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Ability of Poisson-Boltzmann Equation to Capture Molecular Dynamics Predicted Ion Distribution around Polyelectrolytes

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Here, we examine polyelectrolyte (PE) and ion chemistry specificity in ion condensation via all-atom molecular dynamics (MD) simulations and assess the ability of the Poisson-Boltzmann (PB) equation to describe the ion distribution predicted by the MD simulations. The PB model enables extracting parameters characterizing the ion condensation. We find that the modified PB equation which contains the effective PE radius and the energy of the ion-specific interaction as empirical fitting parameters describes ion distribution accurately at large distances but close to the PE, especially when strongly localized charge or specific ion binding sites are present, the mean field description of PB fails. However, the PB model captures the MD predicted ion condensation in terms of Manning radius and fraction of condensed counterions for all the examined PEs and ion species. We show that the condensed ion layer thickness in our MD simulations collapses on a single master curve for all the examined simple, monovalent ions (Na^+ , Br^- , Cs^+ , Cl^- , and Br^-) and PEs when plotted against the Manning parameter (and consequently the PE line charge density). The significance of this finding is that, contrary to the Manning radius extracted from the mean field PB model, the condensed layer thickness in the all atom detail MD modelling does not depend on the PE chemistry or counterion type. Furthermore, the fraction of condensed counterions in the MD simulations exceeds the PB theory prediction. The findings contribute toward understanding and modelling ion distribution around PEs and other charged macromolecules in aqueous solutions, such as DNA, functionalized nanotubes, and viruses.

Introduction

Polyelectrolytes (PEs) are polymers that contain ionic or ionisable repeating electrolyte groups. In aqueous solution, the electrolyte groups dissociate to solvated counterions and a charged polymer. Depending on the PE and the counterion species, as well as, solution characteristics including excess salt, the solvated ions can condense onto the polyions. The degree and extent of this ion condensation, and its influence on PE-PE interactions, is at key role in dictating PE materials characteristics, for example for using them in industrial solubilisation and flocculation,^{1–3} separation,^{4–6} drug delivery,^{7–10} tunable and responsive coatings,^{8,11–13} adhesives,¹⁴ sensors,^{6,15–17} and tissue engineering.^{18,19} Besides technological interest, many important biopolymers, such as DNA, RNA and proteins, are PEs and experience ion condensation.

Excess salt contributes to the ion atmosphere around the PEs. Therefore, it is not surprising that the responses of hydrated PE assemblies, namely complexes and multilayers, are sensitive to the addition of salt. The presence of ions can lead to responses such as shrinking, swelling, loosening, or even dissociation at high enough concentration.^{20–26} Furthermore, the counterion

type has been linked to the solubility,²⁷ kinetics,²⁸ stability,²⁹ and composition of PE complexes,^{30–33} as well as their thermal response.²³

Most commonly, ion condensation in PE systems is described by Manning's theory, a mean field Poisson-Boltzmann (PB) description that models the polyion as an idealized, infinitely long line charge and the counterions within Debye-Huckel approximation.^{34,35} Sharp has elaborated the Manning picture by investigating the effect of excess salt in the system through the nonlinear Poisson-Boltzmann equation.³⁶ For monovalent ions and low charge densities, the PB approach is consistent with simple numerical models^{37,38} and is able to predict various PE solution properties including electrophoretic migration, surface adsorption or osmotic pressure in a concentration range from 0.0003 to 0.15 M.^{38–40} Notably, the Manning mean field picture breaks down in the presence of additional divalent salt, or strongly interacting systems.^{37,41–43} Specifically, several studies in which the PE is defined as a rigid rod or a line charge with varying charge density,^{37,44} or a flexible chain of beads,⁴⁵ have pointed out the importance of charge correlations in ion condensation around PEs in strongly interacting systems.

Mean-field models do not take into account the molecular level structure and inhomogeneity in the PE charge distribution. Ion type specific effects can be incorporated partially to the PB description via modifications, see e.g. Refs.^{46,47}. All these effects in PE-ion systems, however, can be captured by particle level descriptions, such as Monte Carlo, or molecular dynamics (MD). Both, primitive numerical models in which the PEs are described as a rigid rod or a line charge with varying charge density^{37,42,48–}

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⁵⁰ and detailed all-atom simulations^{20,46,51,52} have outlined the significance of chemistry specific effects via charge correlations. Specifically, the effect of ion species on the condensation of ions has been demonstrated in Refs.^{20,53–56}. However, systematic studies of the effect of ion type and PE chemistry on the ion condensation are lacking.

In this work, the ion condensation around several different PEs is examined using two different theoretical approaches: 1) all-atom MD simulations and 2) a modified mean-field PB model. The detailed atomistic molecular dynamics simulation model takes into account the local atomistic structure of the polyelectrolyte and water, as well as, finite size and chemistry specificity of the ions. It also captures van der Waals interactions between the atoms and steric effects. The second approach is a simplistic Poisson-Boltzmann equation. This mean-field electrostatic model neglects atomistic detail, solvent-polymer interactions, and all non-Coulombic interactions but the ion specificity is partially retained via an additional term; the all-atom MD model serves as a reference to the PB. The current study provides both a systematic study of the effect of ion type and PE chemistry on the ion condensation in all-atom detail and a charting of the extent to which the mean-field level PB model captures the distribution. The examined PEs differ in charge per length, chemistry and the degree of ionisation. The ion condensation of different monovalent ions is compared via the fraction of condensed counterions and the Manning radius r_M , and crucial parameters describing the ion condensation are extracted.

To our knowledge, this is the first study where the all-atom ion condensation response of a large number of different PEs and ions are compared with the PB model: the mapping enables capturing molecular detail features that govern the quality of the PB fit. Furthermore, we find that the condensed ion cloud thickness falls on a master curve for all the examined ion types and PEs. This means that although both the PE effective diameter and the Manning radius r_M are PE chemistry or counterion type dependent in the mean field description, the condensed layer thickness in the all-atom MD modelling is not.

Methods

Molecular Dynamics simulations

The all-atom molecular dynamics simulations employ the Gromacs 4.6.5 package.^{57,58} Polystyrene sulfonate (PSS), polydiallyldimethylammonium (PDA), polyacrylic acid (PAA), polyallylamine (PAA), α -poly-L-lysine (PLL), and polyglutamic acid (PGA) chains with Na^+ , K^+ , Cs^+ , Cl^- , and Br^- as counterions were examined. Figure 1c) shows the PE structures. The polyelectrolytes and polypeptides chosen for the study are very common and provide a set that varies in both line charge density and molecular structure significantly. To describe the PEs and the ions, the OPLS-aa force field⁵⁹ was used. The ammonium and carboxylate groups parameters follow Ref.⁶⁰. Cation parameters originate from Ref.⁶¹ and chloride and bromide ion parameters from Refs.⁶² and⁶³ respectively. For

Figure 1. a) A snapshot of the molecular dynamics simulation box for PDA, its Cl^- counterions, and the explicit water molecules and b) the corresponding PB cylindrical cell model with the effective PE radius r_0 , counterion cloud cylinder length L_z , and counterion cloud cylinder radius R specified. c) The examined PE chemical structures.

water, in compliance with the force-field choice, the explicit TIP4P water model⁶⁴ was employed.

For NVT ensemble simulations, the V-rescale thermostat⁶⁵ with coupling constant 0.1 ps was applied at reference temperature $T=300$ K. The NPT ensemble simulations used the same thermostat scheme and additionally the semi-isotropic Parrinello-Rahman barostat⁶⁶ with the coupling constant 1 ps and reference pressure 1 bar. To calculate long-range electrostatic interactions, the PME method was used.⁶⁷ Van der Waals interactions were described using the Lennard-Jones potential with a 1.0 nm cut-off (direct cut-off, no shift). Throughout the simulations, all the bonds in the PEs and water molecules were controlled by the LINCS⁶⁸ and SETTLE⁶⁹ algorithms, respectively. A 2 fs time step within the leap-frog integration scheme was applied and the trajectories were written every 1 ps to obtain a frequent sampling of the ion positions. This setup provides a classical empirical force-field based all-atom detail molecular dynamics simulations model with explicit solvent and ions present and rigorous treatment of both electrostatics and van der Waals interactions in addition to intramolecular and steric considerations. VMD software package⁷⁰ was used for all simulation snapshots.

To achieve a cylindrical setup that can be compared with the PB theory, the MD simulation configurations were constructed so that the PE chains spanned the cuboid simulation box as straight, z-axial chains, see Figure 1a). To straighten the PE chains, they were first aligned in the z-axial direction and then stretched by a force of $1000 \text{ kJ mol}^{-1} \text{ nm}^{-1}$ along the z-axial direction in vacuum in a 1 ns MD simulation with time step 0.5 fs. Next, the terminal groups were connected over the periodic boundary conditions via introducing a bond between the termini monomers, defining the appropriate angle and dihedral interactions, as well as, excluding the neighbouring 1-4 interactions. The simulation box volume is $V = L_x L_y L_z$, where $L_x=L_y$, and L_z is defined by the stretched chain length, see Figure 1a).

The straight PE chain that spans the simulation box axially was solvated by water molecules. An appropriate number of counterions was introduced in the simulation box via replacing

solvent molecules. To remove initial strain, a 10 ps NVT simulation was performed. The *xy*-dimensions of the system, as well as, water and ion distribution around the PE were equilibrated by a 5 ns NPT simulation in which the PE was under position restraints. Next, the PE was released and an NVT run of 100 ns for decamers and 50 ns for icosamers was performed. The ion distribution is calculated from this run.

The stretched PE configuration used in the all-atom simulations is a simplification that we adopt to obtain an equilibrated ion distribution in a cylindrical geometry which enables comparison with the PB equation. Additionally, employing a stretched, infinite chain in the simulation description avoids finite size and end effects, as well as, time scale issues in equilibration because of the PE structural fluctuations that flexible PE chains are subject to. Furthermore, strongly charged PEs and PEs in low ionic strength have extended straight sections: electrostatic repulsion between monomers increases the effective persistence length.^{71–75} The omission of chain flexibility in our description most certainly affects, for example ion condensation sites, see e.g. Refs.^{20,51,76}, and through that also the ion distribution and condensation.

All ion density profiles were calculated from the cylindrical radial distribution functions axed onto the centre of mass of the C_α atoms of the PE backbone (*z*-axial orientation). Here, the C_α atom is the carbon atom to which the PE side chain is attached. The radial (number) density function is defined by $\rho(r) = \rho g(r)$ where $\rho = N/V$ is the mean ion number density in the simulation box, N is the number of ions and V is the respective volume. Here, $g(r)$ is the cylindrical radial distribution function and r the radial distance from the PE backbone (*z*-axis).

The fraction of the ions within r , $x(r)$, is obtained by volumetric integration of the number density function

$$x(r) = \frac{1}{N} G(r) = \frac{1}{N} \int_V d^3r \rho(r') = \frac{2\pi L_z}{N} \int_0^r \rho(r') r' dr', \quad (1)$$

In this, L_z is the box length (PE length). Actually, the ion fraction $x(r)$ is the cumulative radial density distribution function $G(r)$ divided by N , see Eq. (1); both the cylindrical radial density distribution function $\rho(r)$ and the cumulative radial density distribution function were calculated using built-in Gromacs tools.

Ion condensation and PE-ion interactions are subject to charge polarization. In this work, a non-polarizable force field which does not allow reorganization of the charge distribution in the course of the simulation was used. For small, hard ions with relatively small polarizabilities, non-polarizable force-fields can be expected to capture the ion response. The description of ions with larger polarizabilities, however, is subject to suffer from the lack of polarizability in the model. Of the examined ions, Cs^+ and Br^- have largest polarizability and omitting the polarizability in their description might influence their predicted condensation strength.

Poisson-Boltzmann model

A common continuum level approach to modelling a PE chain and its counterions is to represent the PE as a featureless charged cylinder with a linear charge density λ .⁷⁷ For example,

the Onsager-Manning-Oosawa mean-field theory uses this approach and the Poisson-Boltzmann (PB) equation, to characterize the counterion condensation in PE systems.^{34–35} The PB equation within a finite cylindrical cell, i.e., the cylindrical cell model, is analytically solvable: the solution gives the electric potential around the PE described as the charged cylinder and enables deriving simple parameters characterizing counterion condensation from the theory. First, partial counterion condensation is expected if a dimensionless linear charge density, the Manning parameter $\xi > 1$.³⁴ The Manning parameter $\xi = q l_B \lambda$ depends on the counterion valency q , the Bjerrum length $l_B = e^2/(4\pi\epsilon\epsilon_0 k_B T)$, $l_B = 0.7$ nm for water at 300 K, and the cylinder line charge density λ (PE charge per length). The theory also gives the well-known equation for the fraction of condensed counterions in PE systems $x_c = 1 - 1/\xi$, when $\xi > 1$.³⁷ Actually, Heyda and Dzubiella have demonstrated that $1 - 1/\xi$ represents the lower limit of the condensed ion fraction at infinite dilution x_c^{min} .⁴⁶ The rest of the neutralising ions remain dilute in the bulk solvent region.

Next, we set a PB model to match as closely as possible the all-atom molecular dynamics PE chain systems. In the PB model, the stretched PE is represented by an infinitely long cylinder of an effective radius r_0 and a linear charge density $\lambda = Q/L$.⁷⁷ In comparison to the all-atom MD model which captures these, this infinitely long cylinder and featureless, uniform line charge density description clearly omits the possibility of capturing any solvent specific or atomic level structural influences in the ion distribution around the PE. The charged rod (PE) is considered to reside in a coaxial cylindrical cell of radius R , see Fig. 1b). The PB cell volume is set equal to the MD simulations box volume after the NPT relaxation. That is, $V = L_z L_x^2 = \pi R^2 L$. Therefore, the PB cell radius $R = L_x/\sqrt{\pi}$ where $L_x = L_y$ is the MD simulation box edge length in the axial directions perpendicular to the PE. The PB cylinder length $L = L_z$.

This sets the framework for solving the modified cylindrical PB equation⁴⁶ for the PE system

$$\left(\frac{d^2}{dr^2} + \frac{d}{r dr}\right) \Phi(r) = -4\pi l_B \sum_i c_i z_i \exp[-z_i \Phi(r) - \beta V_s(r)], \quad (2)$$

where $\Phi = e\beta\phi$ is the dimensionless electrostatic potential, i the ion type index, $z_i = \pm 1$ the ion valency, and c_i the ion i concentration. For the counterions, $c_i = 0.14$ ions/nm³. Furthermore, e is the elementary charge, ϕ the electrostatic potential, ϵ the relative permittivity of the solvent, ϵ_0 the vacuum permittivity, and $\beta = (k_B T)^{-1}$, where k_B is the Boltzmann constant and T the temperature. The extra term $V_s(r)$ is introduced in line with Heyda and Dzubiella⁴⁶ to capture the specific interaction between the ions and the PE rod. For the fully ionized (strong) PE systems, the summation on the right-hand side reduces to a single term. However, the partially ionized (weak) PE systems have a second term as counterions are added to the system to match the counterion density of the

Figure 2. (a) The ion density profile and (b) the corresponding ion fraction profile in the MD simulations and predicted by the fitted PB equation, and (c) a typical chain conformation with a condensed sodium ion for the PGA system. (d) and (e) show the corresponding data, and (f) the corresponding sodium ion snapshot for the PSS system, respectively.

fully charged PE systems (0.14 ions/nm³). The second term corresponds to the co-ions that neutralize the charge of the added counterions (c_i is 0.03, 0.07, 0.10 or 0.14 ions/nm³). Physically, the $V_s(r)$ is based on hydration⁴⁷ but a shifted Gaussian functional form is used to approximate $V_s(r)$:⁴⁶

$$V_s(r) = V_0 \exp[-(r - r_0)^2 / \sigma^2] \quad (3)$$

Here, V_0 sets the energy scale and σ the length scale of the ion-specific interaction. While $V_0 < 0$ and r_0 are ion specific fitting parameters in the work, σ is set to 0.6 nm following Heyda and Dzubiella.⁴⁶ Significant deviation from $\sigma = 0.6$ nm resulted in worse fits when we tested the parameter sensitivity. In general, the magnitude of the ion specific interactions increases with the absolute value of V_0 and a smaller r_0 value means that the ions condense closer to the PE backbone.

The cylindrical PB equation, Eq. (2), was numerically solved using the *bvp4c* function of Matlab with the boundary conditions $\phi'(R) = 0$ and $\phi'(r_0) = -2\xi/r_0$. The electric field at the surface of a charged cylinder was obtained by Gauss' law. After this, the charge density of ions of type i is given by

$$\rho_i = c_i \exp[-z_i \phi(r) - \beta V_s(r)]. \quad (4)$$

Now, Equation (1) provides the ion fraction $x(r)$ within a cylindrical region of radius r . The ion specific parameters V_0 and r_0 were fitted so that the resulting ion fraction matches with the $x(r)$ profiles of the MD simulations trajectories with focus being on the long-distance fit as atomic level correlations in the MD simulations are most dominant at short radial distances.

Polyelectrolytes and their computational setups

First, ion-specific counterion condensation was studied on four fully ionised strong PEs with different counterions in all-atom detail, and later via the PB model. These PEs are PGA, PSS, PDA and PLL. The counterions for the polyanions are Na⁺, K⁺, and Cs⁺ and for the polycations Cl⁻ and Br⁻. Monovalent counterions were chosen for the study based on the known basic description accuracy ranges of the two models: the PB approach fails to describe multivalent counterions³⁷ and the employed atomistic detail model does not capture the polarizability effects needed for accurate description of the larger ions, such as iodide. All the PE systems had a counterion concentration of 0.14 ions/nm³. As all the monomers are monovalent, the net charge of a fully ionized PE chain is equal to the number of monomers in the simulation box. For all PEs except PDA, chains of 20 monomers (icosamers) and for PDA chains of 10 monomers (decamers) were examined. PDA has the smaller number of monomers because PDA monomers are longer. Finite size effects were mapped for PGA via comparing the PGA icosamers with decamers.

Next, the ion condensation to a weak polyanion (PAA) and a weak polycation (PAH) at different degrees of ionization was examined again first in all-atom detail, and later via the PB model. As PAA and PAH are weak PEs, their degree of ionization, and hence also net charge, varies with pH. Degrees of ionization 100%, 75%, 50%, 25% and 0% were examined. These correspond to pH-values around >9.5, 7.5, 6.5, 5.7, and <2 for PAA and <4.0, 7.7, 8.8, 10.3, and >12 for PAH.⁷⁸

Figure 3. (a) The ion density profile and (b) the corresponding ion fraction profile in the MD simulations and predicted by the fitted PB equation, and (c) a typical chain conformation with a condensed chloride ion for the PLL system. (d) and (e) show the corresponding data, and (f) the corresponding chloride ion snapshot for the PDA system, respectively.

The systems at different degrees of ionization are referred to as PAA-20, PAA-15, PAA-10, PAA-5, and PAA-0 for PAA, and correspondingly for PAH. The number indicates the number of ionized monomers in the icosamer system, that is, PAA-20 and PAH-20 are 100% ionized. In all systems, the ionized monomers are uniformly distributed. The systems were studied with only one type of counterion: PAH counterion is Cl^- and PAA counterion is Na^+ . The counterion concentration was set at 0.14 ions/ nm^3 as this results in a constant counterion concentration in the systems. For the partially ionized PEs, the excess counter charge is neutralized by adding a sufficient number of Na^+ or Cl^- co-ions. Table 1 summarizes the simulations set up information and MD parameters. Fig. 1c) contains the chemical structures of all the studied PEs. The finite size effects of the results, as well as, the dependency of the results on the force-field choice were checked. Two force-fields, i.e., OPLS-aa⁵⁹ and Amber03⁷⁹ with the Dang's ion parameters⁸⁰ and SPC/E water model⁸¹ were compared. Finite size effects were examined by comparison of the counterion condensation around 10 and 20 monomer long PGA chains. The mean number count of ions adsorbed directly on the PE differed slightly between the PGA systems of different length but the calculated overall fraction of condensed counterions x_c varied very little.

Based on the comparison, we concluded PE chains of 20 monomers or comparable length, are sufficiently long to examine the x_c response. On the other hand, the two examined force-fields result in different ion binding characteristics but follow very similar overall trends. The observation that the atomic detail ion binding characteristics bear some dependency on the force-field and ion model is not really surprising; ion

binding dependencies have been reported earlier, for example in Ref.⁷⁶. The details of these checks, the resulting ion distributions, and their detail comparison can be found in the Electronic Supplementary Information.

For fitting the PB model to the all-atom MD simulations data and extracting parameters from the fit, it is instructive to introduce some terms: The range where the ion condensation occurs in the Manning model is called the Manning radius r_M . Here, it is determined by the inflection point criteria^{37,38,46,82} that is commonly used with the PB theory. The fraction of condensed ions x_c is obtained, by definition, as the fraction of ions closer to the PE than the Manning radius: $x_c \equiv x(r_M)$. The PB theory predicts also a scaling $r_M \propto R^{1/2}$.³⁷ This dependency on R was not taken into account in the comparison of the r_M values, as R differs relatively little between the PE systems.

In the Manning theory, a PE is a uniformly charged line. However, the PEs in the MD simulations have a finite radius. In the PB model, this is captured by representing the PEs as charged cylinders with an effective radius r_0 that depends on the PE and ion species. As the PE effective radius varies significantly for the examined PEs and also depends on the counterion species, instead of directly comparing the values of the Manning radii, a parameter $r_{cl} = r_M - r_0$ is introduced to describe the condensed ion cloud thickness. This condensed ion cloud thickness proves out to be a convenient parameter that allows comparison between the different PEs and counterions.

Table 1. The examined PE systems and the corresponding model parameters. Q is the net charge of the PE in the simulation box, $L=L_z$ the periodic box z-axial length (PE length), λ the line charge density of the PE, and L_x the lateral length of the equilibrated periodic box. Notably, $L_x=L_y$, and all the systems have volume per counterion number $V/N=LL_x^2/N = 7.20 \pm 0.11$ [nm³/ion].

System	Q [e]	L [nm]	λ [e/nm]	Ion species	L_x [nm]
PGA	-20	7.37	-2.71	Na ⁺	4.40
				K ⁺	4.42
				Cs ⁺	4.44
PSS	-20	5.51	-3.63	Na ⁺	5.12
				K ⁺	5.12
				Cs ⁺	5.14
PDA	10	6.05	1.65	Cl ⁻	3.47
				Br ⁻	3.48
PLL	20	7.49	2.67	Cl ⁻	4.41
				Br ⁻	4.42
PAH-20	20	5.78	3.46	Cl ⁻	4.95
PAH-15	15	5.78	2.59	Cl ⁻ (Na ⁺)	4.94
PAH-10	10	5.78	1.73	Cl ⁻ (Na ⁺)	4.93
PAH-5	5	5.78	0.86	Cl ⁻ (Na ⁺)	4.93
PAH-0	0	5.78	0	Cl ⁻ (Na ⁺)	4.94
PAA-20	-20	6.12	-3.32	Na ⁺	4.83
PAA-15	-15	6.12	-2.45	Na ⁺ (Cl ⁻)	4.83
PAA-10	-10	6.12	-1.63	Na ⁺ (Cl ⁻)	4.88
PAA-5	-5	6.12	-0.82	Na ⁺ (Cl ⁻)	4.88
PAA-0	0	6.12	0	Na ⁺ (Cl ⁻)	4.90

The error bars for the Manning radius r_M and the fraction of the condensed ions x_c were estimated by the sensitivity of these quantities to small variation in V_0 and r_0 values in the fitting. By examination of the data fits, a variation of ± 0.1 for both parameters was used in determining the error bars.

Results and discussion

Effect of PE chemical structure and ion specificity

First, the counterion condensation on the fully ionised PEs was studied. As expected, the all-atom simulation ion distribution profile depends strongly on the chemical structure of the PE and the counterion type. Fig. 2a) shows that the counterion density profiles around PGA have for all the examined cations two condensation peaks. These correspond to ions residing just beyond the two oxygen groups of PGA in radial distance from the PE backbone axis. Note that the even though the PGA monomer is monovalent, the carbonyl and carboxylate oxygens have partial negative charges -0.59e and -0.82e, respectively. The counterion peak of the carboxylate oxygens is much wider than the peak corresponding to the carbonyl oxygen. The counterion density profiles of PSS, see Fig. 2d), show an ion condensation peak only at the position of the PSS sulfonate oxygens. The peak is relatively wide due to the dispersed charge of the sulfonate group.

The all-atom simulation density profiles for the PDA systems presented in Fig. 3a) have two peaks separated by 0.25 nm. The first one is situated just outside the N⁺ atoms of PDA and the second one corresponds to the methyl groups of PDA. The

counterion density profiles of PLL, Fig. 3d), contain a single wide peak that corresponds to the amine group.

Figures 2b), 2e), 3b), and 3e) present the ion fraction profiles resulting from the all-atom simulations for PGA, PSS, PDA, and PLL, along with the fitted PB curves. Table II presents the corresponding PB fitting parameters V_0 and r_0 and the resulting condensation parameters. Examination of the MD data reveals that the ion-specific differences in the data sets are more distinct between the counter cations than the counter anions. This is because the examined counter cations vary more in ionic radii in aqueous solution than the counter anions:⁸³ $\Delta r_{Na^+ \rightarrow K^+} = 45.4\%$, $\Delta r_{K^+ \rightarrow Cs^+} = 22.7\%$ for cations and $\Delta r_{Cl^- \rightarrow Br^-} = 10.0\%$ for anions, where the relative difference of ionic radii is calculated as $\Delta r_{i \rightarrow j} = (r_j - r_i)/r_i$. This leads to a much larger difference in the charge density of the cations than of the anions and to different behaviour of the ions around the PE. Table II reveals that the ion-specific interaction parameters V_0 of the PB fits quite expectedly follow the effective ionic radii.

The data also shows that the chemistry of the PEs plays a significant role in both the quality of the PB fit and the condensation of the different counterions. Notably, the PB equation fits are not able to capture the ion distribution features of the all-atom simulations near the PE, i.e. at distances close to r_0 (see Table II). This result is expected as the PB model, even with the additional term, is a mean-field model which is unable to accurately describe ion-specific interactions and the PE structure at atomistic level. However, the PB solutions match well the MD simulations data at radial distances $r > 1$ nm. Therefore, using the PB fits to extract condensation parameters r_M and x_c is well founded as the r_M values exceed 1 nm.

Let us next consider the ion and polymer chemistry specific features in the observed ion condensation that are captured by the MD simulations, the extent to which the PB equation solution can reproduce the all-atom MD simulation ion distribution features, and via that assess the applicability range of the PB model based on the PE structure. Figures 2-4 show the MD predicted ion density distribution $\rho(r)$ and snapshots of PE chain fragments with the counterions situated at positions corresponding to the first maximum of $\rho(r)$. As obvious, the PE chemical structure, as well as, for these examined monovalent ions the counterion effective hydrated size determine the condensation site and strength. This is both due to charge distribution in the PE and steric considerations. A comparison with the PB parameters presented in Table II reveals that the first peak of $\rho(r)$ correlates well with the effective PE radius r_0 but the PE and the ion specific features dictate the finer characteristics of the ion condensation.

For PGA, Fig. 2c), in the all-atom MD simulations the sodium ion fits between the PE charge groups. The strongly localized charge on the PGA monomers, together with the small size of the hydrated sodium ion, lead to significant ion condensation at the PE surface. For the larger ions that can be considered to have a lower surface charge density, such as the here examined K⁺ and Cs⁺, condensation occurs to a lesser degree and the PE effective radius r_0 shifts significantly towards larger distances from the PE axis. This response is related with the spatial spacing of the neighbouring PGA groups which introduces size-selectivity to

the condensation response in atomistic detail; for a flexible chain, the size-selectivity is smaller. These charge-charge correlations in the ion positioning result in the strong deviations between the PB fitting and the $x(r)$ derived from the all-atom MD simulations of PGA, especially at distances $r < 0.7$ nm. In total, the comparison to the PB model fit reveals that an ion distribution that has charge-charge correlations, such as the ion distribution in the close vicinity of a PE with localized charges or specific condensation sites, cannot be accurately described using the PB model.

On the other hand, fully charged PSS chains have elongated shape and the carbon backbone is in all-trans conformation.⁷² The aromatic ring in the side chain, as well as, the short length of the monomer unit prevents ion condensation between the functional groups in the atomistic detail simulations model, see Fig. 2f). The counterions are located further out around the sulphate groups which makes the condensation less selective to the ion type than in the case of PGA. With PSS, the PB model predicted change in the effective radius r_0 corresponding to different counterions is relatively small. Furthermore, agreement between the ion fraction obtained from the PB equation and the MD simulations is better than for the PGA but inaccuracy of the PB solution persists very near the PE. Additionally, the counterion condensation of PSS and PGA correlates with the Hofmeister series⁸⁴ with Na^+ condensing more strongly than K^+ and Cs^+ .

The ion condensation around the polycations PDA and PLL show yet different features in the all-atom simulations. PDA has a longer monomer length than the other PEs examined in this work: Figure 3c) shows that the counterions of PDA are located around the isolated charge groups. The ion distribution is much less sensitive to the counteranion species because of the longer separation between the PE charge groups and the similar ionic radii of the counteranions. This leads to the effective radius r_0

obtained from the PB model fit shifting very little for the two counterions. As expected since the assumption of uniform charge distribution is clearly not met, the PB model fits poorly close to the PDA backbone. PLL which has long flexible functional groups provides yet another example: the spacing and flexibility of the PLL functional groups enables the counterions to reside between the monomer units analogous to PGA in the all-atom simulations. However, the small difference in the examined counteranion ionic radii and the side chain flexibility result in much smaller selectivity between the ions than observed with PGA. Also, the agreement with the Hofmeister series for anions cannot be clearly stated.

Figs. 4c) and f) present snapshots of fully charged PAA and PAH chain fragments with the condensed counterions from the all-atom simulations. Both PEs have small side chains and their shape is much more cylindrical than the shapes of the other PEs studied in this work. Their main difference is that PAA has strongly localized charge groups while the PAH charge is more spread out. Of these two, PAH satisfies the PB assumptions of a cylindrical shape and uniform surface charge better. Indeed, the PB model predicts even the fraction of counterions near the PE backbone for PAH, see Fig. 4b). For PAA, the agreement between the MD data and the PB fit is exceptionally bad despite the cylindrical shape of it, see Fig. 4e). This suggests that the strong localization of the charges (non-uniform charge distribution) reduces crucially the ability of the PB equation to capture the ion distribution. Additionally, similar to PGA, the PAA charge groups are compensated efficiently by the small counterions which fit between the charged groups.

The data of Figure 4e) indicates that a very high fraction, almost 80%, of the counterions condense on the fully charged PAA-20 in our all-atom simulations. The PE chains are stretched straight which could enhance the ion condensation.

Table 2. The calculated Poisson-Boltzmann parameters. The table presents the radius of the PB cell R , the Manning parameter ξ , the fraction of condensed ions as predicted by the PB theory x_c^{min} (the lower limit of the fraction of condensed ions), the effective radius of the PE r_0 (PB fitting parameter), the ion-specific interaction V_0 (fitting parameter), the Manning radius r_M , the fraction of condensed ions x_c , and the radius of the condensed layer r_d . The values in the parentheses correspond to the error estimate of the fitting procedure.

System	R [nm]	ξ	x_c^{min}	Ion	r_0 [nm]	V_0 [kBT]	r_M [nm]	x_c	r_d [nm]
PGA	2.52	2.12	0.53	Na ⁺	0.34	-1.8	1.28 (0.01)	0.78 (0.01)	0.94 (0.01)
				K ⁺	0.46	-1.4	1.39 (0.01)	0.75 (0.01)	0.93 (0.01)
				Cs ⁺	0.60	-1.2	1.52 (0.01)	0.73 (0.01)	0.92 (0.01)
PSS	2.92	2.83	0.65	Na ⁺	0.66	-2.0	1.70 (0.01)	0.82 (0.01)	1.04 (0.01)
				K ⁺	0.68	-1.5	1.71 (0.01)	0.78 (0.01)	1.03 (0.01)
				Cs ⁺	0.70	-1.2	1.72 (0.01)	0.76 (0.01)	1.02 (0.01)
PDA	1.97	1.29	0.22	Cl ⁻	0.49	-0.9	1.19 (0.04)	0.63 (0.03)	0.70 (0.04)
				Br ⁻	0.49	-0.9	1.19 (0.04)	0.63 (0.03)	0.70 (0.04)
PLL	2.50	2.08	0.52	Cl ⁻	0.60	-1.3	1.52 (0.01)	0.74 (0.01)	0.92 (0.01)
				Br ⁻	0.63	-1.2	1.55 (0.01)	0.74 (0.01)	0.92 (0.01)
PAH-20	2.85	2.70	0.63	Cl ⁻	0.35	-2.5	1.36 (0.01)	0.83 (0.01)	1.01 (0.01)
PAH-15	2.85	2.02	0.50	Cl ⁻	0.35	-2.0	1.21 (0.01)	0.62 (0.01)	0.86 (0.01)
PAH-10	2.85	1.35	0.26	Cl ⁻	0.35	-1.1	0.99 (0.03)	0.38 (0.02)	0.64 (0.02)
PAH-5	2.85	0.67	-	Cl ⁻	0.45	-0.1	--	--	--
PAH-0	2.85	0	-	Cl ⁻	0.52	0.0	--	--	--
PAA-20	2.77	2.55	0.61	Na ⁺	0.32	-3.5	1.34 (0.03)	0.89 (0.01)	1.02 (0.03)
PAA-15	2.77	1.91	0.48	Na ⁺	0.32	-2.8	1.22 (0.02)	0.69 (0.01)	0.90 (0.02)
PAA-10	2.77	1.27	0.21	Na ⁺	0.35	-1.4	1.06 (0.02)	0.43 (0.01)	0.71 (0.02)
PAA-5	2.77	0.64	-	Na ⁺	0.35	-0.5	--	--	--
PAA-0	2.77	0	-	Na ⁺	0.47	0.0	--	--	--

To examine whether the stretched, straight PE configuration influences the condensation here, the corresponding simulation with a finite length, flexible PAA chain was performed. The condensation and general behaviour of the sodium ions was similar for also the flexible PAA chain.

Effect of ionisation degree

To investigate the influence of the PE ionisation degree on the counterion condensation, PAA and PAH with degrees of ionization of 75%, 50%, 25%, and 0% were examined in addition to the fully charged 100% ionized PEs. The all-atom MD predicted density profiles for the ion condensation around PAA and PAH at varying degree of ionization are presented in Figs. 4a) and 4d). For both PEs, the major peak in ion density $\rho(r)$ of the all-atom simulations is located just outside the N⁺ of PAH or the carboxylate O⁻ of PAA. The peak is followed by some oscillations at larger r values. For PAH, the ion distribution peak is wider than for PAA because PAH amine group charge is more spread out than the PAA carboxylate group charge. As the degree of ionization in the PEs decreases, the peak decreases and the relative amplitude of the oscillations increases. For the neutral chains PAA-0 and PAH-0 no condensation occurs, as

expected. The ion condensation peaks of the PAH-5, PAA-10, and PAA-5 systems shift slightly toward larger radial distances in comparison to the more ionized PEs. The same shift translates to the effective PE radius in the PB model fits.

Further examination of Table II reveals that the V_0 values for the PAA-20, -15, and -10 are much higher than for the other PEs with comparable linear charge density. This is associated with high fraction of condensed counterions that results from the strongly localized charge on the PAA group and suitable spacing between the groups. On the other hand, in agreement with the Manning theory prediction that $\xi = l_B \lambda / e > 1$ is the condensation threshold, for the PAH and PAA systems that correspond to $\xi < 1$, that is, PAA-5, PAH-5, PAA-0, and PAH-0, the PB fittings do not have an inflection point, see Figs. 4b) and 4e). This means that the systems do not exhibit by this criterion a clear limit between condensed and solvated ions; no Manning radius can be defined.

Due to keeping the counterion concentration constant for each degree of ionization of PAH and PAA, co-ions were added to neutralize the partially ionised PE systems (PAH/PAA-15, -10, -5 and -0) in the all-atom simulations. Hence, the partially ionized PE systems correspond to "added salt" conditions instead of "counterions only" conditions. This necessitates the introduction of a new parameter, the Debye length $l_D =$

Figure 4. (a) The density profile and (b) the corresponding ion fraction profile in the MD simulations and predicted by the fitted PB equation for PAH at different degrees of ionization, and (c) a typical chain conformation with a condensed chloride ion for the fully charged PAH-20 system. (d) and (e) show the corresponding data for PAA, and (f) the corresponding sodium ion snapshot for the fully charged PAA-20 system, respectively.

$(8\pi l_B z_s^2 c_s)^{-1/2}$ where $z_s = 1$ is the valency of a symmetric salt and c_s is the salt concentration. Deserno et al.³⁷ have showed that counterion condensation can be treated in the presence of added salt analogous to the case where only counterions are present if the salt concentration c_s is low enough for the Debye length l_D to exceed the Manning radius r_M . As the PE has finite radius, we compared l_D with the condensed ion layer thickness r_{cl} . For both PAH-15/PAA-15 (~ 0.05 M NaCl) and PAH-10/PAA-10 (~ 0.1 M NaCl), l_D exceeds r_{cl} (for PAH-15/PAA-15, $l_D = 1.10$ nm $>$ $r_{cl} \approx 0.88$ nm and for PAH-10/PAA-10, $l_D = 0.73$ nm $>$ $r_{cl} \approx 0.68$ nm).

Heyda and Dzubiella⁴⁶ report a decrease of V_0 upon introducing salt in the system. This could mean that the V_0 values corresponding to the ion condensation of the partially ionised systems decrease with the salt addition. Both Heyda and Dzubiella⁴⁶ and Deserno et al.³⁷ have reported a decrease in the quality of the PB fit when added salt is present. Fig. 4b) and 4e) show that in this work the quality of the PB fit persists. This is very likely due to the relatively low salt concentration in this study.

Effect of PE line charge density

In the Manning theory, or actually considering the PE as a uniformly charged rod, the crucial parameter determining the ion condensation is the line charge density λ . If the screening is taken into account, the Manning parameter $\xi = l_B \lambda / e > 1$ sets the limit for ion condensation. For the PE systems studied here, the limiting line charge density $|\lambda| > |e/l_B| = 0.933$ e/nm. The value is calculated using the dielectric constant of the TIP4P water model that was employed in the all-atom MD simulations at 300

K, $\epsilon = 52$.⁸⁵ The Manning theory is a simplistic approach with relatively light theoretical foundation – ion condensation response that is derived from all-atom MD simulations could deviate from it. However, all the examined systems followed the Manning counterion condensation criteria, i.e. condensation occurs when $\xi > 1$ (PGA, PSS, PDA, PLL, PAH-20/PAA-20, PAH-15/PAA-15, and PAH-10/PAA-10) and no clear condensation is observed when $\xi < 1$ (PAH-5/PAA-5 and PAH-0/PAA-0).

Next, the three parameters characterizing the ion condensation in the PE systems, i.e., x_c , r_M , and r_{cl} , are examined as the function of ξ . The fraction of the condensed counterions x_c for the different ion types as a function of the Manning parameter ξ is presented in Fig. 5. Table II shows a summary of the data. All the calculated x_c values based on the all-atom simulations are consistently over the PB prediction that sets the lower limit of the fraction of condensed counterions $x_c^{\min}$.³⁷ Furthermore, comparison of the x_c values of fully ionised PEs and the x_c values of partially ionised PAH and PAA (empty symbols in Fig. 5) reveals that the partially ionised PEs at low line charge density result in smaller x_c values than the data points corresponding to fully charged PEs with similar line charge density. The smaller x_c values could originate from an underestimation of V_0 values of PAH-15/PAA-15 and PAH-10/PAA-10 due to the presence of added salt.

In Fig. 6, the Manning radius r_M (small symbols) and the condensed ion layer radius $r_{cl} = r_M - r_0$ (large symbols) determined from the PB fits to the MD data are presented as the function of the Manning parameter of the PE system. Direct plotting of r_M results in a relatively large data scatter which

Figure 6. The fraction of condensed counterions x_c for the different ion types as a function of the Manning parameter ξ . The empty symbols correspond to the partially charged PEs.

persist also for $\log(r_M/r_0)$ as a function of ξ .⁴⁹ However, a plot of r_{cl} vs. ξ leads to the data collapsing in an ion-independent way on a curve that follows $r_{cl} = A(\xi - 1)^\alpha = 0.90(\xi - 1)^{0.22}$. Here, the fitting of the parameters $A=0.90$ and $\alpha=0.22$ has been done by using the least mean square deviation as a measure of goodness of the fit. Even though r_M and r_0 depend on the PE and counterion type, the collapse of the data on this single curve shows that r_{cl} depends just on the Manning parameter (line charge density), even for the partially charged PEs. For $\xi = 1$, the Manning radius r_M is located at the surface of the cylinder r_0 ³⁷ and r_{cl} equals zero. Furthermore, the Manning radius depends on the counterion concentration (or PB cell radius R).³⁷ On the other hand, the PE effective radius r_0 depends only on the PE and counterion chemistry.⁴⁶ This means, that the fitting parameters A and α are ion concentration dependent and the fitting curve is expected to shift as the ion concentration changes.

Figure 5. The calculated Manning radius r_M (small symbols) and the condensed layer radius r_{cl} (large symbols) as the function of the Manning parameter ξ . The empty symbols correspond to the partially charged PEs. The solid line is a fit to equation $r_{cl} = A(\xi - 1)^\alpha$. Table II presents the ξ values of the different PEs.

Conclusions

The relation between the PE chemical structure and condensation of counterions was studied via all-atom MD simulations and the ability of a modified PB model to describe the counterion distribution was examined via fitting the model solution to the all-atom MD data and comparing the fit. The study shows that a modified PB equation, with two ion-specific fitting parameters r_0 and V_0 , deviates from the all-atom MD prediction close to the PE. This is because localized charge, atomic level steric considerations, and ion-specific interactions play an important role in this region, as specified by the all-atom MD modelling results. However, if the PE satisfies well the PB model assumptions of cylindrical geometry and evenly distributed charge, as in case of PAH, the PB prediction of ion condensation matches even close to the PE. In general, the findings show that the PB model enables investigating the counterion condensation at larger distances from the PE: the results match with the MD prediction for determining the Manning radius r_M , the condensed ion layer thickness r_{cl} , and the fraction of condensed counterions x_c . Furthermore, ion condensation occurred in the MD simulations only when the Manning parameter $\xi > 1$, in agreement with the Manning theory. The fraction of condensed counterions x_c determined from the MD simulations exceeded consistently the lower limit predicted by PB theory.

The examination also showed that the radius of the ion condensation layer r_{cl} falls on a single master curve as function of ξ . The observed collapse of the r_{cl} values to depend solely on the PE line charge density signifies independency of ion condensation layer r_{cl} on the counterion and PE chemistry specifics beyond the line charge density. The result confirms that the major parameter guiding the counterion condensation onto a PE chain in aqueous solutions is the Manning parameter ξ , and via it the line charge density. Additionally, we presented a new simple way for rough estimation of the Manning radius via the relationship $r_M = r_0 + r_{cl}$. The r_{cl} can be determined from the PE linear charge density while the effective PE radius r_0 can be estimated roughly based on the PE molecular structure or quantitatively determined from the position of the first maximum in the cylindrical radial distribution of the ions with respect to the PE backbone.

Our findings indicate that the simplistic Manning theory which considers the PE as a uniformly charged cylinder can describe ion condensation around a PE with complex chemical structure and also capture ion specificity to a reasonable accuracy at distances > 1 nm. The here presented considerations for applicability range of the modified PB model and the all-atom simulations derived ion distribution dependencies on PE charge distribution, side chain chemistry, and ion specificity, as well as, description of the ion condensation by the PB equation are directly applicable to a whole class of PE structures.

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