

Hydrophilic and Apolar Hydration in Densely Grafted Cationic Brushes and Counterions with Large Mobilities

Raashiq Ishraq,¹ Tanmay Sarkar Akash,² Arka Bera,³ and Siddhartha Das^{4*}

¹Department of Mechanical Engineering, University of Maryland, College Park, MD 20742,
United States

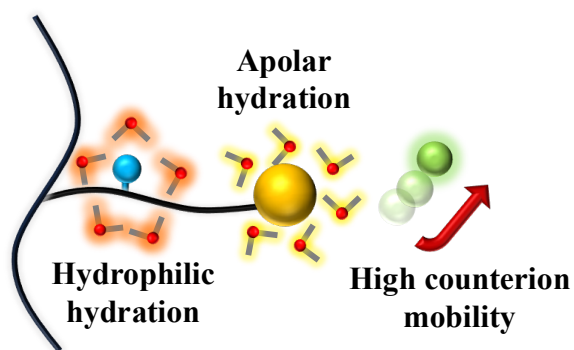
²Department of Mechanical Engineering, University of Maryland, College Park, MD 20742,
United States

³Department of Mechanical Engineering, University of Maryland, College Park, MD 20742,
United States

⁴Department of Mechanical Engineering, University of Maryland, College Park, MD 20742,
United States

*Corresponding Author Email: sidd@umd.edu

TOC Graphic



Abstract

We employ all-atom molecular dynamics (MD) simulation framework to unravel water microstructure and ion properties for cationic [Poly(2-(methacryloyloxy)ethyl trimethylammonium chloride) (PMETAC) brushes with chloride ions as counterions. First, we identify locally separate water domains (or first hydration shells) each around the $\{\text{N}(\text{CH}_3)_3\}^+$ and the C=O functional groups of the PMETAC chain and one around the Cl^- ion. These first hydration shells around the respective moieties overlap and the extent of the overlap depends on the nature of the species triggering it. Second, despite the overlap, the water molecules in these domains demonstrate disparate properties dictated by the properties of the atoms/groups around which they are located. For example, the presence of the methyl groups make the $\{\text{N}(\text{CH}_3)_3\}^+$ group trigger apolar hydration as evidenced by the corresponding orientation of the dipole of the water molecules around the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety. These water molecules around the $\text{N}(\text{CH}_3)_3^+$ group also have enhanced tetrahedrality as compared to the water molecules constituting the hydration layer around the C=O group and the Cl^- counterion. Our simulations also identify that there is an intervening water layer between the Cl^- ion and $\{\text{N}(\text{CH}_3)_3\}^+$ group: this layer prevents the Cl^- ion from coming very close to the $\{\text{N}(\text{CH}_3)_3\}^+$ group. As a consequence, there is a significantly large mobility of the Cl^- ions inside the PMETAC brush layer. Furthermore, the C=O group of the PE chain, due to the partial negative charge on the oxygen atom and the specific structure of the PMETAC brush system, demonstrates strongly hydrophilic behavior and enforces a specific dipole response of water molecules analogous to that experienced by water around anionic species of high charge density. In summary, our findings confirm that PMETAC brushes undergo hydrophilic hydration at one site, apolar hydration at another site, and ensures large mobility of the supported Cl^- counterions.

INTRDOCUTION

Polymer or polyelectrolyte (PE) chains, when grafted to a solid surface at close-enough proximity to one another, stretch away from the solid surface in the form of brushes.¹⁻³ These brushes are often responsive to environmental stimuli, such as the pH or the salt concentration of their surrounding solvent. Such responsiveness has been widely leveraged for functionalizing solid surfaces, such as planar surfaces, inner walls of nanochannel or a nanopore, outer surface of nanoparticles, etc., for a vast range of applications such as fabricating smart surfaces,⁴ developing biofouling-resistant surfaces,⁵ nanofluidic current rectification,^{6,7} nanofluidic diode fabrication,⁸ ion and biosensing,^{9,10} targeted drug and gene delivery,^{11,12} oil recovery,¹³ water harvesting,¹⁴ and many more. The significance of the problem has prompted extensive research on the topic, with the research methods including theory,¹⁵⁻²⁰ simulations,²¹⁻³⁰ and experiments.³¹⁻³⁵ In terms of the simulations, the primary approach for studying the polymer and PE brushes has been coarse-grained simulations. Given the fact that the problem primarily focuses on capturing the behavior of long polymer chains and coarse-grained methods are very much adept in simulating large sizes of the polymer chains, coarse grained approaches²¹⁻³⁰ continue to remain the tools of choice for simulating the behavior and properties of polymer and PE brushes.

Very recently, however, there has been a keen interest to probe the behavior of the polymer and PE brushes with a greater degree of granularity. To achieve such a thing, Dormidontova and co-workers studied the behavior of the uncharged PEG (poly-ethylene glycol) polymer brushes using *all-atom molecular dynamics (MD) simulations*.³⁶⁻³⁸ These simulations captured the hydration behavior and the tail mobility of PEO brushes for different grafting densities as well as for different substrate curvatures. Other notable studies that have employed all-atom MD simulations for studying the behavior of the uncharged polymer brushes and the brush-supported

water molecules include the papers by Kubo and co-workers,³⁹ and Yagasaki and co-workers.⁴⁰ Very recently, we started to explore in great detail, using all-atom MD simulations, the behavior of *charged polyelectrolyte (PE) brushes* and the brush-supported water molecules and the counterions.⁴¹⁻⁴⁹ Our simulations primarily focused on anionic PE brushes, such as PAA [poly(acrylic acid)] or PSS [poly(styrene sulfonate)] brushes and yielded several interesting findings such as identifying water-in-salt electrolyte (WISE) like behavior of the PAA-brush-supported counterions and water molecules,^{41,42} the alteration of the hydrogen bonding energetics inside the PE brush layer,⁴⁴ the role of multivalent counterions in regulating the counterion bridging effect inside the brush layer,⁴⁵ the PE brush charge density dependent changes in the orientation between the PAA and PSS brushes,⁴⁶ and coion-driven electrokinetic transport in nanochannels grafted with PAA brushes.⁴⁷⁻⁴⁹ In this regard, there has been very little work in probing the behavior of *cationic brushes* and such brush-supported water molecules and counterions (anions) using all-atom MD simulations. Very recently, we studied PMETAC brushes using all-atom MD simulations and used machine learning methods to identify the alterations in the characteristics of the water-water hydrogen bonds inside such brush layer.⁵⁰ Santos *et al.* also employed all-atom MD simulations for studying the PMETAC brushes: however, their findings primarily focus on the structure, configuration, and hydration of the brushes (with changing salt type) with little analysis of the behavior and properties of the brush-supported water molecules and counterions.⁵¹ Under such circumstances, a detailed understanding of the structure, configuration, and properties of the cationic-brush-supported water molecules and counterions and the role of different atoms of such cationic brushes in dictating these water and ion behaviors, only discernible by the detailed all-atom MD simulations accompanied by deep statistical analysis, remain largely missing.

In this study, we employ all-atom MD simulations to reveal several interesting facets of the PMETAC brush-supported water molecules and counterions. First, the water supported by the PMETAC-brush-Cl⁻-ion-counterion system is found to form three water domains (or local regions) centered around three entities, namely the N atom [of the {N(CH₃)₃}⁺ moiety] of the PMETAC chain, the C=O group of the PMETAC chain, and the Cl⁻ ion. These water domains are nothing but the first hydration shells formed around these respective moieties. We shall use the word “domain” and “first hydration shell” interchangeably throughout the paper. These domains overlap, i.e., the water molecules in one domain are shared by the other domains, and the extent of this overlap depends on the nature of the species triggering these domains. Second, the properties of the water molecules in these domains are dictated by the effects introduced by the different atomic/molecular entities of the PMETAC chains. For example, the N atom is present as the {N(CH₃)₃}⁺ group: due to the presence of the three methyl groups, the {N(CH₃)₃}⁺ group induces apolar hydration. This is supported by the corresponding dipole orientation of the water molecules in the hydration shell (or the water domain) of the {N(CH₃)₃}⁺ group. Furthermore, the tetrahedral order parameter (q) of these water molecules in the domain around the {N(CH₃)₃}⁺ group is also greater (i.e., the water molecules in the domain around the {N(CH₃)₃}⁺ group are more structured) as compared to the water molecules in the domain around Cl⁻ and C=O. Also, there is an intervening water layer between the {N(CH₃)₃}⁺ group and the Cl⁻ ion; this layer prevents the Cl⁻ ion from coming into close vicinity of {N(CH₃)₃}⁺ group despite the strong electrostatic attraction between Cl⁻ and {N(CH₃)₃}⁺. Accordingly, the Cl⁻ ions are only weakly attracted to the {N(CH₃)₃}⁺ moieties; as a result, the Cl⁻ ions demonstrate significant mobility inside the PMETAC brush layer. Such large mobilities are not witnessed for counterions associated with other types of densely grafted PE brushes, such as poly-acrylic or PAA brushes;⁴¹ however, despite such large

mobilities, the Cl^- ions mostly remain confined within the brush layer and do not escape into the bulk. The $\text{C}=\text{O}$ group of the PMETAC chain, on the other hand, demonstrates strongly hydrophilic behavior: due to the partial negative charges on the oxygen atom and the specific structure of the system, the $\text{C}=\text{O}$ group enforces the dipole response of water molecules to be similar to that experienced by water around anionic species (e.g., Cl^- ion). Please note that by this “specific structure”, we point to the fact that the $\text{C}=\text{O}$ group is a part of the PMETAC chain in brush-like configuration and the brush configuration is such that the $\text{C}=\text{O}$ group is significantly away from other influencing entities of the PMETAC chain. Overall, our findings show that despite being a well-known *cationic* PE chain, PMETAC brushes, demonstrate local hydrophilic hydration at one site and apolar hydration at another site and triggers very large mobilities of the Cl^- counterions.

METHODS

Our all-atom MD simulations considered three separate brush systems with varying grafting density (namely, $\sigma_g = 0.15, 0.2$ and 0.25 chain/nm²). These grafting density values have been previously considered in experiments.⁵²⁻⁵³ Each system consisted of 25 PMETAC chains arranged in a 5 x 5 square array. The PMETAC chains were solvated in water and the water was modeled explicitly using the SPC/E water model.⁵⁴ Every PMETAC chain consisted of 24 monomers with methyl capping (see Fig. 1). Such chain length of the PE brushes is sufficient for capturing the structure and properties of the brush-supported water and counterions.⁴⁴

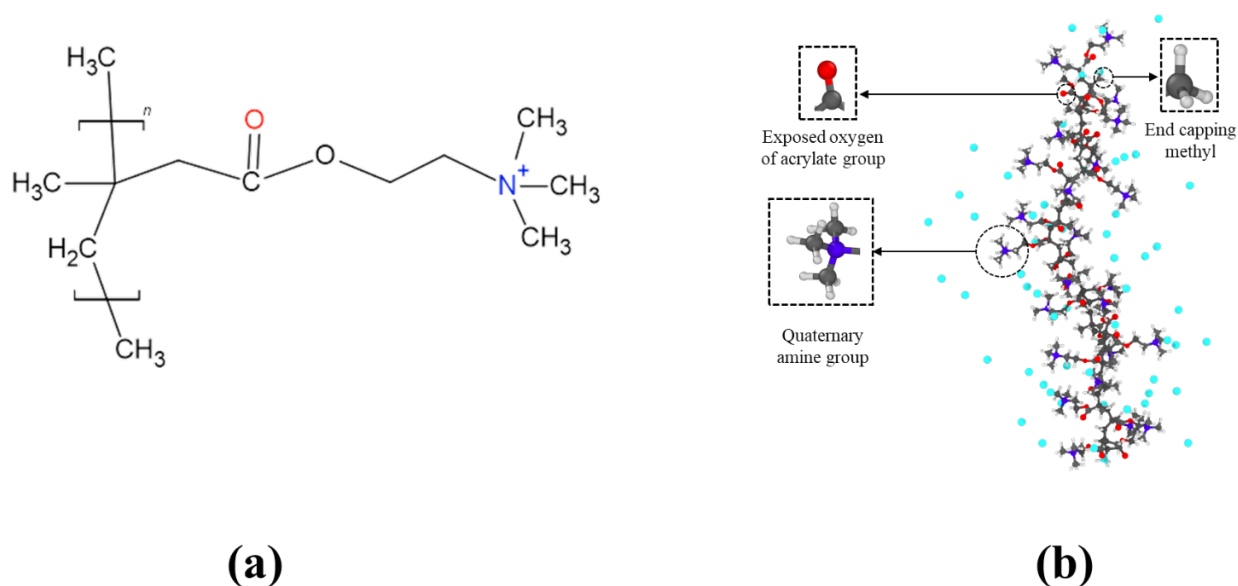


Figure 1: (a) Representation of the chemical structure of a single PMETAC monomer (for our simulations, $n=24$). (b) A snapshot of the chain structure. In (b), black, white, blue, red spheres represent the carbon, hydrogen, nitrogen and oxygen respectively.

We carried out all-atom MD simulation using LAMMPS software package.⁵⁵ Following our previous papers,^{42,44} the initial structure was created as a straight array of chains where columns of counterions were placed adjacent to each chain. We consider an additional added NaCl salt of 0.01 M concentration, with the salt ions (Na^+ and Cl^-) being placed randomly in the bulk water above the brush layer. The structure was built using Moltemplate.⁵⁶ OPLS all-atom forcefield, which is one of the most widely applied forcefields for modelling of polymeric systems⁵⁷ and has been previously used to model PMETAC brushes⁵⁸ (see section S1 in the supporting information for more details), was used to model the interactions between the brush atoms. The water was modeled using the SPC/E model, while for modeling the mobile ions, the parameters from the Joung-Cheatham (J/C) ion model were used.⁶⁰ The J/C ion model considers a non-polarizable and spherical force field and the parameter sets were obtained by reproducing the solvation-free energies, radial distribution function, ion-water interaction energies, and lattice constants.⁶⁰ Long-range Coulombic interactions were calculated using a PPPM (particle-particle particle-mesh) algorithm. The cutoff for the Coulombic interactions was chosen as 10.5 Å. On the other hand, geometric rules were used in all cases for finding the Lennard Jones (LJ) interaction parameters except for the case of the ion-ion and ion-water LJ interactions (for which the Lorentz-Berthelot mixing rule was used to be consistent with Cheatham *et al.*⁶⁰) Also, the cut-off for the shifted-truncated 12-6 LJ potential was considered as 13 Å.⁴¹ The simulation boundary was considered to be periodic in the x-y direction, while a fixed boundary condition was implemented in the z-direction. LJ walls were maintained at both ends in the z-direction in order to prevent mobile counterion and water from escaping the system.

At first, energy minimization was performed to remove any overlap of atoms. Then the system was run under NP_zT ensemble (where dimensions along the z axis is varied) in order to equilibrate

the pressure at 1 atmospheric pressure. After the pressure equilibration, the result of the simulation was run in an NVT ensemble using a Nosé-Hoover thermostat at 300 K.³⁶ The equilibration was confirmed by ascertaining that the average brush height fluctuated around a constant value (see Fig. S2 in the SI). After equilibration, the production run was performed for each system for 12 ns. The simulation, the potentials, the system modelling, and the sampling protocols were kept similar to our previous studies.^{41,42} The brush height calculation, the brush height autocorrelation function, and all other details of the force fields (including the force field parameters) used in this study have been provided in sections 1 and 2 of the Supporting Information (SI).

RESULTS AND DISCUSSION

Configuration of the PMETAC Brushes

Figure 2(a) shows a snapshot of the brush system, depicting the brushes, water molecules, and the counterions. Figure 2(b) provides the variation of the brush height as a function of the grafting density. The brush height, as expected, increases with an increase in the grafting density. Figure 2(c) provides the reduced monomer number density: for all the different grafting density values, the monomer density profiles demonstrate a step-like behavior, which is common for brushes at high grafting densities.^{41,61} Finally, Fig. 2(d) shows the endpoint distribution of the brushes: this distribution provides a measure of the flexibility of the chains in the axial direction. An increase in the grafting density leads to a weak increase in the brush height [i.e., the brush height changes from 13σ to 15σ as the grafting density increases from 0.15 to 0.25 chains/nm²; please see Fig. 2(b)]. Accordingly, the peak of the end point distribution of the brushes for a greater grafting density shifts slightly to the right [see Fig. 2(d-inset)]. Furthermore, given that for a greater grafting density the number of chains per unit volume is more (i.e., there are a greater number of chains whose end points are counted), the magnitude of the $\rho_e\sigma^3$ peak increases progressively with an increase in the grafting density.

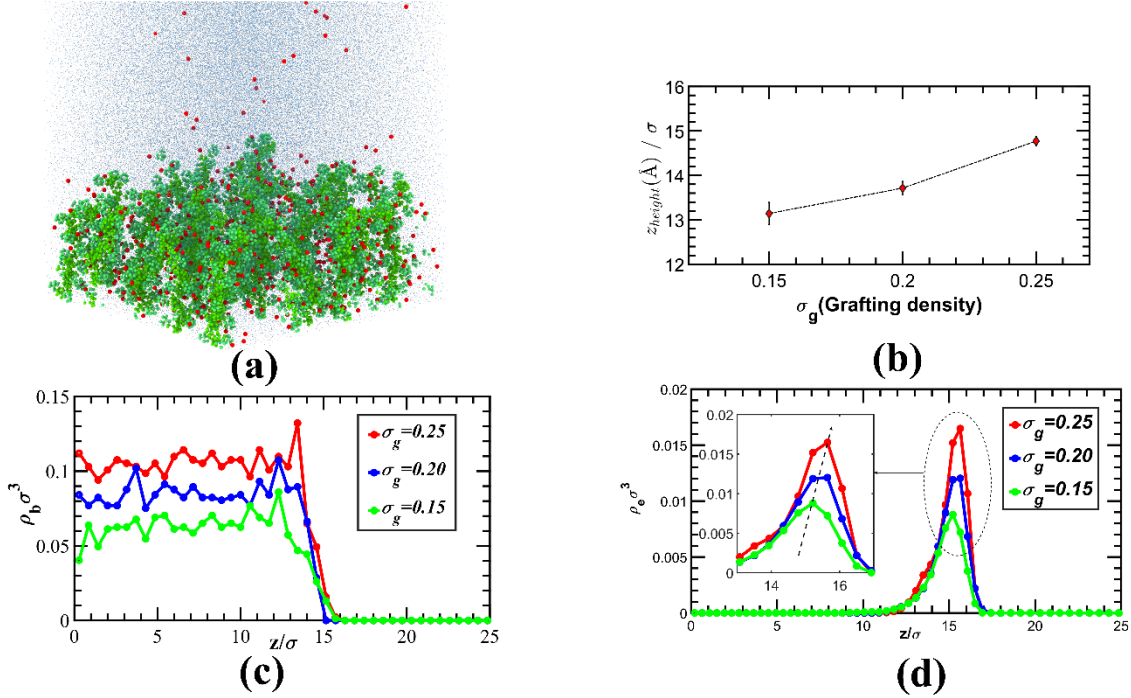


Figure 2. (a) MD simulation snapshot (for a grafting density of 0.15 chains/nm²) showing the PMETAC brushes, water molecules, and Cl⁻ counterions. Green, red and blue (background) respectively represents the brush, counterion and water. (b) Variation of the mean brush height (z_{height}) with the grafting density (σ_g) (see the caption of Fig. S2 in the SI for a detailed procedure employed to calculate the brush height). The unit of the grafting density is in chains/nm² (c) Profile of the dimensionless monomer density ($\rho_b \sigma^3$), where ρ_b is the monomer density and σ is equal to 3.5 Å and the maximum uncertainty ($\Delta\delta_{max}$) among the points reported in the plot is $\pm 0.0031 \rho_b \sigma^3$. (d) Profile of the dimensionless end point density ($\rho_e \sigma^3$) (with the maximum uncertainty among the points reported in the plot being $\Delta\delta_{max} = \pm 0.0016 \rho_e \sigma^3$). The dimensionless monomer and endpoint density profiles are measured along the z -axis (normal to the grafting plane). The distance from the plane is also measured in nondimensionalized units (z/σ). In the inset of (d), we magnify the end-point distributions for the z values where the peaks in the distributions occur. The black dotted line (in the inset) shows the trend of the peaks.

Structure and Properties of the PMETAC-Brush-Supported Water Molecules

We study the structure and properties of water confined within the PMETAC brush layer. In Fig. 3(a), we show the variation of the average number density of the water molecules with distance from the grafting surface both inside and outside of the PMETAC brush layer. As has been observed for anionic brushes,^{41,42} here too, the number density of the water molecules inside the brush layer (i.e., in the space between $z=5\text{\AA}$ to $z=45\text{\AA}$, measured from the grafting surface) decreases with an increase in the grafting density [see the inset of Fig. 3(a)]. A larger grafting density implies the presence of a greater number of monomers (for a given volume) inside the brush layer, which reduces the available space (for a given volume) for the water molecules inside the brush layer. This leads to the presence of a reduced number of water molecules, leading to a reduced water number density inside the brush layer (i.e., between $z=5\text{\AA}$ to $z=45\text{\AA}$). Figure 3(b) confirms this grafting-density-driven reduction in the percentage of atoms belonging to water molecules inside the brush layer (i.e., between $z=5\text{\AA}$ to $z=45\text{\AA}$). It is useful to note here that several of the main qualitative findings of Figs. 2 and 3, namely a decrease in water number density with an increase in grafting density, an increase in brush height with an increase of grafting density, etc., are common for any densely grafted PE brushes. For example, in our previous papers,^{19,41} where all-atom MD simulations were employed to probe the structure and configuration of the anionic PAA (poly-acrylic acid) brushes, we have seen such qualitative results.

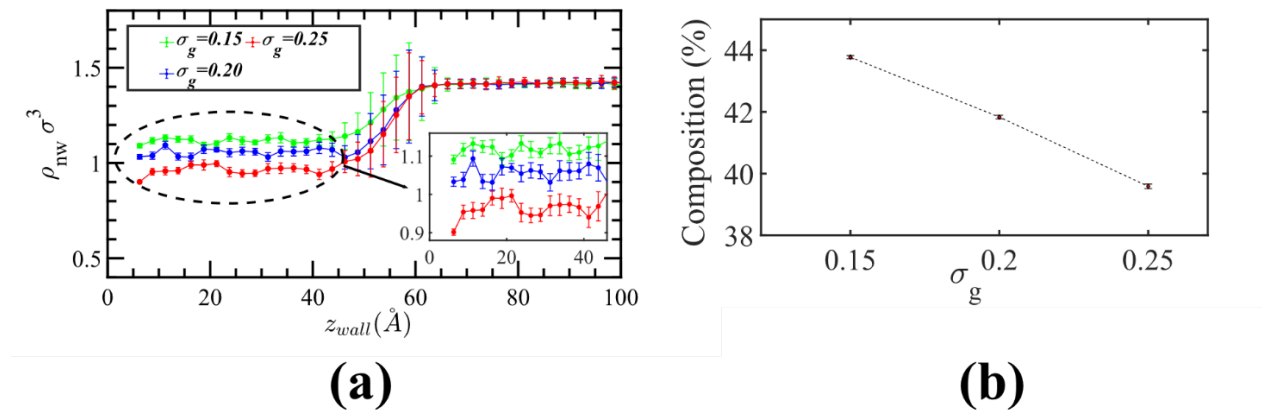


Figure 3. (a) Dimensionless density distribution of the water molecules inside and outside the PE brush layer as functions of the PE grafting density (σ_g). The unit of the grafting density is in chains/nm². In the inset of (a), we magnify the distribution inside the brush layer (i.e., in the space between $z=5\text{\AA}$ to $z=45\text{\AA}$, measured from the grafting surface). (b) Grafting-density-driven variation in the percentage of atoms belonging to water molecules inside the brush layer (i.e., in the space between $z=5\text{\AA}$ to $z=45\text{\AA}$, measured from the grafting surface).

A deeper analysis of the water microstructure inside the brush layer (i.e., between $z=5\text{\AA}$ to $z=45\text{\AA}$) confirms that there are multiple regions or domains of water molecules inside this PMETAC brush layer in the presence of the Cl^- counterions. These domains (or 1st hydration shells) are centered around distinct ionic entities of the PMETA- Cl^- system: there is one water domain around the N atom [of the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety] of the PMETAC brush, another domain around the $\text{O}^{\delta-}$ or the oxygen of the $\text{C}=\text{O}$ group of the PMETAC brush, and the final domain around the Cl^- counterions [see Fig. 4(a)]. The region identified as the “water domain”, in line with the definition of the first solvation shell, is considered as the space between the central atom ($X = \text{C}, \text{N}$ or Cl) and the first minima of the X-O ($X = \text{C}, \text{N}$ or Cl ; O: Oxygen of the water molecule) RDF. These “water domains” are characterized by the fact that although the water domains around different central atoms ($X = \text{C}, \text{N}$ or Cl) overlap [see Figs. 4(a,c) and Fig S4 in the Supporting Information], the moieties maintain their specific influence on the water present inside the water domain that are formed around them. As already pointed out, these water domains centered around these separate ionic species are nothing but the 1st solvation shell of these species. This is confirmed by Fig. 4(b): we calculate the solvation number (see section S3.2 of the SI for the calculation procedure) around the N atom [of the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety], Cl^- ion, and $\text{O}^{\delta-}$ atom (of the $\text{C}=\text{O}$ group). In each case, the solvation number is close to the number predicted by the experiments as well as *ab-initio* simulations.⁶²⁻⁶⁶

At first, we calculate the extent of overlap of these domains: in other words, we are interested to understand to what extent the water molecules in the domain centered around a given species is shared in the water domain centered around another species. Figure 4(c) provides a pie chart that shows the extent to which the water molecules centered around a given species is shared by other species for a grafting density of $\sigma_g = 0.25$ chains/nm². For other grafting densities, the results remain

qualitatively similar (see section S3.2 of the SI for more details). For example, for $\sigma_g = 0.25$ chains/nm², for the water molecules in the domain centered around the N atom [of the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety], 65% of the water molecules are not shared with any other species, 6% is shared with C=O group, 28% is shared with Cl⁻ ion and 1% is common (shared among all moieties). On the other hand, for the water molecules in the domain centered around the Cl⁻ ion, the majority (78%) is shared with the $\{\text{N}(\text{CH}_3)_3\}^+$ group and almost nothing (i.e., less than 1% of the total number of water molecules) is shared with the C=O group, while a small fraction (19%) is retained to itself. Finally, for the water molecules in the domain centered around the C=O group, the majority (79%) is shared with the $\{\text{N}(\text{CH}_3)_3\}^+$ group and almost nothing (<1%) is shared with the Cl⁻, while a small fraction (6%) is retained to itself. The C=O group of the PMETAC chain, due to the partial negative charge on the oxygen atom, will remain significantly away from the Cl⁻ counterion: this explains the very little mutual sharing of the water molecules between these two species.

It is important to note here that even though there is a significant overlap between the water domains (as elucidated above), the different moieties maintain their specific influence on the water molecules in their respective water domains. This influence maintained can be attributed to the specific structure of the PMETAC polyelectrolyte brushes, where (1) the chains, being in the “brush-like” configuration, are stretched in a unidirectional manner and (2) the atoms are separated due to bonds [atoms such as N and O (of C=O)] or due to the presence of the methyl groups (atoms such as Cl and N).

In order to further investigate the microstructure, we plot the N-O_w, Cl⁻-O_w, and O^{δ-}-O_w radial distribution functions (RDFs) [see Fig. 4(d)]. Here O_w refers to the oxygen atom of the water molecule, while O^{δ-} refers to the oxygen of the C=O group. The magnitude of the RDF peaks around these moieties varies significantly, indicating that the density of water molecules varies

significantly inside these domains. The peaks of both the Cl⁻-O_w and O^{δ-}-O_w RDFs occur at a very small distance, confirming that the water molecules are very close to the Cl⁻ counterion and the C=O group of the PMETAC chains. Also, the height of the first O^{δ-}-O_w RDF peak is less than unity, indicating that water molecules are less accessible in that region. This phenomenon can be attributed to the fact that the C=O moiety is close to the base of the polymer, resulting in poor hydration of the moiety. On the other hand, the peak of the N-O_w RDF occurs at a much larger distance due to the steric hinderance of the CH₃ groups. Moreover, the peak of the N-O_w RDF is much blunter as compared to the peaks of the Cl⁻-O_w and O^{δ-}-O_w RDFs. This indicates that the water molecules around {N(CH₃)₃}⁺ moiety is not strongly affected by its charge and demonstrate only weak interactions with the {N(CH₃)₃}⁺ group. Such a trend for the RDFs is observed for other grafting densities as well (see section S3.1 of SI). Additionally, we plotted the N-Cl⁻ RDF (see section S4 of SI) for different grafting densities. In Fig. 4(e), we show that for all grafting densities, the values of the locations of the peaks the N-O_w RDF remains smaller than the values of the N-Cl⁻ RDF peaks: this indicates that for the {N(CH₃)₃}⁺ group, water molecules are closer than the Cl⁻ ion. This trend persists even when there is an increase in the grafting density (i.e., there are a greater number Cl⁻ ions in a given volume around the PMETAC brush). The N-O_w RDF starts to rise at a shorter distance than N-Cl⁻ RDF (see section S4 of SI), which also indicates that water molecules and not Cl⁻ ion, is closer to {N(CH₃)₃}⁺ moiety. These information confirm the presence of an intervening water layer between the {N(CH₃)₃}⁺ moiety and Cl⁻ ion; in other words, for the present case, {N(CH₃)₃}⁺ moiety and Cl⁻ ion behave as solvent-separated ion pair. The consequence of such intervening water layer (and the fact that this water layer is very stable) is that the Cl⁻ ions remain excluded from close vicinity of the {N(CH₃)₃}⁺ moiety despite the obvious electrostatic attraction between Cl⁻ and {N(CH₃)₃}⁺. In summary, Figs. 4(a-e) confirm the presence

of distinct water domains around different entities of the PMETA-Cl⁻ ion system: these water domains are localized at disparate average distances from these different entities and are also shared by other entities.

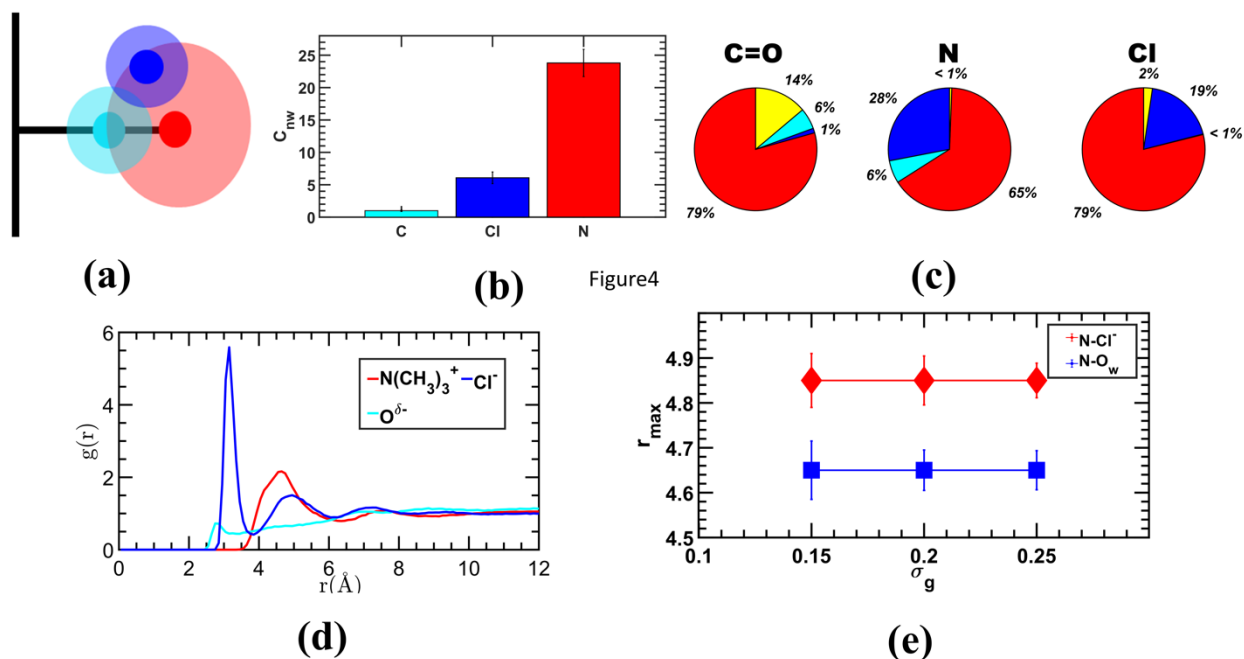


Figure 4. (a) Schematic showing the formation of three distinct water domains around the three moieties [N atom (of the $\{N(CH_3)_3\}^+$ moiety) and C=O group of the PMETAC chain] and Cl⁻ ion. (b) Solvation number around the N atom [of the $\{N(CH_3)_3\}^+$ moiety] and the C=O group of the PMETAC chain and Cl⁻ ion. (c) Pie charts showing the percentage of the water molecules present in the domains around the C=O (left), N atom [of the $\{N(CH_3)_3\}^+$ moiety] (center), and Cl⁻ (right) that are shared by other species. Red, blue and cyan respectively represents the % of shared water molecules only with $N(CH_3)_3\}^+$, Cl⁻ and C=O group. Yellow represents % of water molecules shared with all the moieties. d) N-O_w, Cl⁻-O_w, and O^{δ-}-O_w RDFs. (e) Values of the locations of the peaks (r_{max}) of the N-O_w and N-Cl⁻ RDFs plotted as functions of the PMETAC grafting densities.

The water molecules in these distinct domains formed around the different species demonstrate disparate properties. However, it is important to understand how the charge (or partial charge) of each functional group affects the surrounding water molecules in such an environment: a quantification of the dipole orientation of the water molecules in these domains formed around different species enable us to do that. Figure 5(a) provides the electrical dipole orientation of the water molecules inside these distinct domains. It has been already pointed out above that these water molecules inside these domains are nothing but the water molecules within the 1st solvation shell of the species, namely, the $\{\text{N}(\text{CH}_3)_3\}^+$ and the C=O groups of the PMETAC chains and the Cl^- counterion. The ideal water dipole orientation around hydrophilic anionic and cationic solutes should be 180° and 0° degrees, respectively [see Fig. 5(b)].⁶⁴ Of course, in actual systems, the orientation of the water dipoles deviates from these ideal values on account of the thermal excitation and the energetic penalty associated with the unfavorable positioning (of these water molecules) relative to the adjacent water molecules. On the other hand, depending on the size and the shape of the solute, the dipole orientation of the water molecules around a hydrophobic solute shows a range, but tends to prefer tangential direction for symmetrical entities.^{64,67} For our case ($\sigma_g=0.25$ chains/nm²), the water dipoles around Cl^- ion is mostly oriented around 130°, which is the typical behavior for water molecules present in the first solvation shell of a hydrophilic anion.⁶⁸ It also indicates the water molecules are strongly bound (due to high attraction) to the Cl^- ion and Cl^- ion has a tightly-bound hydration shell. On the other hand, though being cationic, the water dipole orientation around the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety peaks around 75° indicating that the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety triggers an apolar-like hydration. This result highlights the manner in which the effect of the charge of the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety is overwhelmed by the hydrophobic influences of the three methyl (-CH₃) groups. Such apolar hydration-inducing tendencies of the $\{\text{N}(\text{CH}_3)_3\}^+$ entity (of

PMETAC brush) can be surmised from two factors. First, a significant amount of the reported literature indicates the strongly hydrophobic nature of the quaternary amines due to the presence of the hydrophobic methyl groups.^{63,65} Second, in our recent machine learning-based analysis of the water structure inside densely grafted PMETAC brushes, it has been revealed that the $H - O' - O$ angle (here “H” is the hydrogen atom, “O” is the donor oxygen atom, and “O’” is the acceptor oxygen atom), characterizing the water-water hydrogen bonding, gets reduced for the water-water hydrogen bonds (HBs) formed inside the PMETAC brush layer as compared to the water-water HBs formed inside the bulk.⁵⁰ Such a reduction in the $H - O' - O$ angle implies that the water-water HBs become more linear and hence stronger. This phenomenon also indicates water-water attraction strength increases due to weak $\{N(CH_3)_3\}^+$ -water interaction or apolar hydration. On the other hand, the dipole orientation of water molecules within the domain around the C=O group (the C=O demonstrates strongly hydrophilic behavior) of the PMETAC chains is similar to that of water molecules around an anion with high charge density, *i.e.*, very much like that around the Cl^- ion. Such a scenario stems from (1) the presence of the partial negative charges on the O atom of the C=O moiety and (2) the fact that the C=O moiety is a part of the PMETAC chains that are stretched out in a “brush-like” 1D configuration (without any coiling) and that the C=O moiety is somewhat separated from other influencing functional groups of the PMETAC chains (due to the specific structure of the PMETAC chains). *Overall, inside the PMETAC brush layer, there is hydrophilic hydration at one site and apolar hydration at another site.*

It is worthwhile to point out here that the dipole orientation of the water molecules around the $\{N(CH_3)_3\}^+$ moiety is calculated by considering the nitrogen atom as the reference point. We did calculate the same dipole moment of the water molecules around the $\{N(CH_3)_3\}^+$ moiety by considering the hydrogen atoms of the $\{N(CH_3)_3\}^+$ moiety as the reference point. Figure 5(c)

compares the two cases, i.e., the water dipole moments around the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety calculated with N and H atoms as reference points: we see very little change in the dipole moment distribution between these two cases. Also, we shall like to point out that the apolar hydration of the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety stems from the fact that the charges of hydrogen atoms present in the moiety ($0.1e$) is much less than the charges of a water molecule. Therefore, water molecules interacts weakly with the $\{\text{N}(\text{CH}_3)_3\}^+$ functional group. Also, there are several experimental studies^{62,69-71} that have specifically pointed out the apolar hydration of the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety [or more specifically, the apolar hydration of the $\{\text{N}(\text{CH}_3)_4\}^+$ ion, i.e., the Tetramethylammonium (TMA) ion].

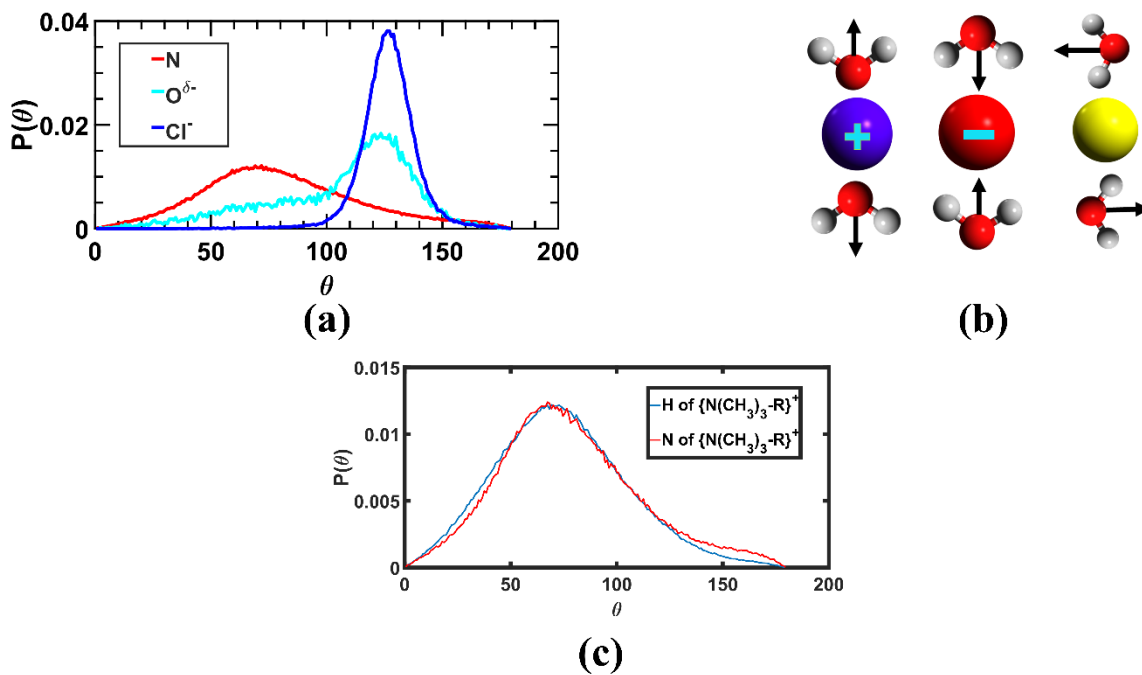


Figure 5. (a) Probability distribution of the orientation angle of the water dipole for the water in the three separate domains, namely water around the N atom [of the $\{N(CH_3)_3\}^+$ moiety], C=O group, and Cl^- ion for a grafting density of $\sigma_g = 0.25$ chains/nm² (results for $\sigma_g = 0.15$ chains/nm² and $\sigma_g = 0.2$ chains/nm² have been provided in section S5 of the SI). (b) Schematic showing the orientation of a water molecule around an ideal cation, an ideal anion, and a hydrophobic solute. (c) Comparison of the probability count distribution of dipole orientation of water molecules in the vicinity of the $\{N(CH_3)_3\}^+$ moiety considering the N atom or the H atoms of the $\{N(CH_3)_3\}^+$ moiety as the reference point. The results are for a grafting density of $\sigma_g = 0.25$ chains/nm².

Finally, in Fig. 6, we provide the probability count distribution (for $\sigma_g=0.25$ chain/nm²) of the tetrahedral order parameter (given by Errington and Debendetti⁷²) of the water molecules in these different domains, or the water molecules associated with the solvation shells of the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety and the C=O group of the PMETAC chains and the Cl⁻ counterions. Such tetrahedral order parameter (q) gives a measure of the structural order: the greater the value of q more structured are the water molecules (see section S6 of SI for more details). A high tetrahedral order parameter (closer to 1) means the solvating water molecules are in a perfect tetrahedron (like ice); that is the reason for which for a greater value of the order parameter, the water molecules are considered to be “more structured”. The water molecules in the solvation shell (or the water domain) of the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety show a greater value of q as compared to the water molecules in the solvation shell or water domain of the Cl⁻ counterion or the C=O group. As mentioned before, the charges of hydrogen atoms present in the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety ($0.1e$) is much lower than water molecules. Therefore, water molecules try to form relatively stronger interactions with other water molecules than the moiety itself, resulting in enhanced q parameter of the water molecules present in the domain around the $\{\text{N}(\text{CH}_3)_3\}^+$ group. On the other hand, the significantly low tetrahedral order parameter of the hydration shell water around the C=O group, which signifies reduced structuring of water molecules around the C=O group, can be attributed partly to the partial charges of the C=O group and the resulting hydrophilic hydration (such hydration, stemming from the strongly hydrophilic behavior of the C=O group, leads to stronger C=O-water interactions causing a reduced water structural order) and partly to the presence of other methyl groups surrounding the C=O group. The low tetrahedral ordering of the water molecules around the Cl⁻ atom can be primarily attributed to its high charge density and its resulting interactions with the surrounding water molecules (such interactions distort the water tetrahedron more and consequently the q

parameter decreases). We also studied the tetrahedral order parameter of the water molecules around these different entities for other grafting densities ($\sigma_g=0.20$ and 0.15 chains/nm²): the results are provided in the SI and demonstrate similar behavior. Moreover, an increase in the grafting density weakly decreases the tetrahedral order parameter, i.e., reduces the extent of water structuring: this is evident in a small decrease in the fraction of the water molecules with greater q values and a slight leftward shift of the peak in the $P(q)$ -vs- q distribution [see Fig. 6-inset and Fig. S7 in the SI].

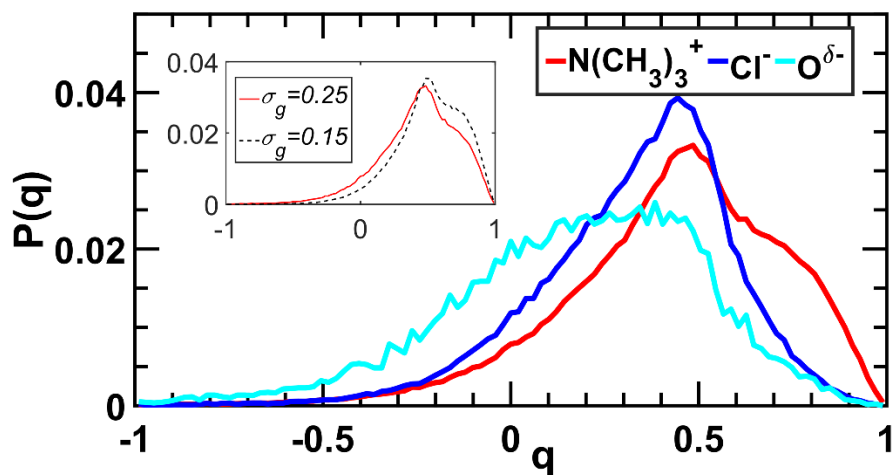


Figure 6. Variation of the tetrahedral order parameter for the water in the three separate domains, namely water around $\{\text{N}(\text{CH}_3)_3\}^+$ group and C=O group of the PMETAC chain and Cl^- ion. These results are all for a grafting density of $\sigma_g = 0.25$ chains/nm². (Inset) Comparison in the variation of the tetrahedral order parameter for the water in the domain formed around $\{\text{N}(\text{CH}_3)_3\}^+$ group between the cases of $\sigma_g = 0.25$ chains/nm² and $\sigma_g = 0.15$ chains/nm².

Structure and Properties of the PMETAC-Brush-Supported Cl⁻ Counterions

The multiple water domains inside the PMETAC brush layers involve the counterions as well, given the fact that one of the domains is around the Cl⁻ ion. Therefore, a complete description of the problem must involve a detailed accounting of the counterion properties and behaviors inside the PMETAC brush layer. First, in Fig. 7(a), we plot the dimensionless counterion number density as a function of the grafting density of the PMETAC brushes. An increase in the grafting density will imply a greater number of charged monomers for a given volume; therefore, in order to balance the monomer charges, there will be a larger number of counterions in a given volume. This ensures that the counterion number density increases as a function of the grafting density. On the other hand, in Fig. 3, we have pointed out that the water density *decreases* with an increase in the grafting density. Despite such opposite trends, the relative distances between the Cl⁻ ion and N atom and the N atom and water molecule remain the same for all values of the grafting density, with N-O_w RDF peak distance being smaller than the N-Cl⁻ RDF peak distance for all grafting densities [see Fig. 4(e)]. Such trends in the N-O_w and N-Cl⁻ RDFs with the PMETAC grafting density, despite the grafting density influencing the counterion and water concentrations differently, can be mainly attributed to the stable intervening water layer between {N(CH₃)₃}⁺ and Cl⁻ that forces the Cl⁻ ion to remain at large-enough distance from the {N(CH₃)₃}⁺ group despite the electrostatic attraction between the {N(CH₃)₃}⁺ moiety and Cl⁻ ions.

We next attempt to quantify the mobility of the counterions inside the PMETAC brush layer. For that purpose, we calculated the probability distribution function of the distances traveled by a Cl⁻ counterion in 40 picoseconds as a function of the PMETAC brush grafting density [see Fig. 7(b)]. We compare this result with the probability distribution function of the distances traveled by a Na⁺ counterion inside a PAA brush layer. All-atom MD simulation data for the PAA

brush layer that has been used for this figure has been generated from the parameters of our previous study.⁴² The grafting density of the PAA brush layer is 1.67 chains/nm², which tantamounts to a brush-brush separation distance of $l = \sqrt{\frac{1}{1.67/\text{nm}^2}} = 7.73\text{\AA}$. On the other hand, the maximum grafting density considered for the PMETAC chains is 0.25 chains/nm² that converts to a brush-brush separation distance of $l = \sqrt{\frac{1}{0.25/\text{nm}^2}} = 20\text{\AA}$. However, there are bulky side chains on two sides of the PMETAC chains, ensuring an effective reduction of the brush-brush separation distance for the PMETAC brushes. Interestingly, the number density of the solvating water molecules for these two separate cases, namely the case of PAA brush layer with a grafting density of 1.67 chains/nm² and the case of the PMETAC brush layer with a grafting density of 0.25 chains/nm², closely resemble with one another [see Fig. 7(c)]. This implies both these systems, with disparate grafting densities, exert a similar degree of confinement to the solvating water.⁴⁶ Accordingly, we can hypothesize that the effective chain-chain separation distance for the PMETAC brushes (for a grafting density of 0.25 chains/nm²), on account of the bulky side chains, will be similar to the chain-chain separation distance of the PAA brushes (for a grafting density of 1.67 chains/nm²). Despite that, we find that the distance traversed by the Cl⁻ ions inside the PMETAC brush layer (for a grafting density of 0.25 chains/nm²) is several times greater than the distances traversed by the Na⁺ ions inside the PAA brush layer (for a grafting density of 1.67 chains/nm²) [see Fig. 7(b)]. This confirms the significantly large mobility of the Cl⁻ counterions inside the PMETAC brush layer and this can be attributed to the weak attraction of the Cl⁻ ions to the {N(CH₃)₃}⁺ groups of the PMETAC chains owing to the failure of the Cl⁻ ions to come to close enough proximity of the {N(CH₃)₃}⁺ group, as confirmed by Fig. 4(e). Additionally, we calculated the probability distribution for $\sigma_g=0.15$ and 0.2 chains/nm² [shown in Fig. 7(d)], which shows a

slight increase in counterion mobility due to the reduction of the steric hindrance at lower grafting densities. Therefore, it can be concluded that the chemical nature of the confining medium plays a greater role on dictating counterion mobility than the degree of confinement (or grafting density). In order to further showcase the enhanced mobilities of the counterions inside the PMETAC layers, we plot the MSD (mean square displacement) of the counterions inside the PMETAC brush (for different grafting densities) and the PAA brush (with a grafting density that enables a similar degree of confinement for the solvating water as the PMETAC brush layer with a grafting density of $\sigma_g = 0.25$ chains/nm²) [see Fig. 7(e)]. This MSD is calculated using eqs.(1) below:

$$MSD(t) = \langle (r(t) - r_0)^2 \rangle. \quad (1)$$

$$D = \frac{1}{6} \lim_{t \rightarrow \infty} \frac{d}{dt} \langle (r(t) - r_0)^2 \rangle. \quad (2)$$

In eqs.(1,2), $r(t)$ is the position of the a particle at time t , r_0 is the initial position of the particle, and $\langle \rangle$ denotes the average over all the particles and different initial positions, and D is the diffusion coefficient. The MSD values clearly demonstrate the significantly large mobilities of the counterions inside the PMETAC brush layer (especially for the case of weak grafting density values). For PAA it shows that the Na⁺ atoms are completely immobilized and are fluctuating in their respective positions. Table 1 shows the diffusion coefficients calculated for all the systems. The diffusion coefficient (D) has been calculated from the Einstein formula by using the slope of the MSD curve ⁸¹ (Eq. 2). From the table we can see that the diffusion coefficient for PMETAC brushes with a grafting density of $\sigma_g = 0.25$ chains/nm² is significantly higher than PAA brushes. Therefore, for a similar degree of confinement, despite Na⁺ ion having lower mass (23 amu) than Cl⁻ (35.5 amu), the mobility and diffusivity of the Na⁺ ions inside PAA-brush-Na⁺-counterion

system is much less than the mobility and diffusivity of the Cl^- ions inside PMETAC-brush- Cl^- counterion system.

Finally, in Fig. 8, we compare the number density distribution of the N atom [of the $\{\text{N}(\text{CH}_3)_3\}^+$ groups] and Cl^- ions and observe that there is very little difference between these number densities within the brush layer. Hence, we can infer that most of the Cl^- counterions remain inside the brush layer despite having high mobility. Therefore, we can hypothesize that inside the brush layer, the counterions are not strongly attracted to a fixed oppositely charged site on the brushes, but rather move around inside the brush layer without actually leaving the brush layer.

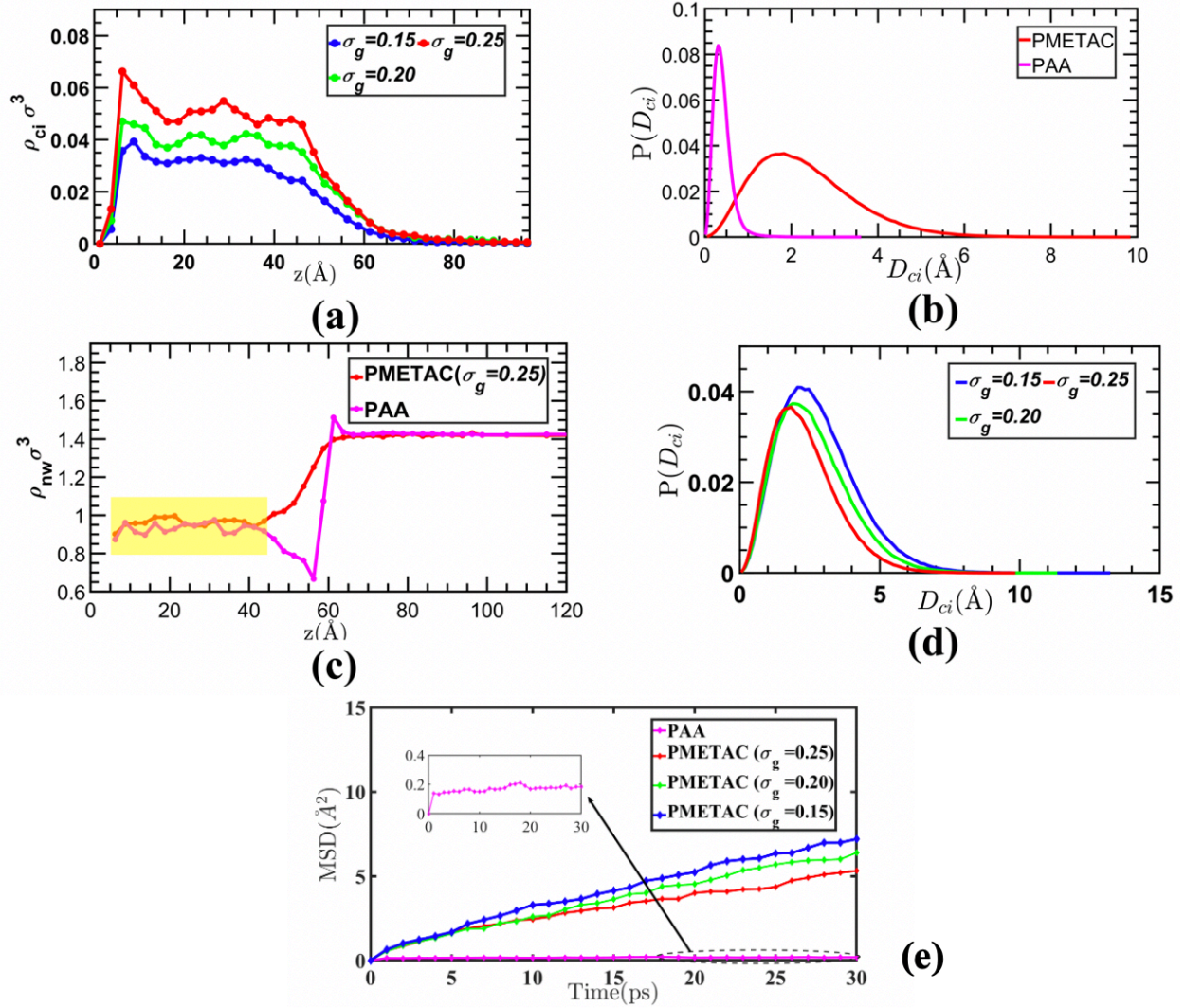


Figure 7. (a) Dimensionless density distribution of the Cl^- counterions inside and outside the PMETAC brush layer as functions of the PMETAC brush grafting densities (the maximum uncertainty among the points reported in the plot being $\Delta\delta_{\text{max}} = \pm 0.0403 \rho_{\text{ci}} \sigma^3$). (b) Distribution of the average distances traversed by the counterions for PAA and PMETAC. The results (of the PMETAC) are compared with the average distances traversed by a Na^+ ion inside the PAA brush layer having $\sigma_g = 1.67$ chains/ nm^2 . (c) Dimensionless water density distribution of PMETAC brush layer ($\sigma_g = 0.25$ chains/ nm^2) and PAA brush layer ($\sigma_g = 1.67$ chains/ nm^2) with Na^+ counterions (the maximum uncertainty among the points reported in the plot being $\Delta\delta_{\text{max}} = \pm 0.136 \rho_{\text{nw}} \sigma^3$). The sampling region (5\AA to 45\AA from lower wall) is shaded in yellow. (d) Distribution of the average

distances traversed by the counterions for of PMETAC for different grafting densities ($\sigma_g=0.15,0.2$ and 0.25 chains/nm²). (e) MSD variation of the counterions inside the PMETAC brush layer (counterions are Cl⁻ ions) and the PAA brush layer (counterions are Na⁺ ions). The results are shown for the PMETAC brush layer with three different grafting density values, while for the PAA brush layer the grafting is $\sigma_g=1.67$ chains/nm² (i.e., a grafting density that enables a similar degree of confinement for the solvating water as the PMETAC brush layer with a grafting density of $\sigma_g=0.25$ chains/nm²). In the inset of Fig. 7(e), the MSD plot for the Na⁺ ions inside the PAA brush layer have been magnified.

Table 1: Diffusivities (D) of the Na^+ ions inside PAA-brush- Na^+ -counterion system and the Cl^- ions inside PMETAC-brush- Cl^- -counterion system.

Counterion	$D \times 10^{-10}$ (m^2/s)
Cl^- (inside PMETAC brushes, $\sigma_g = 0.15$ chains/ nm^2)	3.61 ± 0.3626
Cl^- (inside PMETAC brushes, $\sigma_g = 0.20$ chains/ nm^2)	3.09 ± 0.3339
Cl^- (inside PMETAC brushes, $\sigma_g = 0.25$ chains/ nm^2)	2.44 ± 0.266
Na^+ (inside PAA brushes, $\sigma_g = 1.67$ chains/ nm^2)	0.016 ± 0.0235

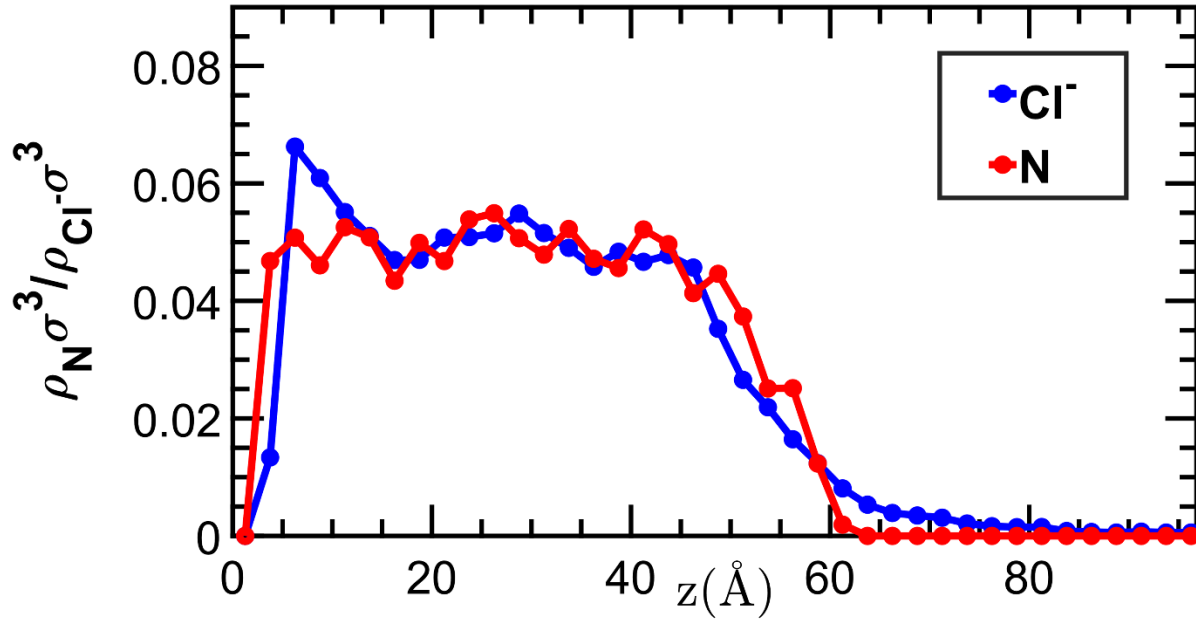


Figure 8. Dimensionless density distribution of the Cl⁻ counterions and N atoms [of the {N(CH₃)₃}⁺ groups] (of the PMETAC brushes) inside and outside the PMETAC brush layer (results are shown for a grafting density of 0.25 chains/nm²) and the maximum uncertainty among the points reported in the plot being $\Delta\delta_{max} = \pm 0.0341 \rho_{N/Cl} \sigma^3$.

CONCLUSIONS

We have studied the microstructure of water and properties of counterions inside the PMETAC brushes using all-atom MD simulations. We reveal that inside water-solvated PMETAC brushes there are multiple water domains, centered around distinct moieties. These water domains overlap, although the specific architecture of the PMETAC brushes ensures that the water molecules inside these domains retain the influence of the moiety triggering these water domains. Water molecules in these domains demonstrate distinctly different properties that point to PMETAC brushes triggering hydrophilic hydration at one site (C=O group) and apolar hydration (with water molecules showing greater structural order) at another site ($\{\text{N}(\text{CH}_3)_3\}^+$ group). Water forms a stable intervening layer between the $\{\text{N}(\text{CH}_3)_3\}^+$ moiety and the Cl^- ion, thereby preventing the Cl^- ion to come in close proximity to the $\{\text{N}(\text{CH}_3)_3\}^+$ group despite strong electrostatic attraction. Such a scenario ensures a significantly high Cl^- ion mobility inside the PMETAC brush layer. The C=O group of the PMETAC chain, on the other hand, demonstrates strongly hydrophilic behavior and the dipole orientation of the water molecules in the water domain around the C=O group resembles that around an anion with high charge density. Overall, our findings unravel highly intriguing water and ion behavior around a very well-studied cationic brush system and we anticipate that these findings will motivate newer discoveries and applications of PE brush grafted systems. For example, this study establishes a most unique scenario where counterions are highly mobile inside a highly charged brush layer with large grafting density: this is usually not the case for highly charged brushes. Such large mobilities of the counterions, for example, can be successfully leveraged to trigger stronger electroosmotic transport⁴⁷ and more efficient electrokinetic energy generation.⁴⁹

Supporting Information

MD simulation details; Results showing the time evolution and autocorrelation function of brush height; Results showing the solvation shell number, percentage and water-moiety RDF; $\text{N}(\text{CH}_3)_3^+$ - Cl^- and $\text{N}(\text{CH}_3)_3^+$ - O_w radial distribution functions (RDFs) for different grafting densities; Water dipole orientation around different moieties for different grafting densities; Tetrahedral order parameter of water around different moieties for different grafting densities.

Acknowledgement: This work has been supported by the Department of Energy Office of Science grant DE-SC0017741. The authors also gratefully acknowledge the Zaratan High-Performance Computing cluster at the University of Maryland for providing necessary computational resources.

References:

1. Zhulina, E. B.; Rubinstein, M. Lubrication by Polyelectrolyte Brushes. *Macromolecules* **2014**, *47*, 5825-5838.
2. Das, S.; Banik, M.; Chen, G.; Sinha, S.; Mukherjee, R. Polyelectrolyte Brushes: Theory, Modelling, Synthesis and Applications. *Soft Matter* **2015**, *11*, 8550-8583.
3. Chen, W. L.; Cordero, R.; Tran, H.; Ober, C. K. Polymer Brushes: Novel Surfaces for Future Materials. *Macromolecules* **2017**, *50*, 4089-4113.
4. Li, M.; Pester, C.W. Mixed Polymer Brushes for “Smart” Surfaces. *Polymers* **2020**, *12*, 1553.
5. Yang, W.; Zhou, F. Polymer Brushes for Antibiofouling and Lubrication. *Biosurface And Biotribology* **2017**, *3*, 97-114
6. Ali, M.; Yameen, B.; Cervera, J.; Ramírez, P.; Neumann, R.; Ensinger, W.; Knoll, W.; Azzaroni, O. Layer-by-layer Assembly of Polyelectrolytes into Ionic Current Rectifying Solid-state Nanopores: Insights from Theory and Experiment. *J. Am. Chem. Soc.* **2010**, *132*, 8338–8348.
7. Yameen, B.; Ali, M.; Neumann, R.; Ensinger, W.; Knoll, W.; Azzaroni, O. Single Conical Nanopores Displaying pH-Tunable Rectifying Characteristics. Manipulating Ionic Transport with Zwitterionic Polymer Brushes. *J. Am. Chem. Soc.* **2009**, *131*, 2070.
8. Ali, M.; Ramirez, P.; Mafé, S.; Neumann, R.; Ensinger, W. A pH-Tunable Nanofluidic Diode with a Broad Range of Rectifying Properties. *ACS Nano* **2009**, *3*, 603–608.
9. Cao, M.; Wang, H.; Tang, H.; Zhao, D.; Li, Y. Enzyme-Encapsulated Zeolitic Imidazolate Frameworks Formed Inside the Single Glass Nanopore: Catalytic Performance and Sensing Application. *Anal. Chem.* **2021**, *93*, 12257–12264.

10. Ali, M.; Ahmed, I.; Nasir, S.; Ramirez, P.; Niemeyer, C. M.; Mafe, S.; Ensinger, W. Ionic Transport through Chemically Functionalized Hydrogen Peroxide-Sensitive Asymmetric Nanopores. *ACS Appl. Mater. Interfaces* **2015**, *7*, 19541–19545.
11. Yang, Q.; Li, L.; Zhao, F.; Han, H.; Wang, W.; Tian, Y.; Wang, Y.; Ye, Z.; Guo, X. Hollow Silica-Polyelectrolyte Composite Nanoparticles for Controlled Drug Delivery. *J. Mater. Sci.* **2019**, *54*, 2552–2565.
12. Jiang, R.; Lu, X.; Yang, M.; Deng, W.; Fan, Q.; Huang, W. Monodispersed Brush-Like Conjugated Polyelectrolyte Nanoparticles with Efficient and Visualized SiRNA Delivery for Gene Silencing. *Biomacromolecules* **2013**, *14*, 3643–3652.
13. ShamsiJazeyi, H.; Miller, C. A.; Wong, M. S.; Tour, J. M.; Verduzco, R. Polymer-coated Nanoparticles for Enhanced Oil Recovery. *J. Appl. Polym. Sci.* **2014**, *131*, 40576.
14. Liu, G.; Cai, M.; Wang, X.; Zhou, F.; Liu, W. Core–Shell–Corona-Structured Polyelectrolyte Brushes-Grafting Magnetic Nanoparticles for Water Harvesting. *ACS Appl. Mater. Interfaces* **2014**, *6*, 11625–11632.
15. Chen, L.; Merlitz, H.; He, S.; Wu, C. X.; Sommer, J. W. Polyelectrolyte Brushes: Debye Approximation and Mean-Field Theory. *Macromolecules* **2011**, *44*, 3109–3116.
16. Borisov, O. V.; Zhulina, E. B. Conformations of Polyelectrolyte Molecular Brushes: A Mean-Field Theory. *J. Chem. Phys.* **2018**, *149*, 184904.
17. Zhulina, E. B.; Wolterink, J. K.; Borisov O. V.; Screening Effects in a Polyelectrolyte Brush: Self-Consistent-Field Theory. *Macromolecules* **2000**, *33*, 4945–4953.
18. Okrugin, B. M.; Richter, R. P.; Leermakers, F. A. M.; Neelov, I. M.; Borisov O. V.; Zhulina, E. B. Structure and Properties of Polydisperse Polyelectrolyte Brushes Studied by Self-Consistent Field Theory. *Soft Matter* **2018**, *14*, 6230-6242.

19. Sachar, H. S.; Sivasankar, V. S.; Das, S. Revisiting the Strong Stretching Theory for Ph-Responsive Polyelectrolyte Brushes: Effects of Consideration of Excluded Volume Interactions and An Expanded Form of The Mass Action Law. *Soft Matter* **2019**, *15*, 559-574.
20. Etha, S. A.; Sivasankar, V. S.; Sachar, H. S.; Das, S. Strong Stretching Theory for Ph-Responsive Polyelectrolyte Brushes in Large Salt Concentrations. *Phys. Chem. Chem. Phys.*, **2020**, *22*, 13536-13553.
21. Yu, J.; Jackson, N. E.; Xu, X.; Brettmann, B. K.; Ruths, M.; de Pablo, J. J.; Tirrell, M. Multivalent Ions induce Lateral Structural Inhomogeneities in Polyelectrolyte Brushes. *Sci. Adv.* **2017**, *3*, eaao1497.
22. Jackson, N. E.; Brettmann, B. K.; Vishwanath, V.; Tirrell, T.; de Pablo, J. J. Comparing Solvophobic and Multivalent Induced Collapse in Polyelectrolyte Brushes. *ACS Macro Lett.* **2017**, *6*, 155–160.
23. Yuan, J.; Antila, S. H.; Luitjen, E. Structure of Polyelectrolyte Brushes on Polarizable Substrates. *Macromolecules* **2020**, *53*, 2983–2990.
24. Luo, Y.; Wang, C.; Pang, A.; Zhang, X.; Wang, D.; Lu, X. Low-Concentration Salt Solution Changes the Interfacial Molecular Behavior of Polyelectrolyte Brushes. *Macromolecules* **2021**, *54*, 6006–6013.
25. Elliott, I. G.; Kuhl, T. L.; Faller, R. Molecular Simulation Study of the Structure of High Density Polymer Brushes in Good Solvent. *Macromolecules* **2010**, *43*, 9131–9138.
26. Verso, F. L.; Egorov, S. A.; Milchev, A.; Binder, K. Spherical Polymer Brushes Under Good Solvent Conditions: Molecular Dynamics Results Compared to Density Functional Theory. *J. Chem. Phys.* **2010**, *133*, 184901.

27. Smook, L. A.; van Eck, G. C. R.; de Beer, S. Friends, Foes, and Favorites: Relative Interactions Determine How Polymer Brushes Absorb Vapors of Binary Solvents. *Macromolecules* **2020**, *53*, 10898-10906.
28. Mensink, L. I. S.; de Beer, S.; Snoeijer, J. H. The Role of Entropy in Wetting of Polymer Brushes. *Soft Matter* **2021**, *17*, 1368-1375.
29. Glišić, I.; Eck, G. C. R. V.; Smook, L. A.; de Beer, S. Enhanced Vapor Sorption in Block and Random Copolymer Brushes. *Soft Matter* **2022**, *18*, 8398-8405.
30. Sethuraman, V.; McGovern, M.; Morse, D. C.; Dorfman, K. D. Influence of Charge Sequence on the Adsorption of Polyelectrolytes to Oppositely-Charged Polyelectrolyte Brushes. *Soft Matter* **2019**, *15*, 5431-5442.
31. Yu, J.; Jackson, N. E.; Xu, X.; Morgenstern, M.; Kaufman, Y.; de Pablo, J. J.; Tirrell M. Multivalent Counterions Diminish the Lubricity of Polyelectrolyte Brushes. *Science* **2018**, *360*, 1434-1438.
32. Farina, R.; Laugel, N.; Pincus, P.; Tirrell, M. Brushes of Strong Polyelectrolytes in Mixed Mono- And Tri-Valent Ionic Media at Fixed Total Ionic Strengths. *Soft Matter*, **2013**, *9*, 10458-10472.
33. Yu, J.; Mao, J.; Yuan, G.; Satija, S.; Chen, W.; Tirrell, M. The Effect of Multivalent Counterions To the Structure of Highly Dense Polystyrene Sulfonate Brushes. *Polymer* **2016**, *98*, 4488-453.
34. Faubel, J. L.; Patel, R. P.; Wei, W.; Curtis, J. E.; Brettmann, B. K. Giant Hyaluronan Polymer Brushes Display Polyelectrolyte Brush Polymer Physics Behavior. *ACS Macro Lett.* **2019**, *8*, 1323–1327.

35. Willott, J. D.; Humphreys, B. A.; Webber, G. B.; Wanless, E. J.; de Vos, W. M. Combined Experimental and Theoretical Study of Weak Polyelectrolyte Brushes in Salt Mixtures. *Langmuir* **2019**, *35*, 2709–2718.
36. Dahal, U. R.; Wang, Z.; Dormidontova, E. E. Hydration and Mobility of Poly(ethylene oxide) Brushes. *Macromolecules* **2017**, *50*, 6722–6732.
37. Dormidontova, E.; Chen, G. PEO-Grafted Gold Nanopore: Grafting Density, Chain Length, and Curvature Effects. *Macromolecules* **2022**, *55*, 5222–5232.
38. Dahal, U.; Dormidontova, E. Chain Conformation and Hydration of Polyethylene Oxide Grafted to Gold Nanoparticles: Curvature and Chain Length Effect. *Macromolecules* **2020**, *53*, 8160–8170.
39. Uehara, S.; Liu, J.; Xu, J.; Ootani, Y.; Ozawa, N.; Kubo, M. Effect of Fluorination on Friction Forces between Concentrated Polymer Brushes in the Dry State: All-atom Molecular Dynamics Simulation Study. *Chem. Lett.* **2018**, *37*, 784-786.
40. Yagasaki, T.; Matubayasi, N. Molecular Dynamics Study of the Interactions Between a Hydrophilic Polymer Brush on Graphene and Amino Acid Side Chain Analogues in Water. *Phys. Chem. Chem. Phys.* **2022**, *24*, 22877-22888.
41. Sachar, H. S.; Pial, T. H.; Desai, P. R.; Etha, S. A.; Wang, Y.; Chung, P. W.; Das, S. Densely Grafted Polyelectrolyte Brushes Trigger “Water-in-Salt”-like Scenarios and Ultraconfinement Effect. *Matter* **2020**, *2*, 1509–1521.
42. Sachar, H. S.; Pial, T. H.; Chava, B. S.; Das, S. All-atom Molecular Dynamics Simulations of Weak Polyionic Brushes: Influence of Charge Density on the Properties of Polyelectrolyte Chains, Brush-supported Counterions, and Water Molecules. *Soft Matter* **2020**, *16*, 7808-7822.

43. Sachar, H. S.; Chava, B. S.; Pial, T. H.; Das, S. All-Atom Molecular Dynamics Simulations of the Temperature Response of Densely Grafted Polyelectrolyte Brushes. *Macromolecules* **2021**, *54*, 6342–6354.
44. Sachar, H. S.; Chava, B. S.; Pial, T. H.; Das, S. Hydrogen Bonding and Its Effect on the Orientational Dynamics of Water Molecules inside Polyelectrolyte Brush-Induced Soft and Active Nanoconfinement. *Macromolecules* **2021**, *54*, 2011–2021.
45. Pial, T. H.; Sachar, H. S.; Das, S. Quantification of Mono- and Multivalent Counterion-Mediated Bridging in Polyelectrolyte Brushes. *Macromolecules* **2021**, *54*, 4154–4163.
46. Pial, T. H.; Prajapati, M.; Chava, B. S.; Sachar, H. S.; Das, S. Charge-Density-Specific Response of Grafted Polyelectrolytes to Electric Fields: Bending or Tilting?. *Macromolecules* **2022**, *55*, 2413–2423.
47. Pial, T. H.; Sachar, H. S.; Desai, P. R.; Das, S. Overscreening, Co-Ion-Dominated Electroosmosis, and Electric Field Strength Mediated Flow Reversal in Polyelectrolyte Brush Functionalized Nanochannels. *ACS Nano* **2021**, *15*, 6507–6516.
48. Pial, T. H.; Das, S. Specific Ion and Electric Field Controlled Diverse Ion Distribution and Electroosmotic Transport in a Polyelectrolyte Brush Grafted Nanochannel. *J. Phys. Chem. B* **2022**, *126*, 10543–10553.
49. Sachar, H. S.; Pial, T. H.; Sivasankar, V. S.; Das, S. Simultaneous Energy Generation and Flow Enhancement (Electroslippage Effect) in Polyelectrolyte Brush Functionalized Nanochannels. *ACS Nano* **2021**, *15*, 17337–17347.
50. Pial, T. H.; Das, S. Machine Learning Enabled Quantification of the Hydrogen Bonds Inside the Polyelectrolyte Brush Layer Probed Using All-Atom Molecular Dynamics Simulations. *Soft Matter* **2022**, *18*, 8945–8951.

51. Santos, D. E. S.; Li, D.; Ramstedt, M.; Gautrot, J. E.; Soares, T. A. Conformational Dynamics and Responsiveness of Weak and Strong Polyelectrolyte Brushes: Atomistic Simulations of Poly (Dimethyl Aminoethyl Methacrylate) and Poly(2-(Methacryloyloxy)Ethyl Trimethylammonium Chloride). *Langmuir* **2019**, *35*, 5047-5049.
52. Wu, B.; Wang, X.; Yang, J.; Hua, Z.; Tian, K.; Kou, R.; Zhang, J.; Ye, S.; Luo, Y.; Craig, V. S. J. et al. Reorganization of Hydrogen Bond Network Makes Strong Polyelectrolyte Brushes Ph-Responsive. *Sci. Adv.* **2016**, *2*, e1600579.
53. Chu, X.; Yang, J.; Liu, G.; Zhao, J. Swelling Enhancement of Polyelectrolyte Brushes Induced By External Ions. *Soft Matter* **2014**, *10*, 5568-5578.
54. Dahal, U.; Dormidontova, E. E. Chain Conformation and Hydration of Polyethylene Oxide Grafted to Gold Nanoparticles: Curvature and Chain Length Effect. *Macromolecules* **2020**, *53*, 8160–8170.
55. Thompson, A. P.; Aktulga, H. M.; Berger, R.; Bolintineanu, D. S.; Brown, W. M.; Crozier, P. S.; in 't Veld, P. J.; Kohlmeyer, A.; Moore, S. G.; Nguyen, T. D. et al. LAMMPS - A Flexible Simulation Tool For Particle-Based Materials Modeling At The Atomic, Meso, And Continuum Scales. *Comput. Phys. Commun.* **2022**, *271*, 108171.
56. Jewett, A. I.; Stelter, D.; Lambert, J.; Saladi, S. M.; Roscioni, O. M.; Ricci, M.; Autin, L.; Maritan, M.; Bashusqeh, S. M.; Keyes, T. et al. Moltemplate: A Tool for Coarse-Grained Modeling of Complex Biological Matter and Soft Condensed Matter Physics. *J. Mol. Biol.* **2021**, *433*, 166841.
57. Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.

58. Pial, T. S.; Das, S. Machine Learning Enabled Quantification of The Hydrogen Bonds Inside the Polyelectrolyte Brush Layer Probed Using All-Atom Molecular Dynamics Simulations. *Soft Matter* **2022**, *18*, 8945-8951.
59. Ghobadi, A. F.; Jayaraman, A. Effects of Polymer Conjugation on Hybridization Thermodynamics of Oligonucleic Acids. *J. Phys. Chem. B* **2016**, *120*, 9788–9799.
60. Joung, I. S.; Cheatham, T. E. III. Determination of Alkali and Halide Monovalent Ion Parameters for Use in Explicitly Solvated Biomolecular Simulations. *J. Phys. Chem. B* **2008**, *112*, 9020–9041.
61. Csajka, F. S.; Seidel, C. Strongly Charged Polyelectrolyte Brushes: A Molecular Dynamics Study. *Macromolecules* **2000**, *33*, 2728–2739.
62. Turner, J.; Soper, A. K.; Finney, J. L. A Neutron-Diffraction Study of Tetramethylammonium Chloride In Aqueous Solution. *Mol. Phys.* **1990**, *70*, 679-700.
63. Hawlicka, E.; Dlugoborski, T. Molecular Dynamics Simulations of The Aqueous Solution of Tetramethylammonium Chloride. *Chem. Phys. Lett.* **1997**, *268*, 325-330.
64. García-Tarrés, L.; Guàrdia, E. Hydration and Dynamics of a Tetramethylammonium Ion in Water: A Computer Simulation Study. *J. Phys. Chem. B* **1998**, *102*, 7448–7454.
65. Biswas, A.; Priyadarshini, A.; Malik, B. S. Dynamics and Spectral Response of Water Molecules around Tetramethylammonium Cation. *J. Phys. Chem. B* **2019**, *123*, 8753–8766.
66. Mancinelli, R.; Botti, A.; Bruni, F.; Ricci, M. A.; Soper, A. K. Hydration of Sodium, Potassium, and Chloride Ions in Solution and the Concept of Structure Maker/Breaker. *J. Phys. Chem. B* **2007**, *111*, 13570–13577.

67. Vaisman, I. I.; Brown, F. K.; Tropsha, A. Distance Dependence of Water Structure around Model Solutes. *J. Phys. Chem.* **1994**, *98*, 5559–5564.
68. Zhou, J.; Lu, X.; Wang, Y.; Shi, J. Molecular Dynamics Study on Ionic Hydration. *Fluid Phase Equilib.* **2002**, *194-197*, 257-270.
69. Nilsson, E. J.; Alfredsson, V.; Bowron, D. T.; Edler, K. J. A Neutron Scattering and Modelling Study of Aqueous Solutions of Tetramethylammonium and Tetrapropylammonium Bromide. *Phys. Chem. Chem. Phys.*, **2016**, *18*, 11193-11201.
70. Van der post, S. T.; Scheidelaar, S.; Bakker, H. J. Water Dynamics in Aqueous Solutions of Tetra-n-alkylammonium Salts: Hydrophobic and Coulomb Interactions Disentangled. *J. Phys. Chem. B* **2013**, *117*, 15101–15110.
71. Turner, J. Z.; Soper, A. K.; Finney, J. L. Ionic versus Apolar Behavior of the Tetramethylammonium Ion in Water. *J. Chem. Phys.* **1995**, *102*, 5438–5443.
72. Duboué-Dijon, E.; Laage, D. Characterization of the Local Structure in Liquid Water by Various Order Parameters. *J. Phys. Chem. B* **2015**, *119*, 8406–8418.
73. Varanasi, S. R.; Guskova, O. A.; John, A.; Sommer, J.-U. Water around Fullerene Shape Amphiphiles: A Molecular Dynamics Simulation Study of Hydrophobic Hydration. *J. Chem. Phys.* **2015**, *142*, 224308.
74. Coe, M. K.; Evans, R.; Wilding, N. B. Understanding the Physics of Hydrophobic Solvation. *J. Chem. Phys.* **2023**, *158*, 034508.
75. Grabowska, J.; Kuffel, A.; Zielkiewicz, J. Revealing the Frank–Evans “Iceberg” Structures within the Solvation Layer around Hydrophobic Solutes. *J. Phys. Chem. B* **2021**, *125*, 1611–1617.

76. Frank, H. S.; Evans, M. W. Free Volume and Entropy in Condensed Systems III. Entropy in Binary Liquid Mixtures; Partial Molal Entropy in Dilute Solutions; Structure and Thermodynamics in Aqueous Electrolytes. *J. Chem. Phys.* 1945, *13*, 507-532.
77. Montagna, M.; Sterpone, F.; Guidoni, L. Structural and Spectroscopic Properties of Water around Small Hydrophobic Solutes. *J. Phys. Chem. B* **2012**, *116*, 11695–11700.
78. Jerie, K., Baranowski, A., Jákli, G.; Gliński, J. Structure of Aqueous Solutions of Tetraethylammonium Chloride Investigated by Positron Annihilation and Ultrasonic Methods. *J. Radioanal. Nucl. Chem.* **1999**, *240*, 223–229.
79. Galamba, N. Water's Structure Around Hydrophobic Solutes and the Iceberg Model. *J. Phys. Chem. B* **2013**, *117*, 2153–2159.
80. Strazdaite, S.; Versluis, J.; Backus, E. H. G.; Bakker, H. J. Enhanced Ordering of Water at Hydrophobic Surfaces. *J. Chem. Phys.* **2014**, *140*, 054711.
81. Kowsari, M. H.; Alavi, S.; Ashrafizadeh, M.; Najafi, B. Molecular Dynamics Simulation of Imidazolium-based Ionic Liquids. 1. Dynamics and Diffusion Coefficient. *J. Chem. Phys.* **2008**, *129*, 224508.