

Structure and self-diffusivity of alkali-halide electrolytes in neutral and charged graphene nanochannels (Electronic supplementary information)

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S1. FORCE-FIELD PARAMETERS

TABLE S1. The Lennard-Jones energy and size parameters, ϵ and σ , respectively, and partial charges, q , for the water atoms, ions and graphene atoms¹⁻⁴ along with the cross Lennard-Jones energy and size parameters for the ion-graphene interactions, ϵ_{iC} and σ_{iC} , respectively.⁵ The cross Lennard-Jones energy and size parameters for the water oxygen-carbon, water oxygen-ion and ion-ion interactions are given by the Lorentz-Berthelot combining rules;⁶ M is the molar mass.

water						
atom	M	ϵ	σ	q		
	(g/mol)	(kcal ^a /mol)	(Å)	(e)		
O	15.9994	0.15535	3.166	-0.8476		
H	1.00794	0.0	0.0	0.4238		
ions						
atom	M	ϵ	σ	q	ϵ_{iC}	σ_{iC}
	(g/mol)	(kcal ^a /mol)	(Å)	(e)	(kcal ^a /mol)	(Å)
Li	6.941	0.33676	1.41	1.0	0.956	2.312
Na	22.9897	0.35253	2.16	1.0	0.717	2.687
K	39.0983	0.42973	2.84	1.0	0.5258	3.027
Cl	35.453	0.01291	4.83	-1.0	0.1434	4.022
graphene						
atom	M	ϵ	σ	q		
	(g/mol)	(kcal ^a /mol)	(Å)	(e)		
C	12.0107	0.11711	3.214	q_C^b		

^a1 kcal=4.184 kJ

^bcorresponds to the surface charge density $\bar{\sigma}_C = \pm 0.064$ C/m² for the charged graphene or $\bar{\sigma}_C = 0$ for the neutral graphene

S2. ADDITIONAL RESULTS AND DISCUSSION

A. Orientation distributions of confined water

We complement the density distributions of water molecules by water orientation distributions described using the z -profile of $\cos \Phi$, $\cos \Phi(z_0)$. It should be noted that $\cos \Phi(z_0)$ characterises an average orientation of water molecules at z_0 and we thus combined it with $\rho_O(z)$ and $\rho_H(z)$ to elucidate water orientations across the graphene nanochannels. Figs. S1, S2, and S3 display $\cos \Phi(z_0)$ for confined LiCl(aq), NaCl(aq), and KCl(aq), respectively. The $\cos \Phi(z_0)$ s are qualitatively rather similar for all the solutions but differ slightly quantitatively from solution to solution in the 9 and 12 Å nanochannels. For comparison, we also show $\cos \Phi(z_0)$ s for pure water confined in the neutral nanochannels.

Confined pure water: Water molecules prefer to align their μ parallel with the walls in the central layers of the 7 and 12 Å nanochannels ($\cos \Phi(z_0) \approx 0$ and the same position of the $\rho_O(z)$ and $\rho_H(z)$ peaks) while they tend to point their μ away from the walls in the surface layers of the 9 and 12 Å nanochannels ($\cos \Phi(z_0)$ up to 0.1 and mutual shifts in the $\rho_O(z)$ and $\rho_H(z)$ peaks).

Confined electrolytes: On the one hand, the orientation distributions of water molecules became enhanced with respect to the confined pure water. On the other hand, they are to a certain extent similar to those for confined pure water in the neutral nanochannels, and in the charged 9 and 12 Å nanochannels. In the 7 Å nanochannels and regardless of the solutions, the positive graphene charge progressively reorients μ away from the surfaces when water molecules approach the surfaces ($\cos \Phi(z_0) \rightarrow 0.2$) due to the electrostatic repulsion between the surface charge and the water hydrogens. Analogously the negative surface charge along with the confined cations reorient μ of surface water molecules towards the surfaces ($\cos \Phi(z_0) \rightarrow -0.4$) as the surface water molecules point their hydrogens towards the graphene surfaces. Similarly in the wider charged nanochannels, the surface charge primarily and directly affects alignment of the surface water molecules which reorient their μ away from the positively-charged graphene ($\cos \Phi(z_0) \rightarrow 0.35$) or towards the negatively-charged graphene ($\cos \Phi(z_0) \rightarrow -0.2$).

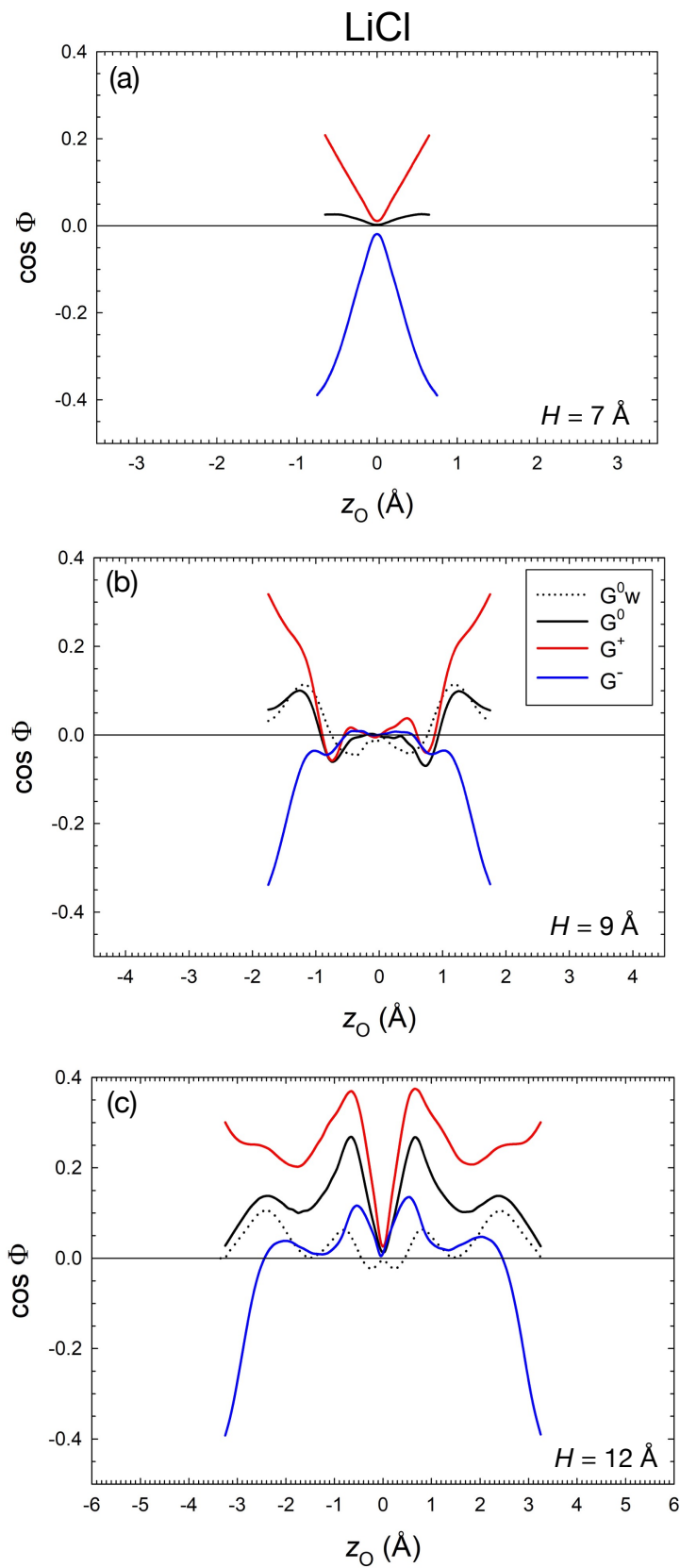


FIG. S1. The z -profile of the water-dipole angle, $\cos\Phi(z_O)$, in the aqueous LiCl solution confined in the neutral (G^0) and positively-charged (G^+), and negatively-charged (G^-) graphene nanochannels of the height (a) $H = 7 \text{ \AA}$, (b) $H = 9 \text{ \AA}$, and (c) $H = 12 \text{ \AA}$; Φ is the angle between the water dipole, μ , and the liquid-facing normal of the nearest graphene walls, \mathbf{n} , $\cos\Phi = \hat{\mu} \cdot \mathbf{n}$ with $\hat{\mu} = \mu/\mu$, and z_O is the distance of water oxygen from the middle of the graphene nanochannel which corresponds to $z_O = 0$. The $\cos\Phi(z_O)$ s for pure water in the neutral graphene nanochannels (G^{0w}) are shown for comparison as dotted lines.

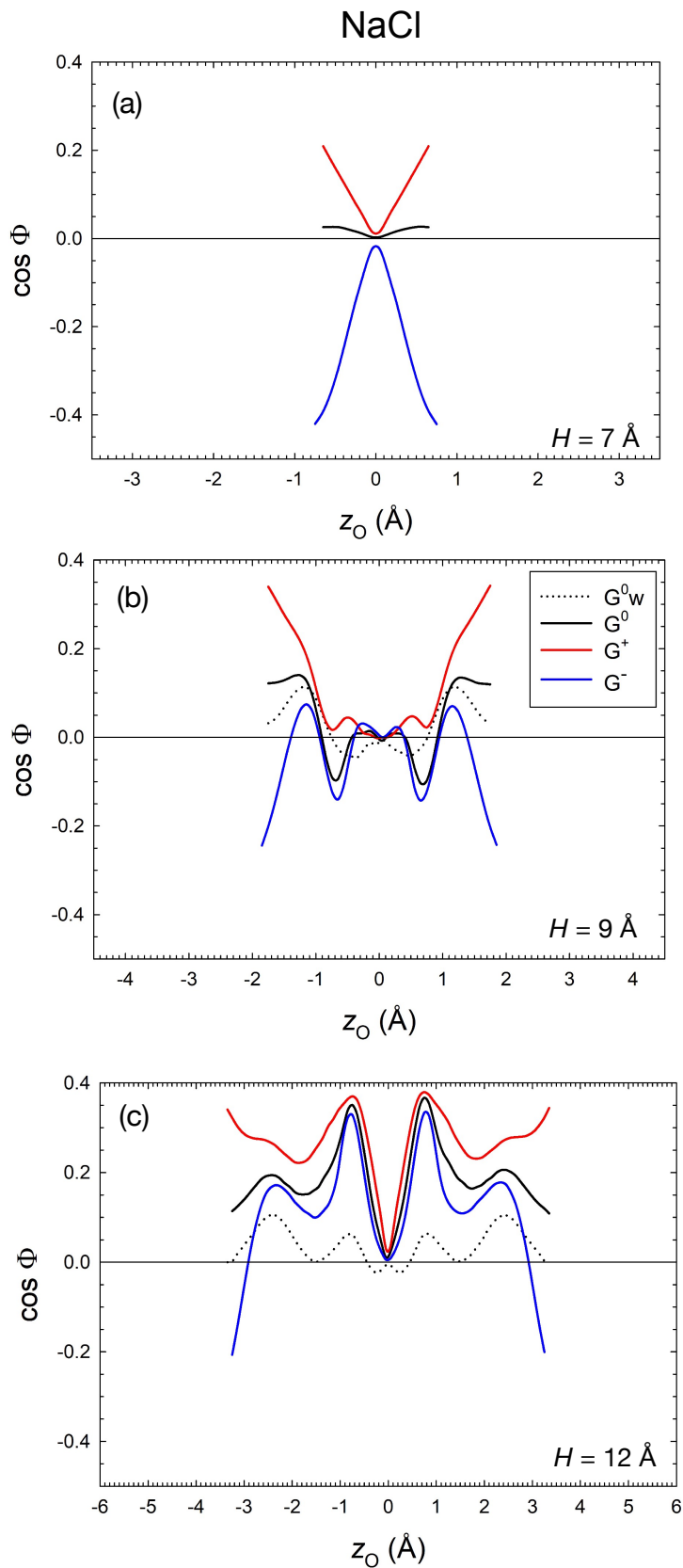


FIG. S2. The z -profile of the water-dipole angle, $\cos \Phi(z_O)$, in the aqueous NaCl solution confined in the neutral (G^0) and positively-charged (G^+), and negatively-charged (G^-) graphene nanochannels of the height (a) $H = 7 \text{ \AA}$, (b) $H = 9 \text{ \AA}$, and (c) $H = 12 \text{ \AA}$; Φ is the angle between the water dipole, $\boldsymbol{\mu}$, and the liquid-facing normal of the nearest graphene walls, \mathbf{n} , $\cos \Phi = \hat{\boldsymbol{\mu}} \cdot \mathbf{n}$ with $\hat{\boldsymbol{\mu}} = \boldsymbol{\mu}/\mu$, and z_O is the distance of water oxygen from the middle of the graphene nanochannel which corresponds to $z_O = 0$. The $\cos \Phi(z_O)$ s for pure water in the neutral graphene nanochannels (G^0w) are shown for comparison as dotted lines.

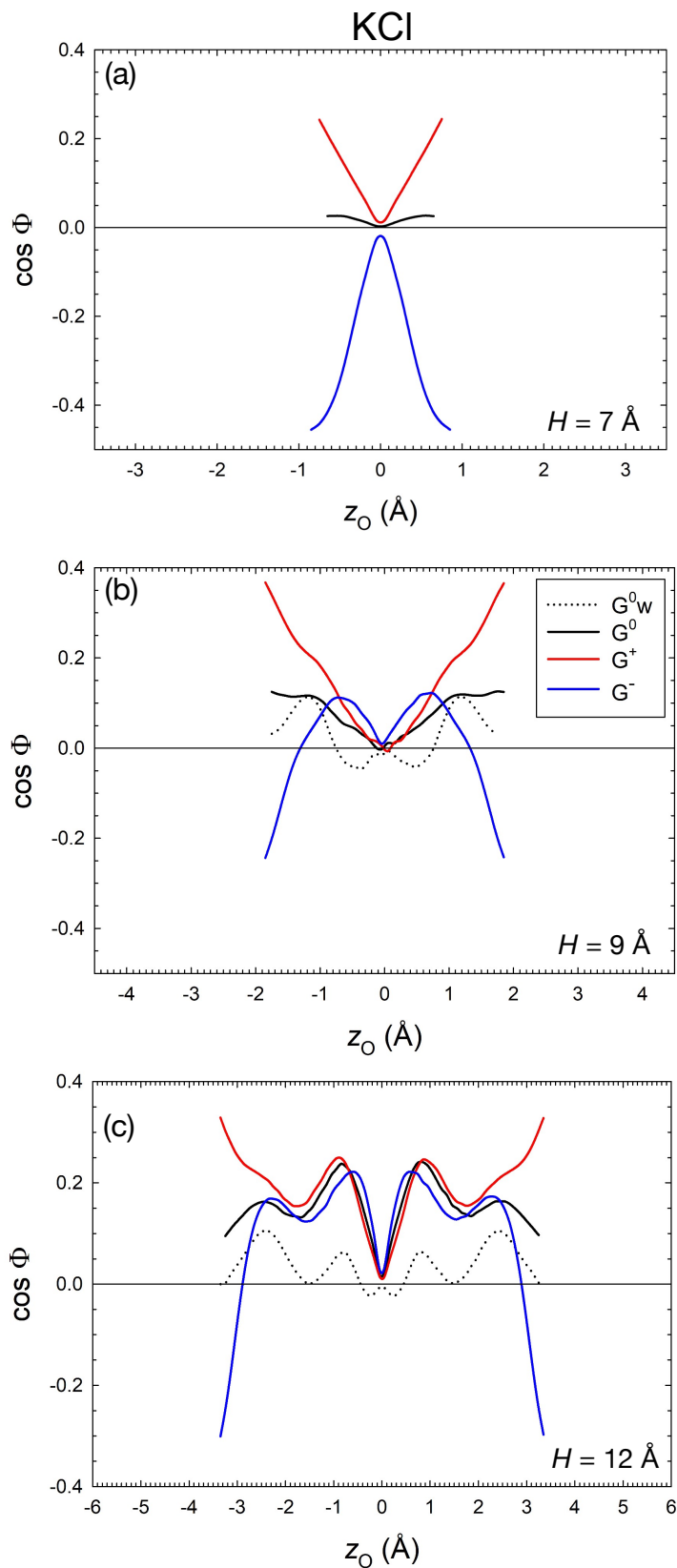


FIG. S3. The z -profile of the water-dipole angle, $\cos\Phi(z_O)$, in the aqueous KCl solution confined in the neutral (0G) and positively-charged (+G), and negatively-charged (-G) graphene nanochannels of the height (a) $H = 7 \text{ \AA}$, (b) $H = 9 \text{ \AA}$, and (c) $H = 12 \text{ \AA}$; Φ is the angle between the water dipole, μ , and the liquid-facing normal of the nearest graphene walls, \mathbf{n} , $\cos\Phi = \hat{\mu} \cdot \mathbf{n}$ with $\hat{\mu} = \mu/\mu$, and z_O is the distance of water oxygen from the middle of the graphene nanochannel which corresponds to $z_O = 0$. The $\cos\Phi(z_O)$ s for pure water in the neutral graphene nanochannels (0Gw) are shown for comparison as dotted lines.

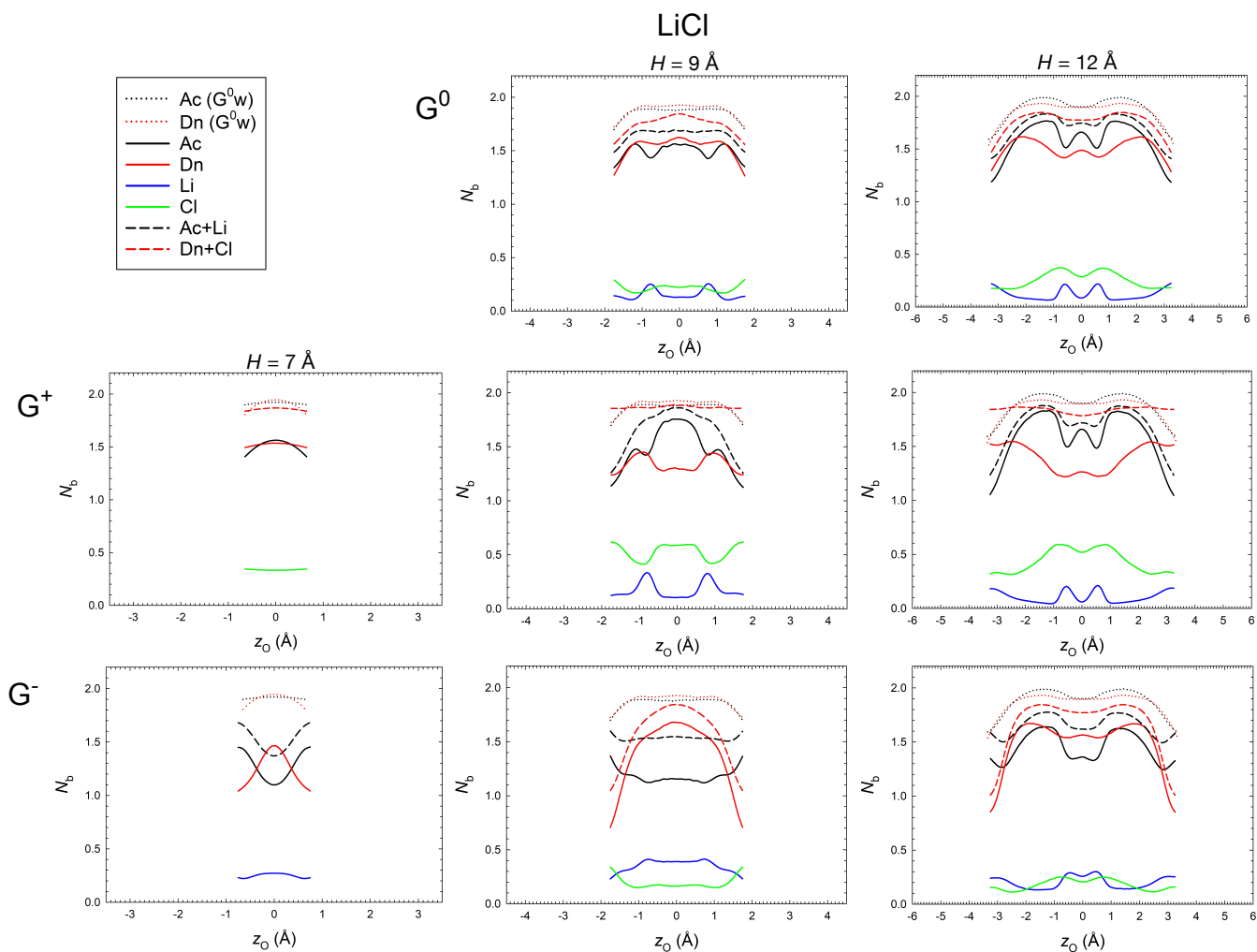


FIG. S4. The z -profile of the numbers of intermolecular bonds per water molecule, $N_b(z_O)$, in the aqueous LiCl solution confined in the neutral (G^0) and positively-charged (G^+), and negatively-charged (G^-) graphene nanochannels of the height H ; z_O is the distance of water oxygen from the middle of the graphene nanochannel which corresponds to $z_O = 0$. The H-bonding profiles for pure water in the neutral graphene nanochannels (G^0_w) are shown for comparison as dotted lines. The H-bonds for acceptor (Ac) and donor (Dn) water molecules, $N_b^{Ac}(z_O)$ and $N_b^{Dn}(z_O)$, respectively, were determined using the standard, distance-angle definition.^{7,8} The following sums are also displayed $N_b^{Ac+Li}(z_O) \equiv N_b^{Ac}(z_O) + N_b^{Li}(z_O)$ and $N_b^{Dn+Cl}(z_O) \equiv N_b^{Dn}(z_O) + N_b^{Cl}(z_O)$ as dash lines. In the bulk SPC/E water, the distance-angle definition gives $N_b^{Ac} = N_b^{Dn} = 1.80$.⁹

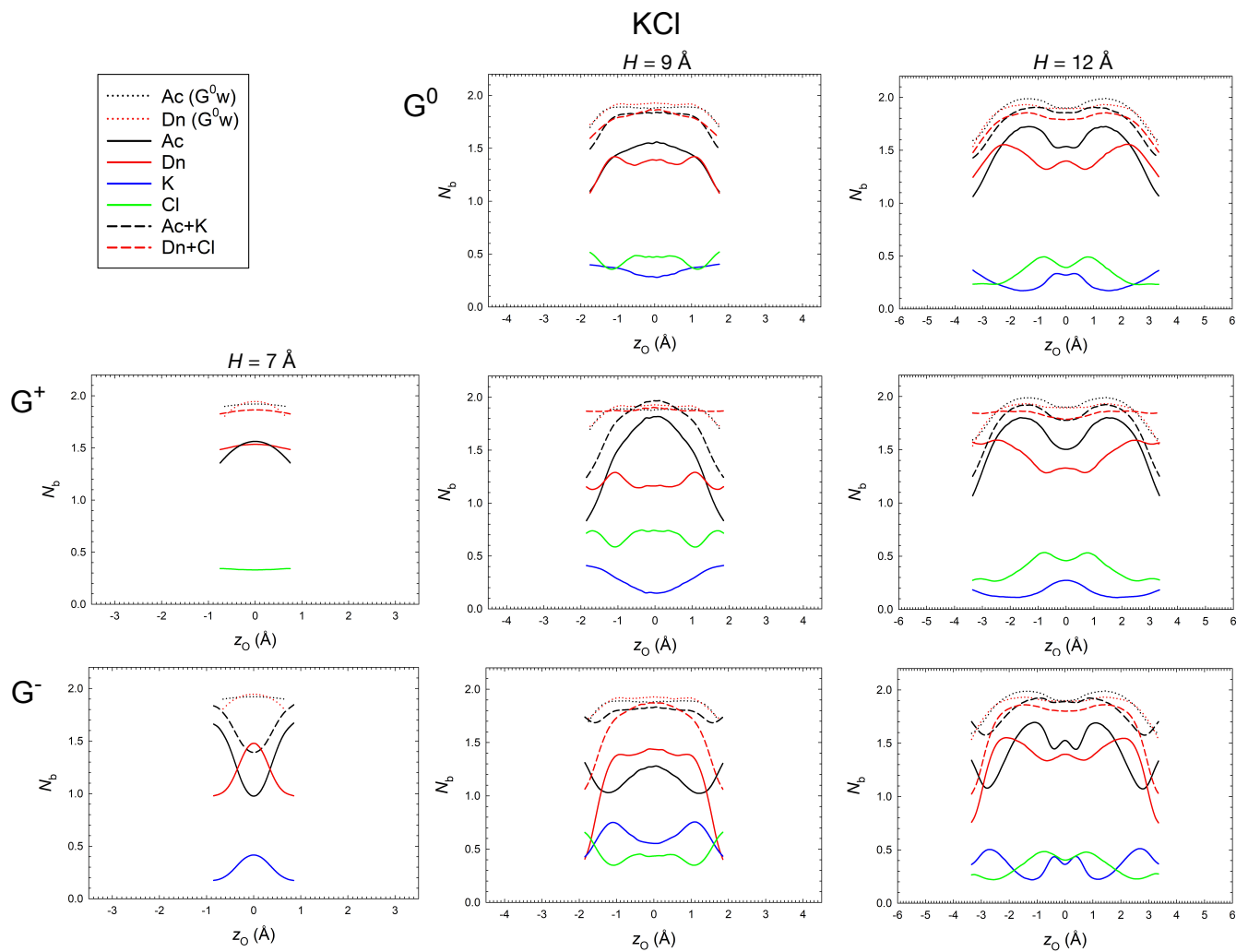


FIG. S5. The z -profile of the numbers of intermolecular bonds per water molecule, $N_b(z_0)$, in the aqueous KCl solution confined in the neutral (G^0) and positively-charged (G^+), and negatively-charged (G^-) graphene nanochannels of the height H ; z_0 is the distance of water oxygen from the middle of the graphene nanochannel which corresponds to $z_0 = 0$. The H-bonding profiles for pure water in the neutral graphene nanochannels (G^0_w) are shown for comparison as dotted lines. The H-bonds for acceptor (Ac) and donor (Dn) water molecules, $N_b^{\text{Ac}}(z_0)$ and $N_b^{\text{Dn}}(z_0)$, respectively, were determined using the standard, distance-angle definition.^{7,8} The following sums are also displayed $N_b^{\text{Ac+K}}(z_0) \equiv N_b^{\text{Ac}}(z_0) + N_b^{\text{K}}(z_0)$ and $N_b^{\text{Dn+Cl}}(z_0) \equiv N_b^{\text{Dn}}(z_0) + N_b^{\text{Cl}}(z_0)$ as dash lines. In the bulk SPC/E water, the distance-angle definition gives $N_b^{\text{Ac}} = N_b^{\text{Dn}} = 1.80$.⁹

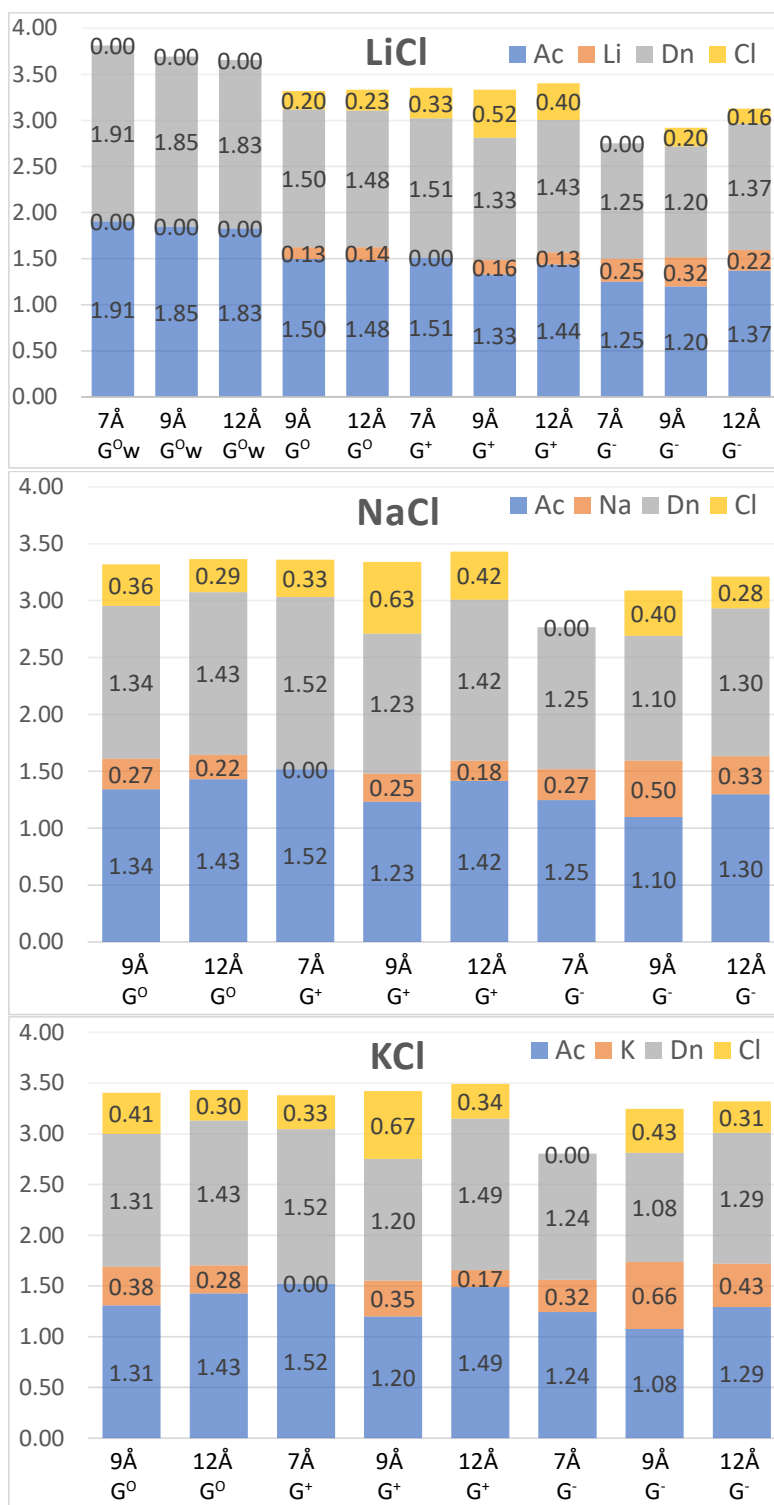


FIG. S6. Average numbers of intermolecular bonds of water oxygen to hydrogens (Ac) or cations (Li, Na or K) and intermolecular bonds of water hydrogens (counted together) to oxygens (Dn) or Cl anions for the aqueous LiCl, NaCl and KCl solutions confined in the neutral (G^0) and positively-charged (G^+), and negatively-charged (G^-) graphene nanochannels of various heights. The total heights of the stacked bars indicate the total numbers of bonds per water molecule. The data for pure water in the neutral (G^0) 7 Å graphene nanochannel are the same as for the G^0 7 Å nanochannel, since no ions enter the nanochannel.

TABLE S2. Average numbers of bonds of water oxygen to hydrogens (Ac) or cations (Li, Na or K), and bonds of water hydrogens (counted together) to oxygens (Dn) or Cl anions for aqueous LiCl, NaCl, and KCl solutions confined in the graphene nanochannels of the height H . The numbers of bonds from acceptors Ac and donors Dn averaged over water molecules in the nanochannel monitored region are the same.

pure water		Ac=Dn		Ac+Dn			
height	surface charge						
H (Å)	$\bar{\sigma}_C$ (C/m ²)						
7	0	1.91			3.81		
9	0	1.85			3.69		
12	0	1.83			3.66		
LiCl(aq)							
height	surface charge	Ac=Dn	Li	Cl	Ac+Li	Dn+Cl	Ac+Dn+Li+Cl
H (Å)	$\bar{\sigma}_C$ (C/m ²)						
7	0	1.91	0	0	1.91	1.91	3.81
	+0.064	1.52	0	0.33	1.52	1.84	3.36
	-0.064	1.25	0.25	0	1.50	1.25	2.75
9	0	1.50	0.13	0.20	1.62	1.69	3.32
	+0.064	1.33	0.16	0.52	1.48	1.85	3.34
	-0.064	1.20	0.32	0.20	1.52	1.40	2.92
12	0	1.48	0.14	0.23	1.62	1.71	3.33
	+0.064	1.44	0.13	0.40	1.57	1.83	3.40
	-0.064	1.37	0.22	0.16	1.59	1.53	3.13
NaCl(aq)							
height	surface charge	Ac=Dn	Na	Cl	Ac+Na	Dn+Cl	Ac+Dn+Na+Cl
H (Å)	$\bar{\sigma}_C$ (C/m ²)						
7	0	1.91	0	0	1.91	1.91	3.81
	+0.064	1.52	0	0.33	1.52	1.84	3.36
	-0.064	1.25	0.27	0	1.52	1.25	2.77
9	0	1.34	0.27	0.36	1.61	1.71	3.32
	+0.064	1.23	0.25	0.63	1.48	1.86	3.34
	-0.064	1.10	0.50	0.40	1.59	1.50	3.09
12	0	1.43	0.22	0.29	1.65	1.72	3.37
	+0.064	1.42	0.18	0.42	1.59	1.84	3.43
	-0.064	1.30	0.33	0.28	1.63	1.58	3.21
KCl(aq)							
height	surface charge	Ac=Dn	K	Cl	Ac+K	Dn+Cl	Ac+Dn+K+Cl
H (Å)	$\bar{\sigma}_C$ (C/m ²)						
7	0	1.91	0	0	1.91	1.91	3.81
	+0.064	1.52	0	0.33	1.52	1.86	3.38
	-0.064	1.24	0.32	0	1.56	1.24	2.80
9	0	1.31	0.38	0.41	1.69	1.72	3.40
	+0.064	1.20	0.35	0.67	1.55	1.87	3.42
	-0.064	1.08	0.66	0.43	1.74	1.51	3.24
12	0	1.43	0.28	0.30	1.70	1.73	3.43
	+0.064	1.49	0.17	0.34	1.66	1.84	3.49
	-0.064	1.29	0.43	0.31	1.72	1.60	3.32

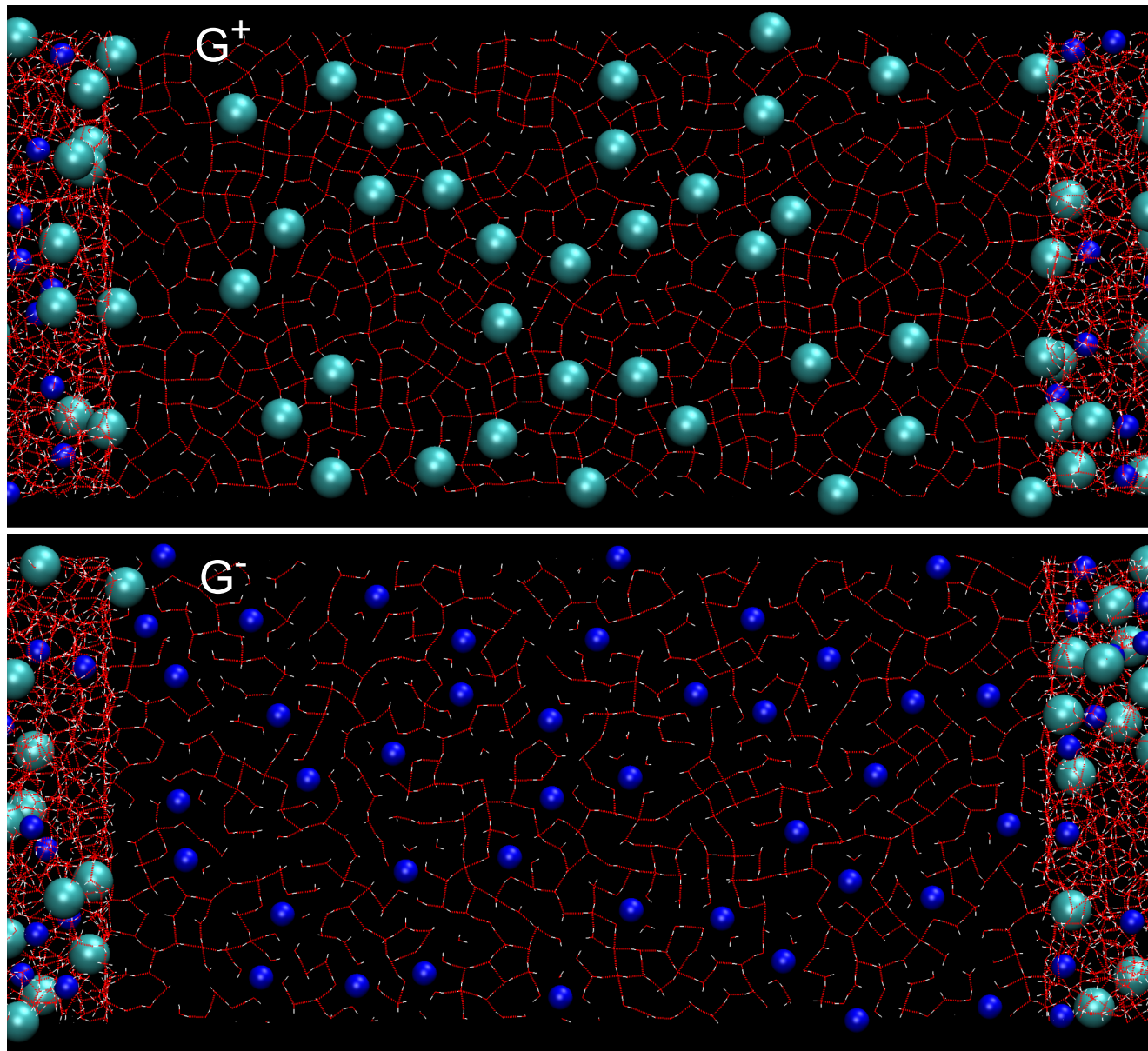
NaCl, $H = 7 \text{ \AA}$ 

FIG. S7. Structure of intermolecular bonds for the aqueous NaCl solution confined in the positively-charged (top, G^+) and negatively-charged (bottom, G^-) 7 \AA graphene nanochannels, showing a more connected intermolecular bond network in the positively-charged nanochannel as compared to the negatively-charged nanochannel. What is displayed is an orthographic projection along the z -axis, with the horizontal x -axis and the vertical y -axis up to the edges of the reservoir. The intermolecular bonds are shown as thick red dashed lines, oxygens are red, hydrogens white, Na^+ s blue, and Cl^- s cyan. The H-bonds were determined using the standard, distance-angle definition, i.e., an H-bond between a pair of water molecules is assumed to form when the O-O intermolecular distance, $\text{O} \cdots \text{O}$, is less than 3.5 \AA , and the angle between $\text{O} \cdots \text{O}$ and water O-H bond is less than 30° .^{7,8}

B. Hydration numbers of ions

Fig. S8 presents $N_{\text{hyd}}^c(z_c)$ s and $N_{\text{hyd}}^{\text{Cl}}(z_{\text{Cl}})$ s for all confined solutions studied. In the charged, one-layer 7 Å nanochannels, $N_{\text{hyd}}^c(z_c)$ s or $N_{\text{hyd}}^{\text{Cl}}(z_{\text{Cl}})$ s are flat due to very narrow distributions of water oxygens or ions, and they are significantly lower than in the bulk solutions except for strongly hydrated Li^+ s with $N_{\text{hyd}}^{\text{Li}}(z_{\text{Li}})$ almost reach the bulk value. Specifically, $N_{\text{hyd}}^{\text{Cl}}(z_{\text{Cl}}) \simeq 5$ in the positively-charged nanochannel while $N_{\text{hyd}}^{\text{Na}}(z_{\text{Na}}) \simeq 4$ and $N_{\text{hyd}}^{\text{K}}(z_{\text{K}}) \simeq 4.5$ in the negatively-charged nanochannels. In the wider 9 and 12 Å nanochannels, the $N_{\text{hyd}}^{\text{Li}}(z_{\text{Li}})$ s are around the bulk value as Li^+ s adsorbed into the interior of the nanochannels and the hydration shell of Li^+ is too strong to be restructured due to the graphene surfaces. The $N_{\text{hyd}}^{\text{Na}}(z_{\text{Na}})$ s have a step-wise character and they are about the bulk value around the middle of the nanochannels. Then in the close vicinity of the graphene surfaces, there is a drop in $N_{\text{hyd}}^{\text{Na}}(z_{\text{Na}})$ s as one water- Na^+ bond is typically broken. Behaviour of $N_{\text{hyd}}^{\text{K}}(z_{\text{K}})$ s is to a certain extent similar to that of $N_{\text{hyd}}^{\text{Na}}(z_{\text{Na}})$ s except for a more pronounced drop in $N_{\text{hyd}}^{\text{K}}(z_{\text{K}})$ s close to the graphene surfaces. The drops in $N_{\text{hyd}}^{\text{Na}}(z_{\text{Na}})$ s/ $N_{\text{hyd}}^{\text{K}}(z_{\text{K}})$ s reflect that Na/K cation forms a larger and weaker hydration shell which abruptly or gradually loses some water molecules as Na^+ s/ K^+ s get closer to the surfaces and in turn, the hydration shell of Na^+ / K^+ becomes qualitatively restructured by the graphene walls. In the wider 9 and 12 Å nanochannels, $N_{\text{hyd}}^c(z_c)$ s differ from solution to solution while $N_{\text{hyd}}^{\text{Cl}}(z_{\text{Cl}})$ s are rather similar. Since the chloride anions are distributed in the interior of the nanochannels the $N_{\text{hyd}}^{\text{Cl}}(z_{\text{Cl}})$ s are not strongly influenced by the graphene walls or the surface charge. They reach approximately the bulk value in the centre of the nanochannels and then slightly or moderately decrease towards the graphene surfaces. The confined Cl^- s form a larger and weaker hydration shell, which gradually loses some water molecules for Cl^- s closer to the graphene walls.

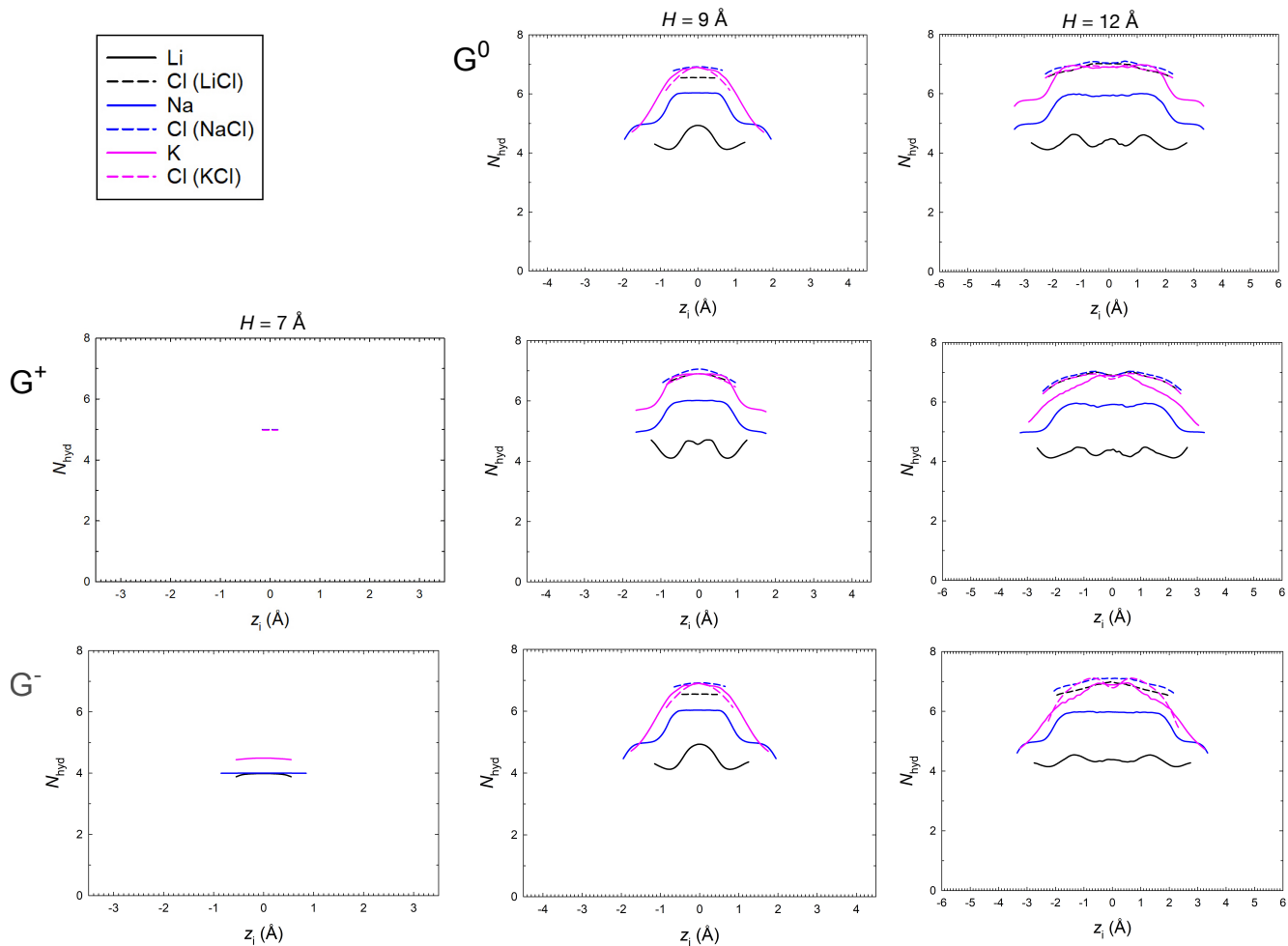


FIG. S8. The z -profile of the hydration numbers of ions, $N_{\text{hyd}}(z_i)$, in the aqueous LiCl, NaCl, and KCl solutions confined in the neutral (G^0) and positively-charged (G^+), and negatively-charged (G^-) graphene nanochannels of the height H ; z_i is the distance of ions from the middle of the graphene nanochannel which corresponds to $z_i = 0$. The neutral 7 Å nanochannel is not displayed since it completely restricts the adsorption of the ions from the bulk reservoir. The hydration numbers in the bulk LiCl solutions are about 4.2 for Li^+ and about 7.0 for Cl^- , in the bulk NaCl solution about 5.8 for Na^+ and about 7.2 for Cl^- , and in the bulk KCl solution about 6.9 for K^+ and about 6.9 for Cl^- .^{10,11}

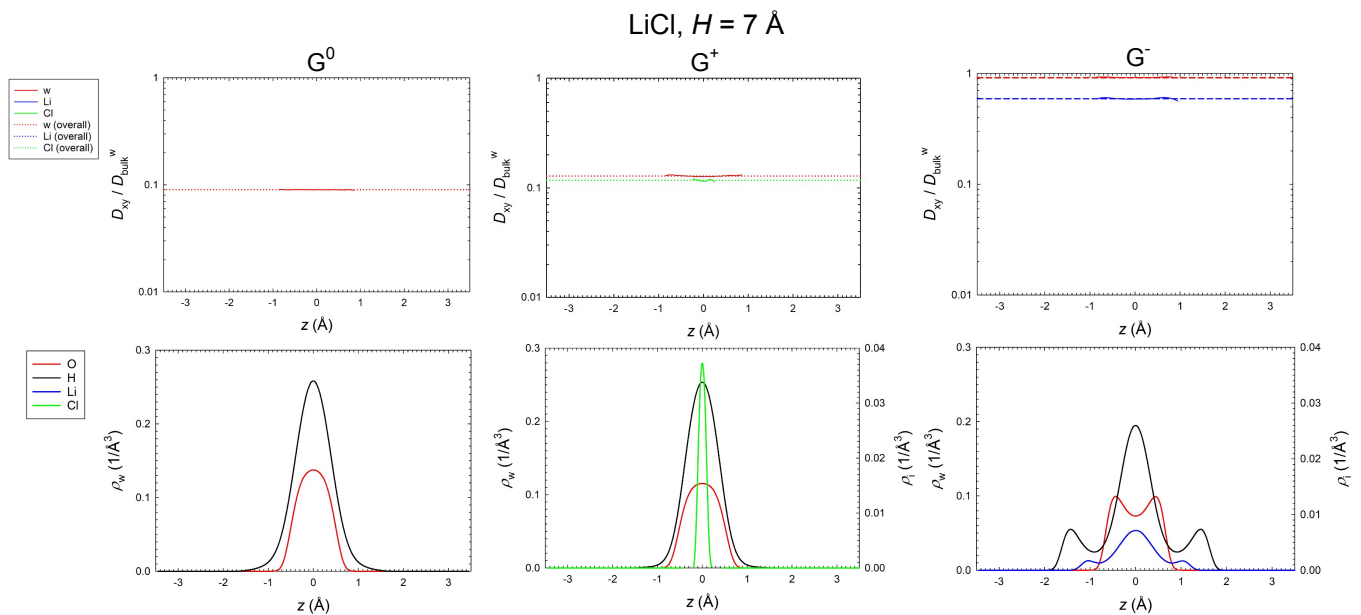
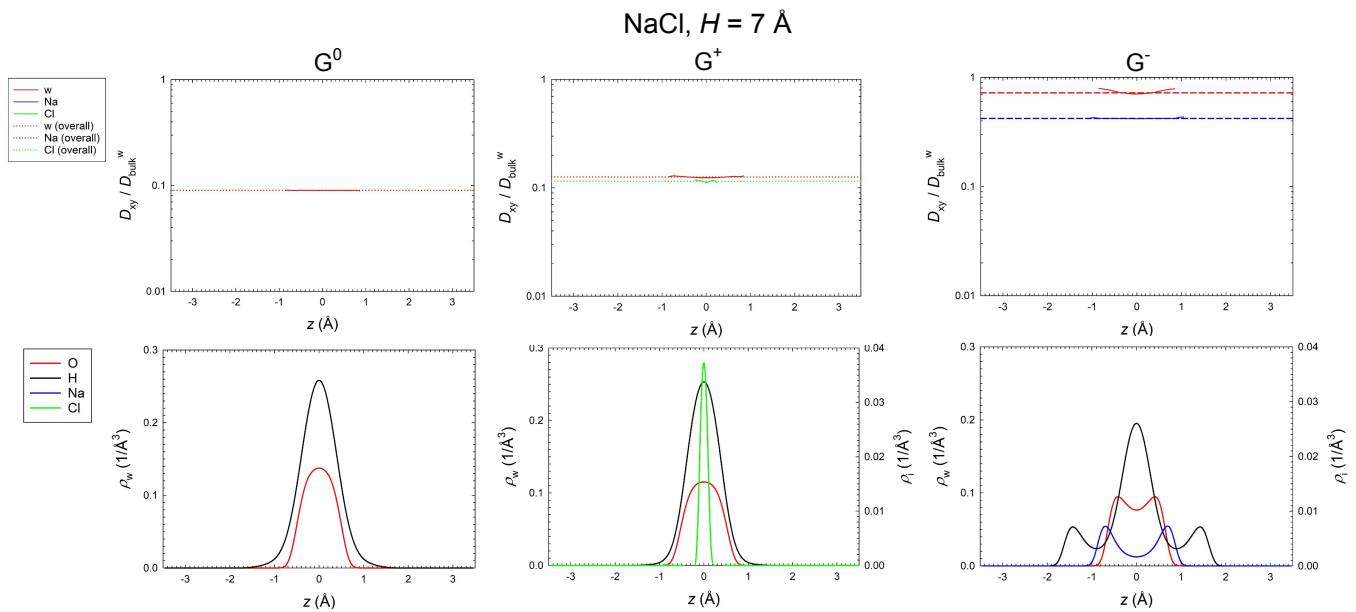


FIG. S10. The z -dependent in-plane self-diffusion coefficients of water molecules and ions, D_{xy} , (top row) along with the corresponding atomic density profiles for water atoms, $\rho_w(z)$, and ions, $\rho_i(z)$, (bottom row) in the aqueous LiCl solution confined in the neutral (G^0) and positively-charged (G^+), and negatively-charged (G^-) 7 \AA graphene nanochannels; z is the distance from the middle of the graphene nanochannel which corresponds to $z = 0$. The D_{xy} s are normalised by the self-diffusion coefficient of the bulk SPC/E water $D_{\text{bulk}}^w = 2.97 \cdot 10^{-9} \text{ m}^2/\text{s}$.¹²

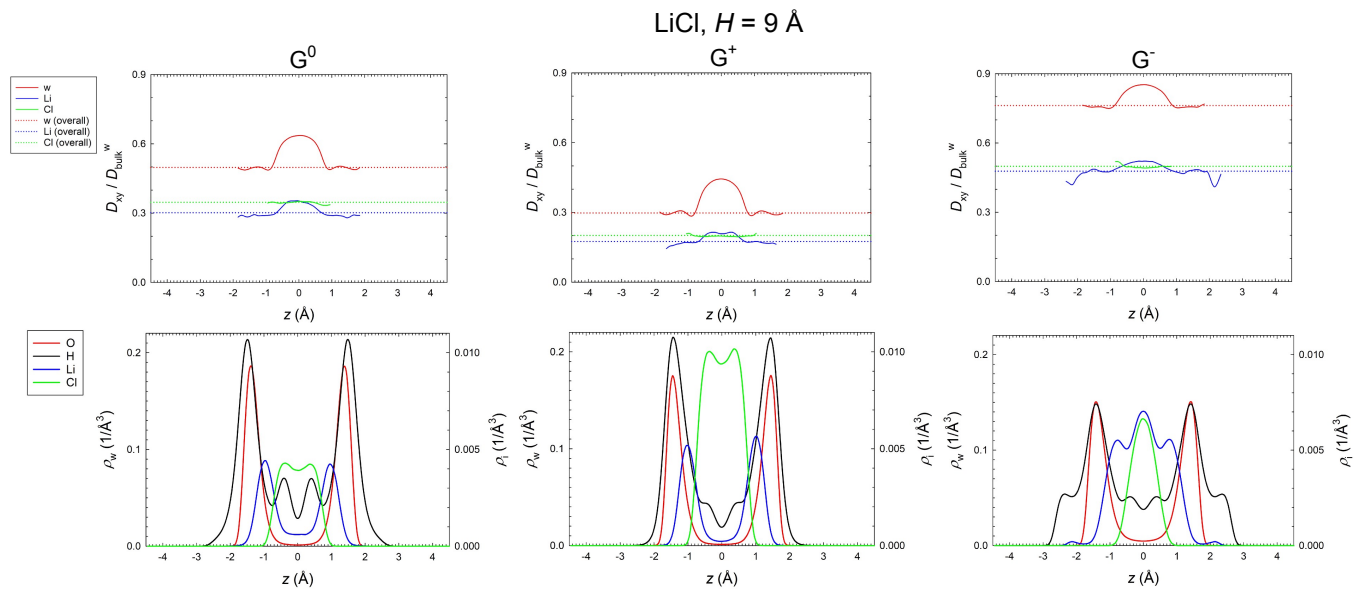


FIG. S11. The z -dependent in-plane self-diffusion coefficients of water molecules and ions, D_{xy} , (top row) along with the corresponding atomic density profiles for water atoms, $\rho_w(z)$, and ions, $\rho_i(z)$, (bottom row) in the aqueous LiCl solution confined in the neutral (G^0) and positively-charged (G^+), and negatively-charged (G^-) 9 \AA graphene nanochannels; z is the distance from the middle of the graphene nanochannel which corresponds to $z = 0$. The D_{xy} s are normalised by the self-diffusion coefficient of the bulk SPC/E water $D_{\text{bulk}}^w = 2.97 \cdot 10^{-9} \text{ m}^2/\text{s}$.¹²

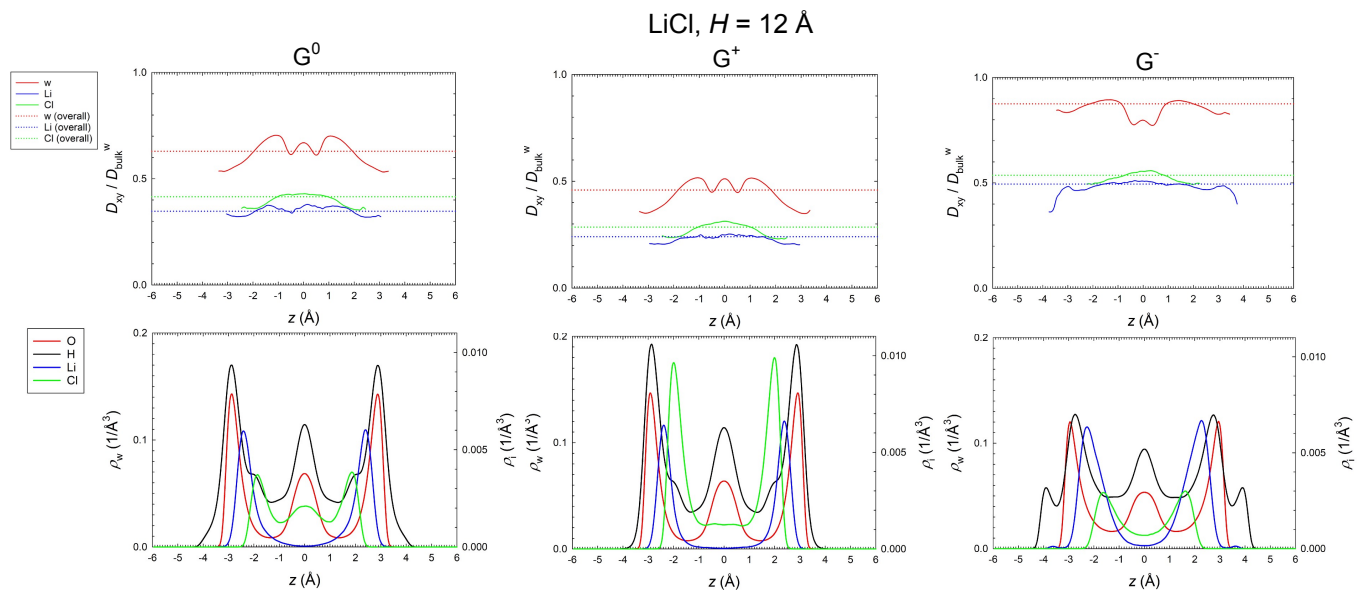
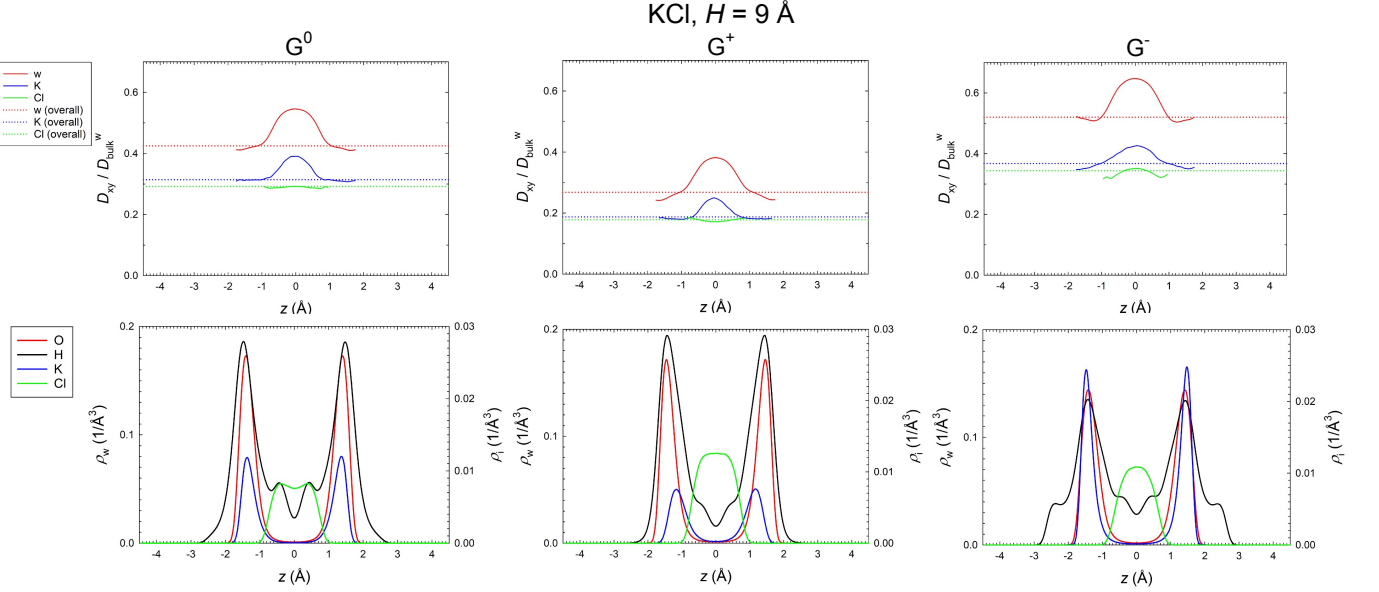
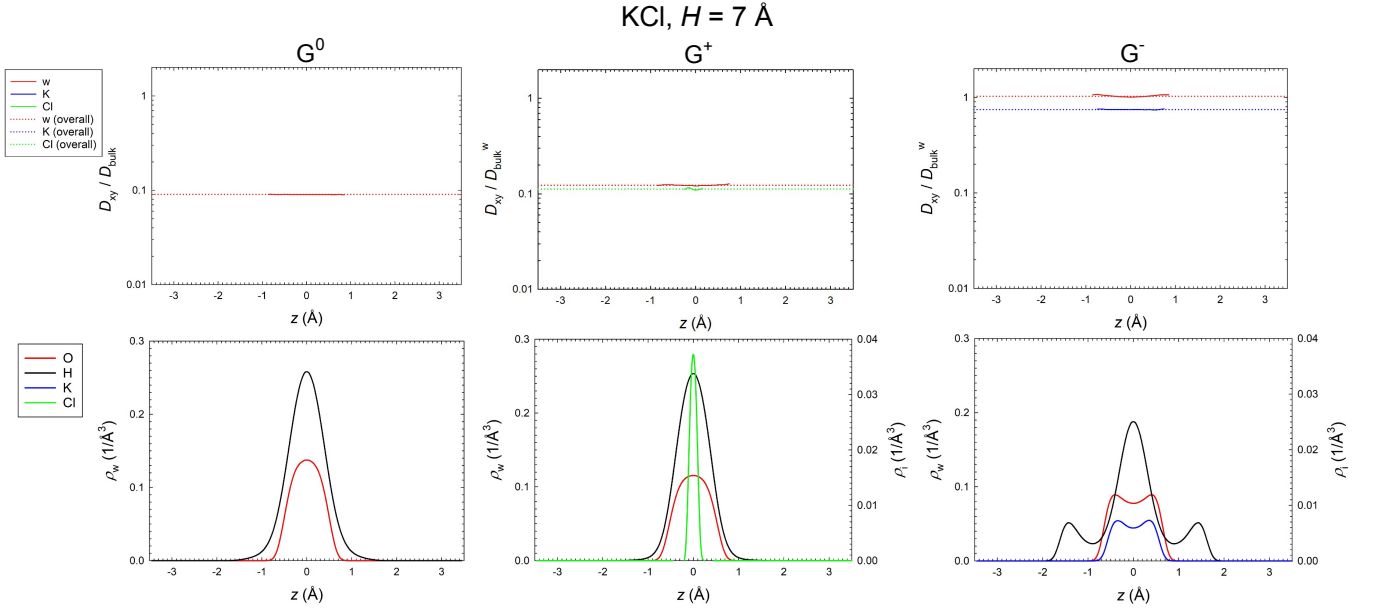


FIG. S12. The z -dependent in-plane self-diffusion coefficients of water molecules and ions, D_{xy} , (top row) along with the corresponding atomic density profiles for water atoms, $\rho_w(z)$, and ions, $\rho_i(z)$, (bottom row) in the aqueous LiCl solution confined in the neutral (G^0) and positively-charged (G^+), and negatively-charged (G^-) 12 \AA graphene nanochannels; z is the distance from the middle of the graphene nanochannel which corresponds to $z = 0$. The D_{xy} s are normalised by the self-diffusion coefficient of the bulk SPC/E water $D_{\text{bulk}}^w = 2.97 \cdot 10^{-9} \text{ m}^2/\text{s}$.¹²



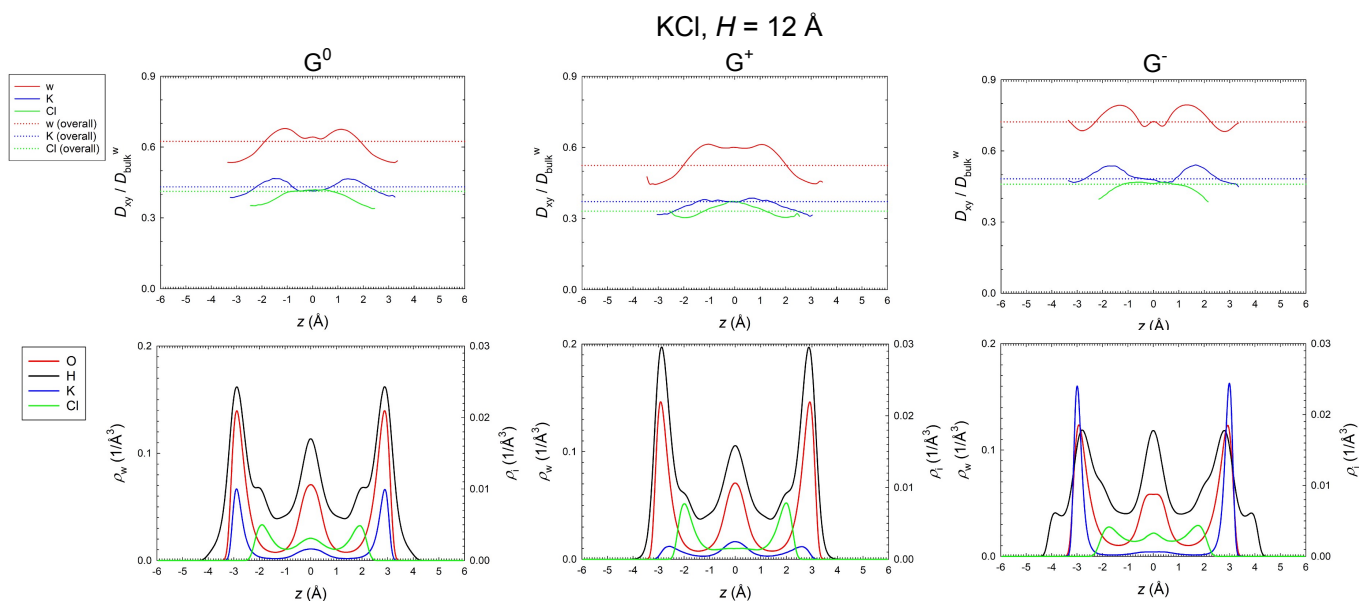


FIG. S15. The z -dependent in-plane self-diffusion coefficients of water molecules and ions, D_{xy} , (top row) along with the corresponding atomic density profiles for water atoms, $\rho_w(z)$, and ions, $\rho_i(z)$, (bottom row) in the aqueous KCl solution confined in the neutral (G^0) and positively-charged (G^+), and negatively-charged (G^-) 12 \AA graphene nanochannels; z is the distance from the middle of the graphene nanochannel which corresponds to $z = 0$. The D_{xy} s are normalised by the self-diffusion coefficient of the bulk SPC/E water $D_{\text{bulk}}^w = 2.97 \cdot 10^{-9} \text{ m}^2/\text{s}$.¹²

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