Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

The Tug of War between Al^{3+} and Na^{+} for Order-Disorder Transitions in Lipid-A Membranes

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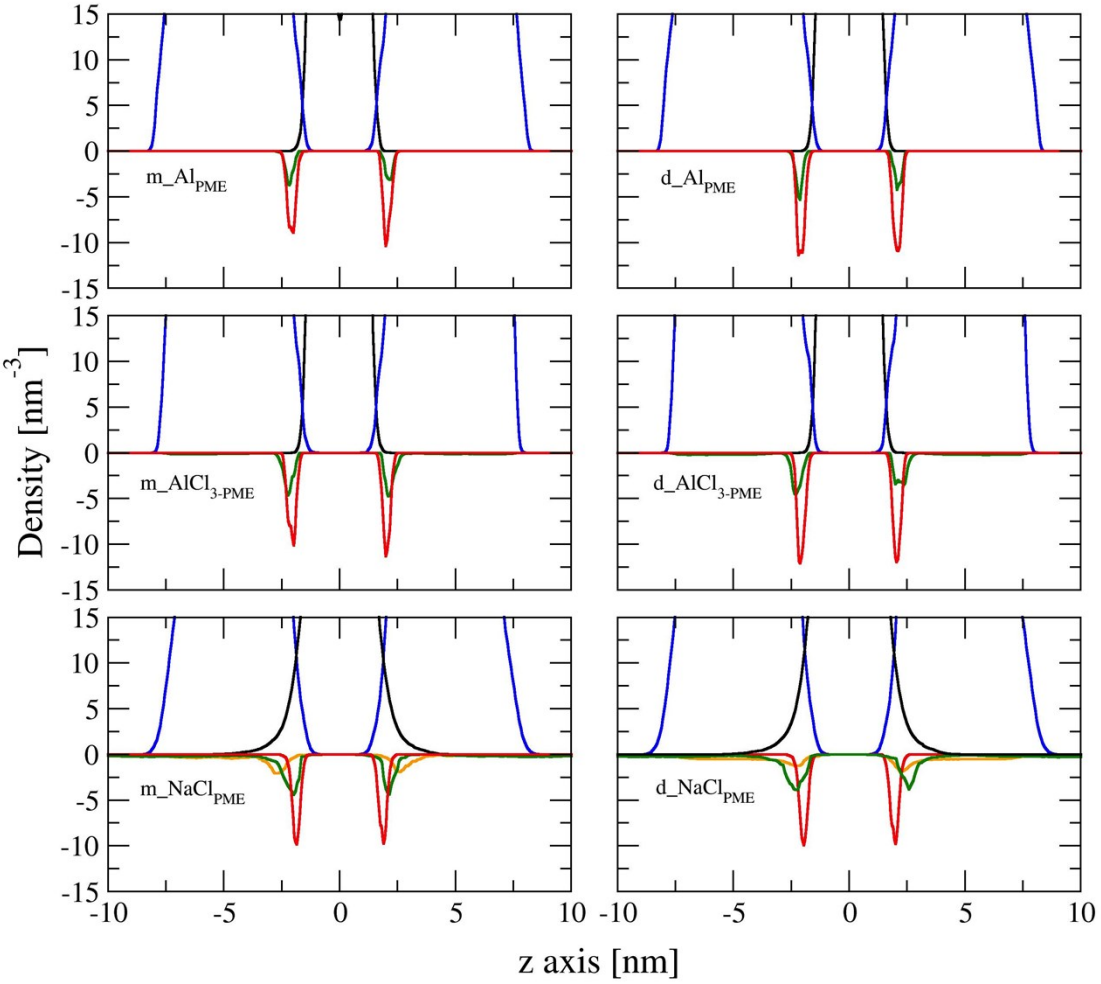

Figure SI-1. Partial density profiles for selected chemical groups of mono- and diphosphorylated Lipid-A in presence of Al^{3+} counterions and in different concentration regimes (0 mM, 150 mM $AlCl_3$, and 150 mM NaCl) using Particle mesh Ewald approximations. Water molecules are represented in blue, lipid acyl chains in black, phosphorus atoms in red, aluminium cations in green and sodium cations in orange. Density values for phosphorus atoms and cations were increased by 4-fold for clarity. Averages ran over the last 100 ns of simulation. The density profiles were calculated with SuAVE by taking the phosphorus atoms as reference for the grid fitting along the bilayer leaflets. The number of grid points for the mesh was chosen to be 100 × 100 grid points.

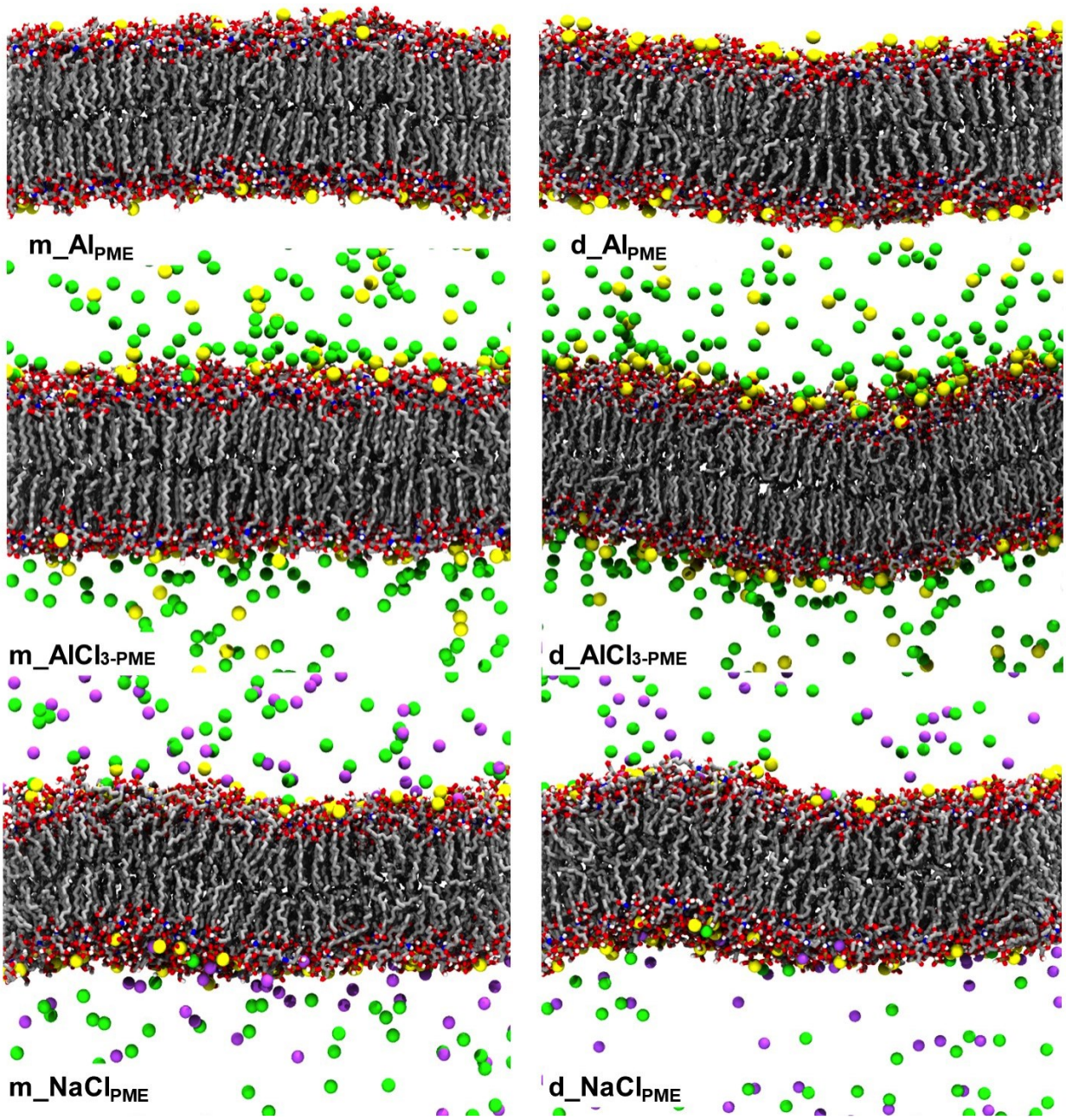

Figure SI-2. Representative conformations from MD simulations of Lipid-A membranes using Particle mesh Ewald approximations. Lipids acyl chains are represented in gray sticks and ions Al^{3+}, Na^{+} and Cl^{-} are show in yellow, magenta and green van der Waals spheres, respectively.

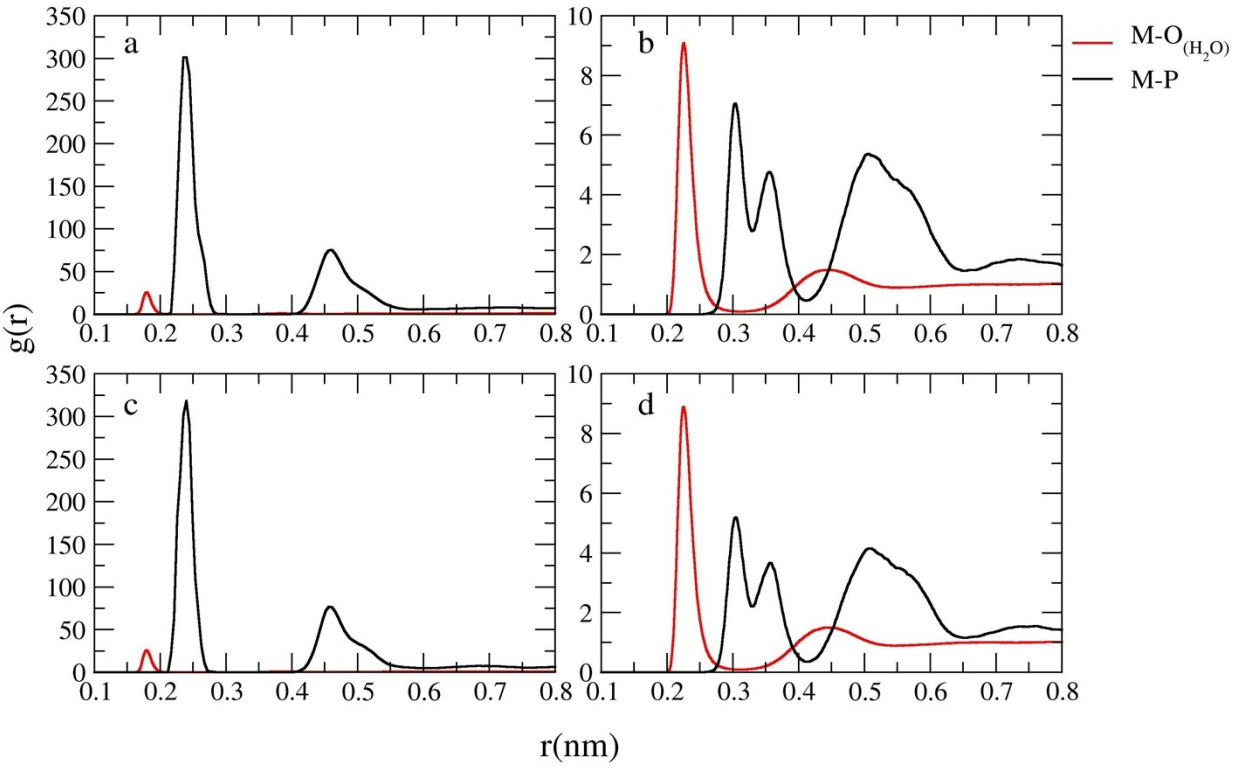

Figure SI-3. Radial distribution g(r) for ions (M = Na^+ or Al^{3+}) with phosphorus atom (black lines) and water oxygens (red lines) for systems (a) Ref1 (M=Al^{3+}), b) Ref2 (M=Na^+) and (c) e (d) for Ref3 system with M=Al^{3+} and M=Na^+ respectively.

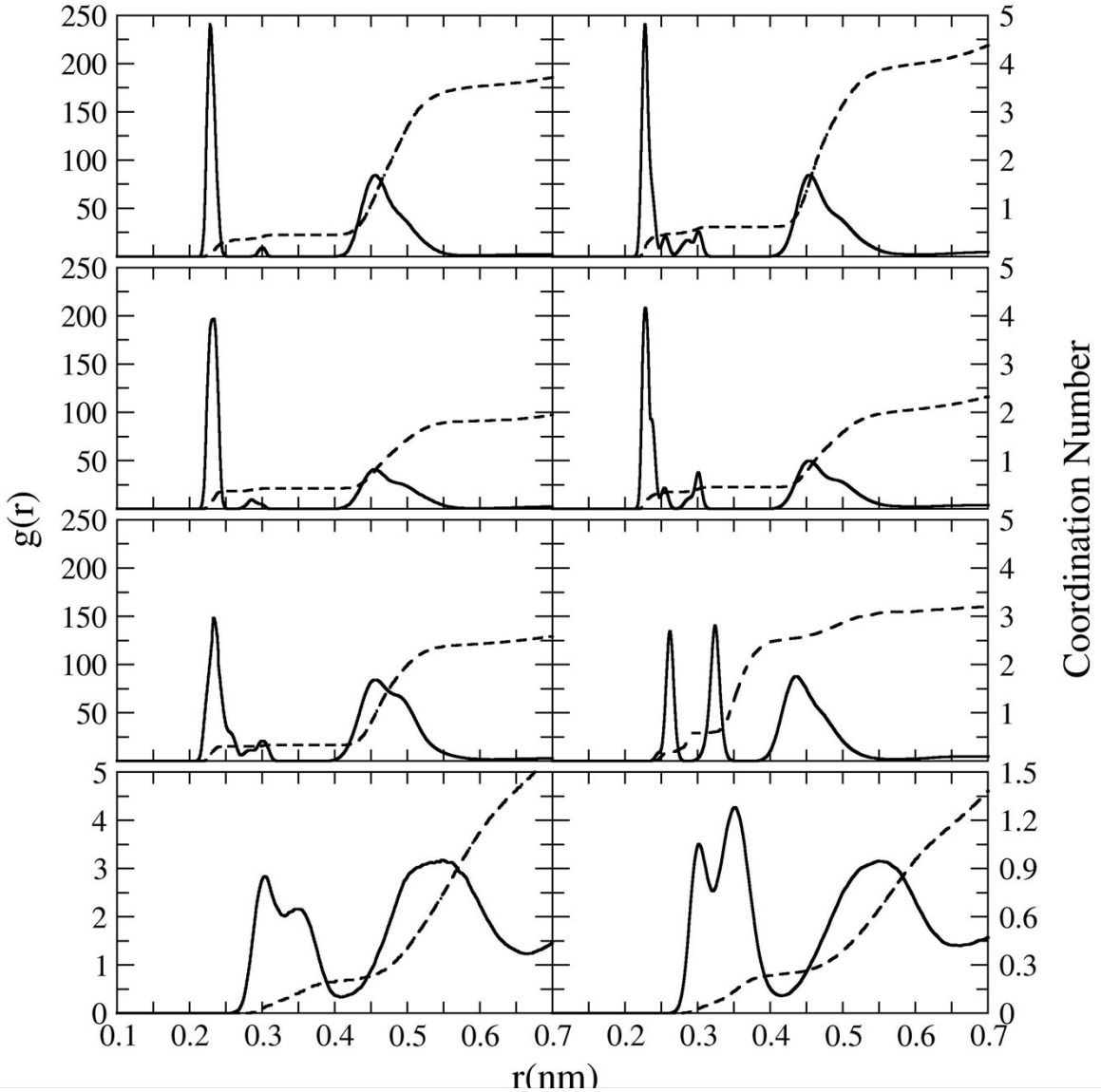

Figure SI-4. Radial distribution g(r) (solid lines) and coordination number Int g(r) (dashed lines) for ions with phosphorus atom for simulated systems. The last two graphs represent the g(r) for the Na^+ ions for the m_NaCl and d_NaCl systems. The cumulative values take into account all the cations present in the simulation boxes.

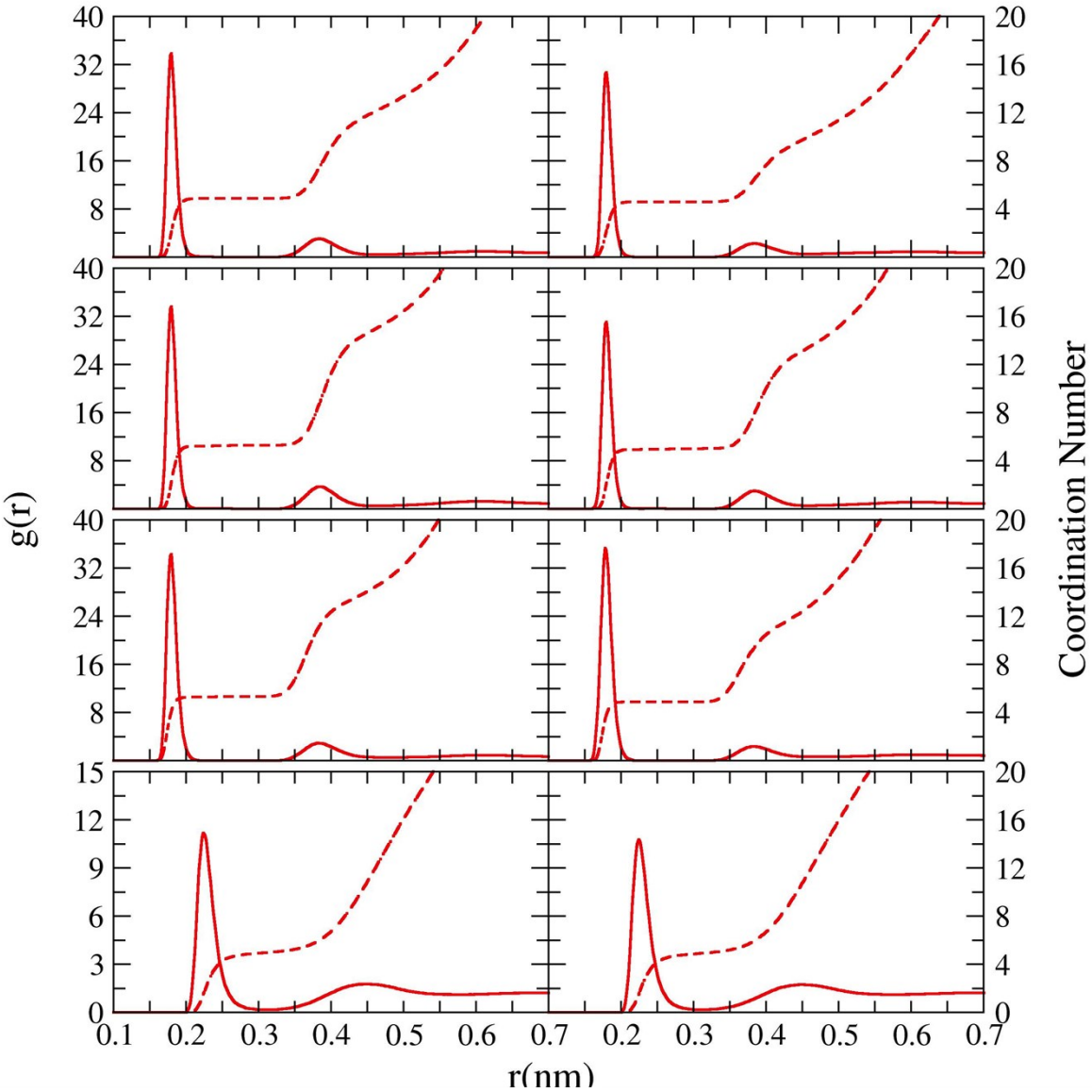

Figure SI-5. Radial distribution g(r) (solid lines) and coordination number Int g(r) (dashed lines) for ions with water molecules for simulated systems. The cumulative values take into account all the cations present in the simulation boxes. The last two graphs represent the g(r) for the Na^+ ions for the m_NaCl and d_NaCl systems.

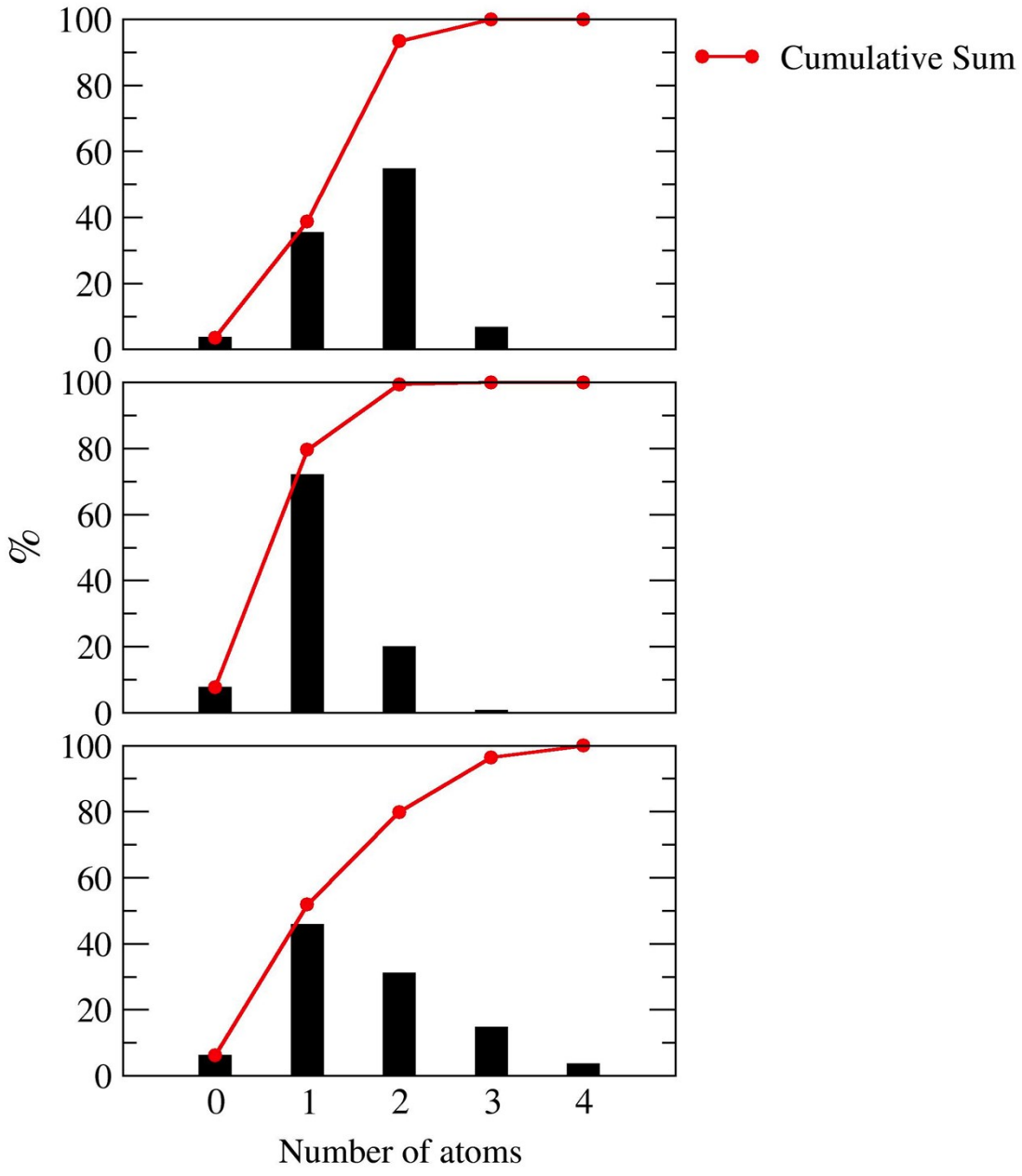

Figure SI-6. Distribution of the time-average number of (top) phosphates within 0.23 nm of Al^{3+} ions on d_Al system, (middle) phosphates within 0.25 nm of Al^{3+} ions on d_NaCl system and (bottom) phosphates within 0.30 nm of Na^{+} ions on d_NaCl system.

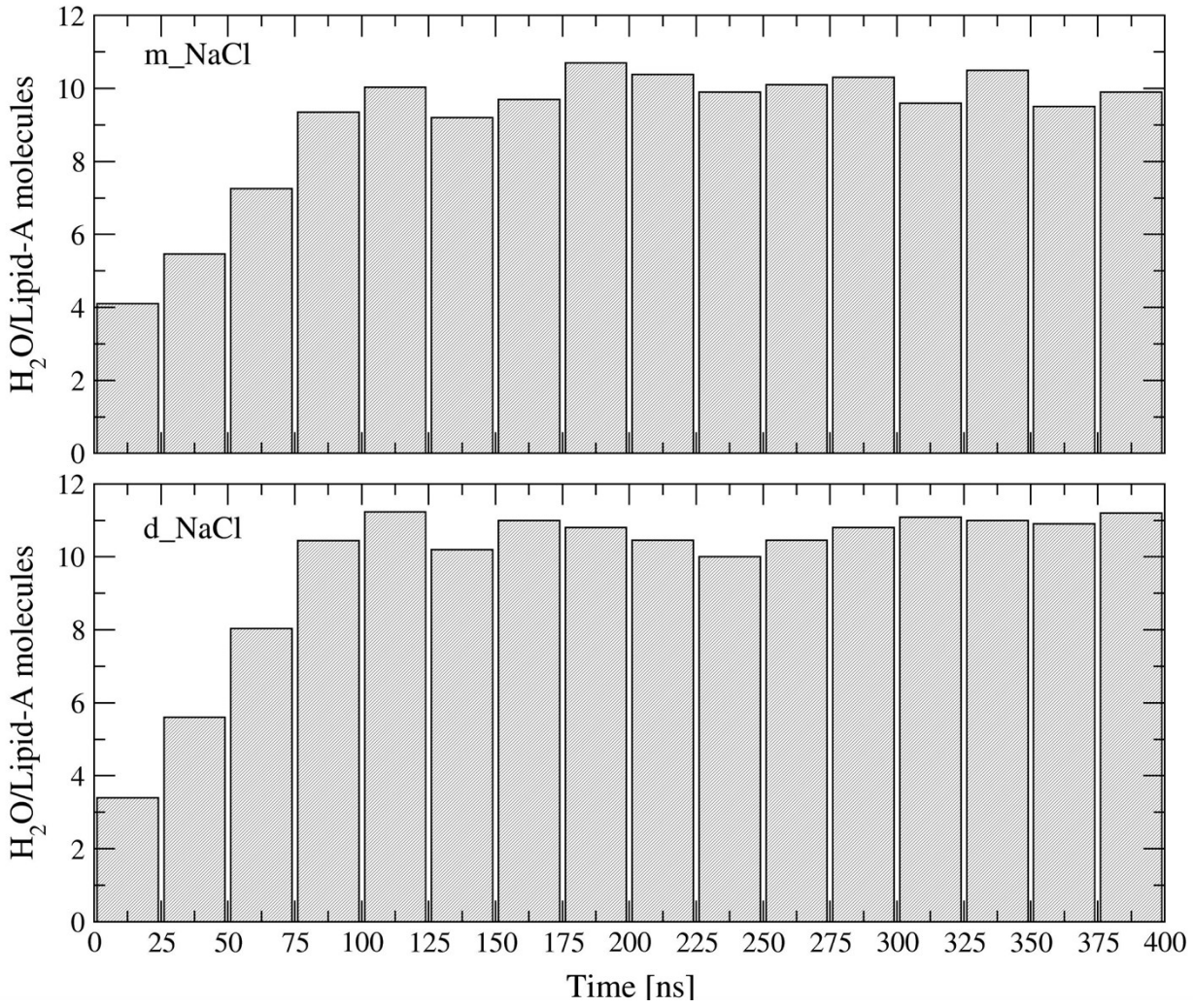

Figure SI-7. Convergence of the average number of water molecules per lipid for mono- and diphosphorylated Lipid-A membranes in presence of Al^{3+} counterions and in 150 mM NaCl solution. Values are normalized by the total number of water molecules in the simulation box. These estimative were calculated with SuAVE by taking the phosphorus atoms as reference for the grid fitting along the bilayer leaflets. The number of grid points for the mesh was chosen to be 100 × 100 grid points.

Table SI-1. Diffusion coefficients (D, 10^{-6} cm^2/s) for cations in mono- and diphosphorylated Lipid-A membranes under varying concentration regimes (0 mM, 150 mM $AlCl_3$, and 150 mM NaCl). Diffusion coefficients for the xy plane (D_{xy}), z axis (D_z) and total (D).

Systems	**Cations**	**Diffusion coefficient [10^{-6} cm^2/s]**		
		D_{xy}	D_z	D
m_Al$_{RF}$	Al^{3+}	0.13 ± 0.01	0.039 ± 0.005	0.14 ± 0.01
m_Al$_{PME}$	Al^{3+}	0.12 ± 0.01	0.040 ± 0.007	0.14 ± 0.01
m_AlCl$_{3\text{-}RF}$	Al^{3+}	2.8 ± 0.1	1.7 ± 0.2	2.4 ± 0.5
m_AlCl$_{3\text{-}PME}$	Al^{3+}	2.6 ± 0.1	1.7 ± 0.2	2.3 ± 0.8
m_NaCl$_{RF}$	Al^{3+}	0.20 ± 0.01	0.13 ± 0.08	0.15 ± 0.07
	Na^+	**18.8 ± 3.9**	**8.7 ± 0.7**	**21.7 ± 1.9**
m_NaCl$_{PME}$	Al^{3+}	0.17 ± 0.01	0.14 ± 0.02	0.15 ± 0.01
	Na^+	**18.0 ± 3.4**	**8.6 ± 0.4**	**20.8 ± 0.5**
d_Al$_{RF}$	Al^{3+}	0.15 ± 0.01	0.035 ± 0.007	0.38 ± 0.01
d_Al$_{PME}$	Al^{3+}	0.15 ± 0.01	0.036 ± 0.005	0.37 ± 0.01
d_AlCl$_{3\text{-}RF}$	Al^{3+}	3.8 ± 0.1	1.5 ± 0.2	4.1 ± 0.1
d_AlCl$_{3\text{-}PME}$	Al^{3+}	3.9 ± 0.2	1.6 ± 0.2	4.1 ± 0.1
d_NaCl$_{RF}$	Al^{3+}	0.28 ± 0.01	0.050 ± 0.002	0.18 ± 0.01
	Na^+	**24.0 ± 6.8**	**10.7 ± 4.1**	**27.3± 2.2**
d_NaCl$_{PME}$	Al^{3+}	0.28 ± 0.01	0.051 ± 0.002	0.18 ± 0.01
	Na^+	**24.8 ± 6.7**	**11.0 ± 4.9**	**26.1 ± 2.1**