

SUPPORTING INFORMATION

Molecular Modelling of Structure and Dynamics of Nafion

Protonation States

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I. Simulation Protocol

All the simulation boxes were energy minimized using the conjugate gradient algorithm in LAMMPS¹. $T= 353$ K, the average operating temperature for PEMFCs, was chosen for the present simulations.

The equilibration and production runs were also carried out using LAMMPS software¹. The NVT runs and annealing protocol followed is the same as employed in our previous study². The system is cycled between 353 K and 600 K as part of the annealing schedule. After annealing and NVT equilibration, the sample was simulated under NpT conditions for another 8 ns at $p=1$ atm and $T=353$ K. The density of the sample has been stabilized after about 1.5 ns of NpT simulations. The last 3 ns of the NpT run was used for analysis.

The Nose-Hoover style thermostat and barostat^{3,4} in LAMMPS¹ were used for maintaining the temperature and pressure, as imposed during the NVT/NpT simulation. The Verlet integration algorithm⁵ was used for time integration of the equations of motion. The PPPM solver was used for the electrostatics. The cutoff for the non-bonded interactions was set at 10 Å. The time step was equal to 1 fs for all the simulations.

During the last 3 ns of the NpT simulation, particles trajectories were saved every 1 ps for structural and dynamic property analysis. The RDFs and average water cluster sizes showed minimal variation during this time.

II. Sulfur-Oxygen (water) Radial Distribution Functions

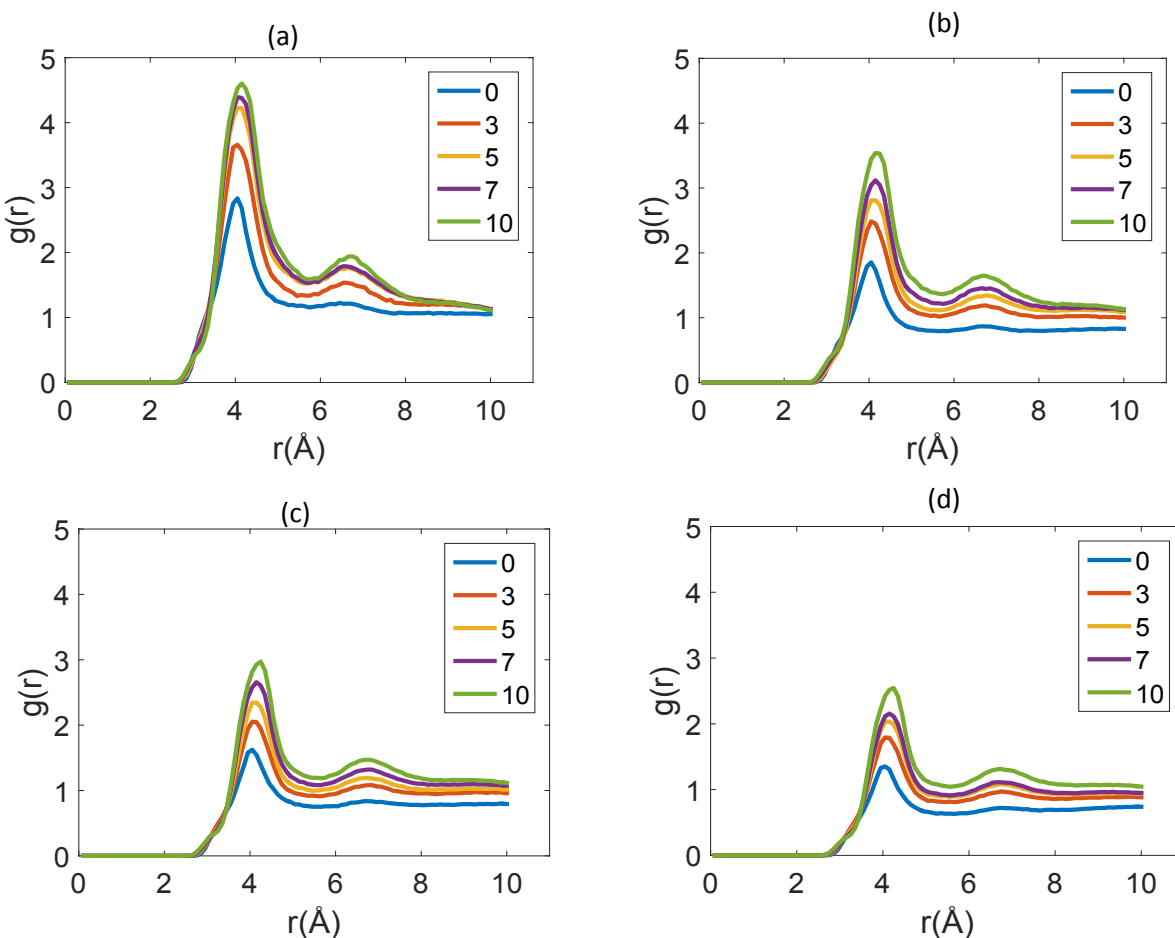


Figure S1. S-Ow (Sulfur- Oxygen (water)) radial distribution functions for DDP= 0, 3, 5, 7, 10 for (a) $\lambda = 5$ (b) $\lambda = 10$ (c) $\lambda = 15$ (d) $\lambda = 20$

III. Sulfur-Oxygen (hydronium) Radial Distribution Functions

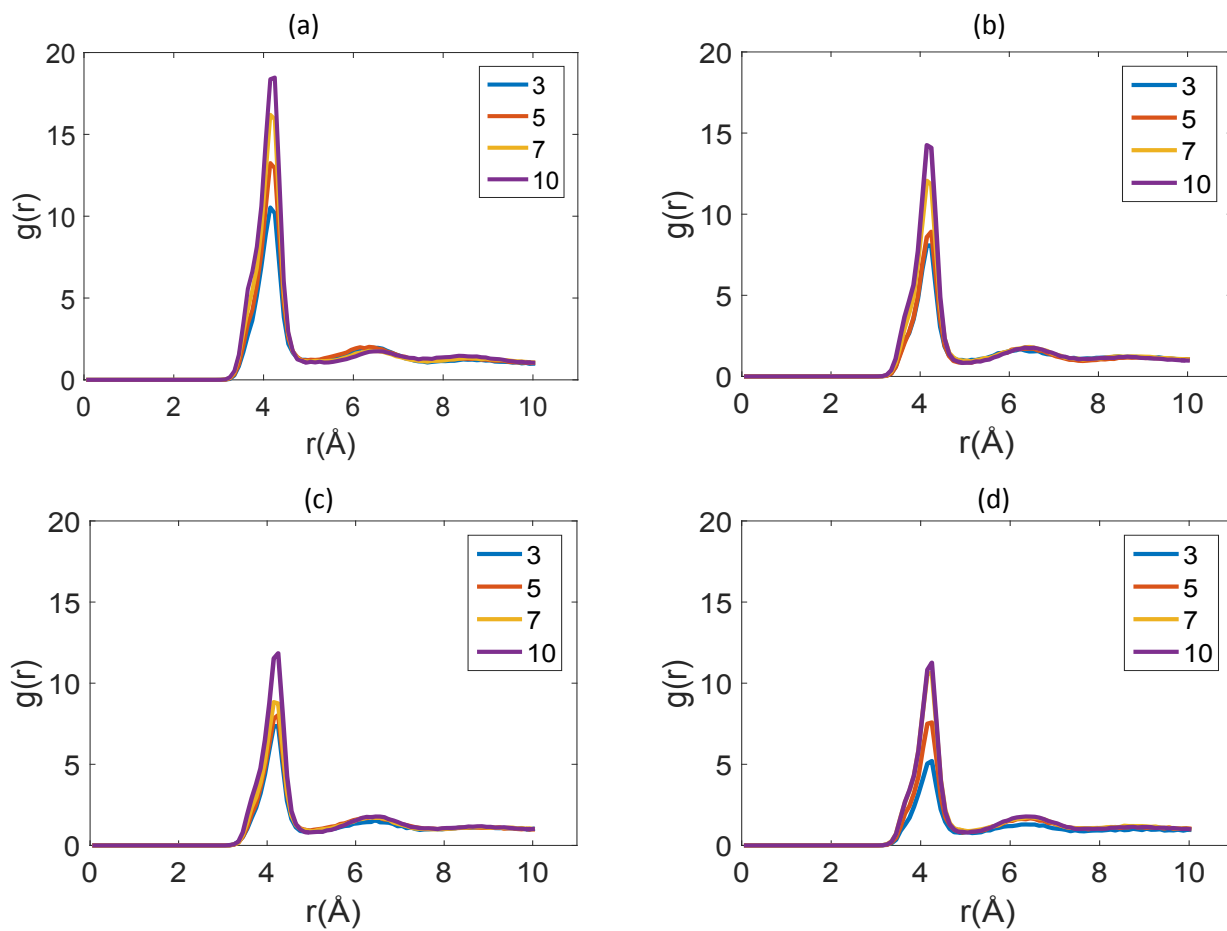


Figure S2. S-Oh (Sulfur- Oxygen (hydronium)) radial distribution functions for DDP= 3, 5, 7, 10 for (a) $\lambda = 5$ (b) $\lambda = 10$ (c) $\lambda = 15$ (d) $\lambda = 20$

IV. Oxygen (Water) -Oxygen (Water) Radial Distribution Functions

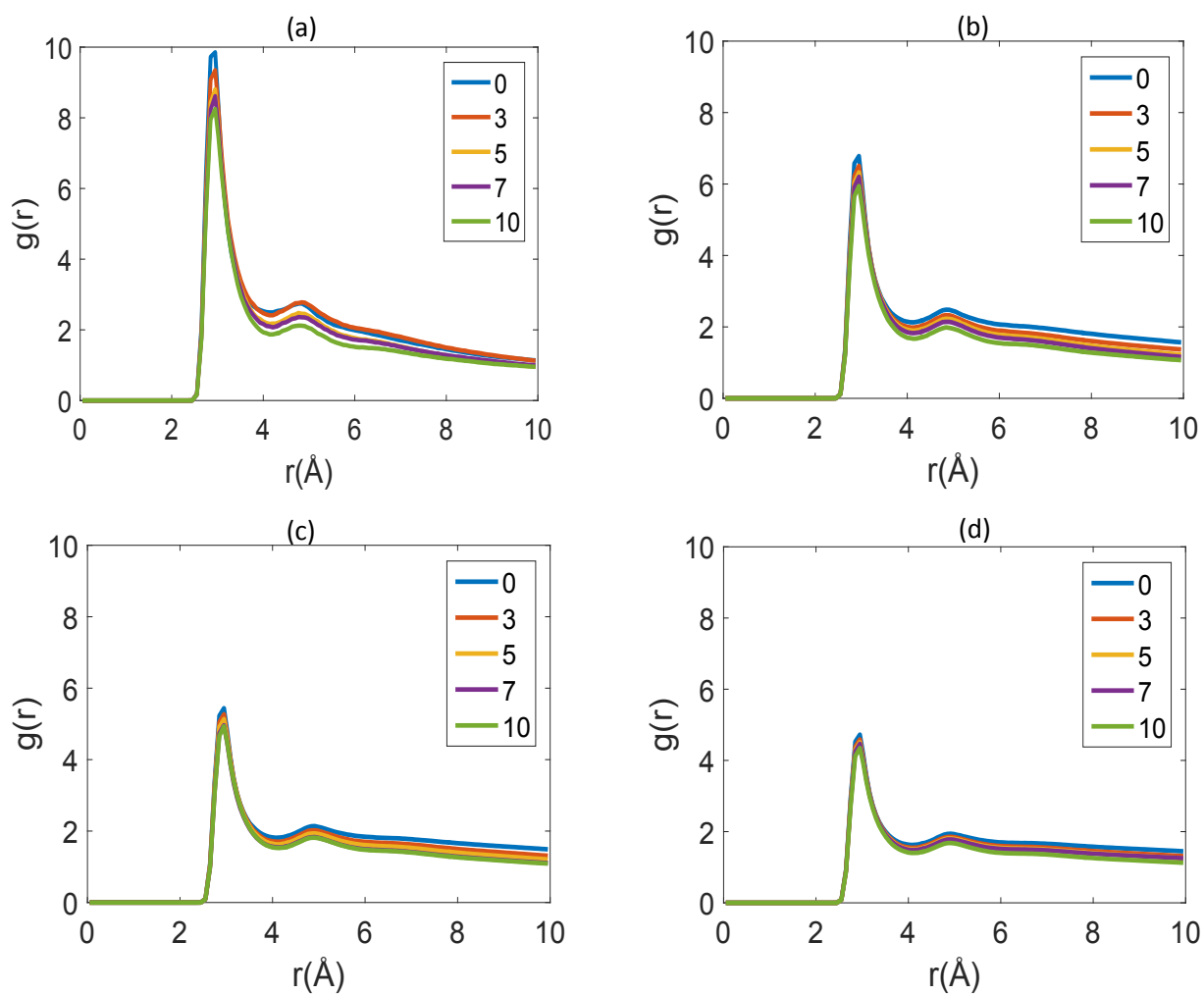


Figure S3. Ow-Ow (Oxygen (water) - Oxygen (water)) radial distribution functions for DDP= 0, 3, 5, 7, 10 for (a) $\lambda = 5$ (b) $\lambda = 10$ (c) $\lambda = 15$ (d) $\lambda = 20$

V. Oxygen (hydronium) -Oxygen (Water) Radial Distribution Functions

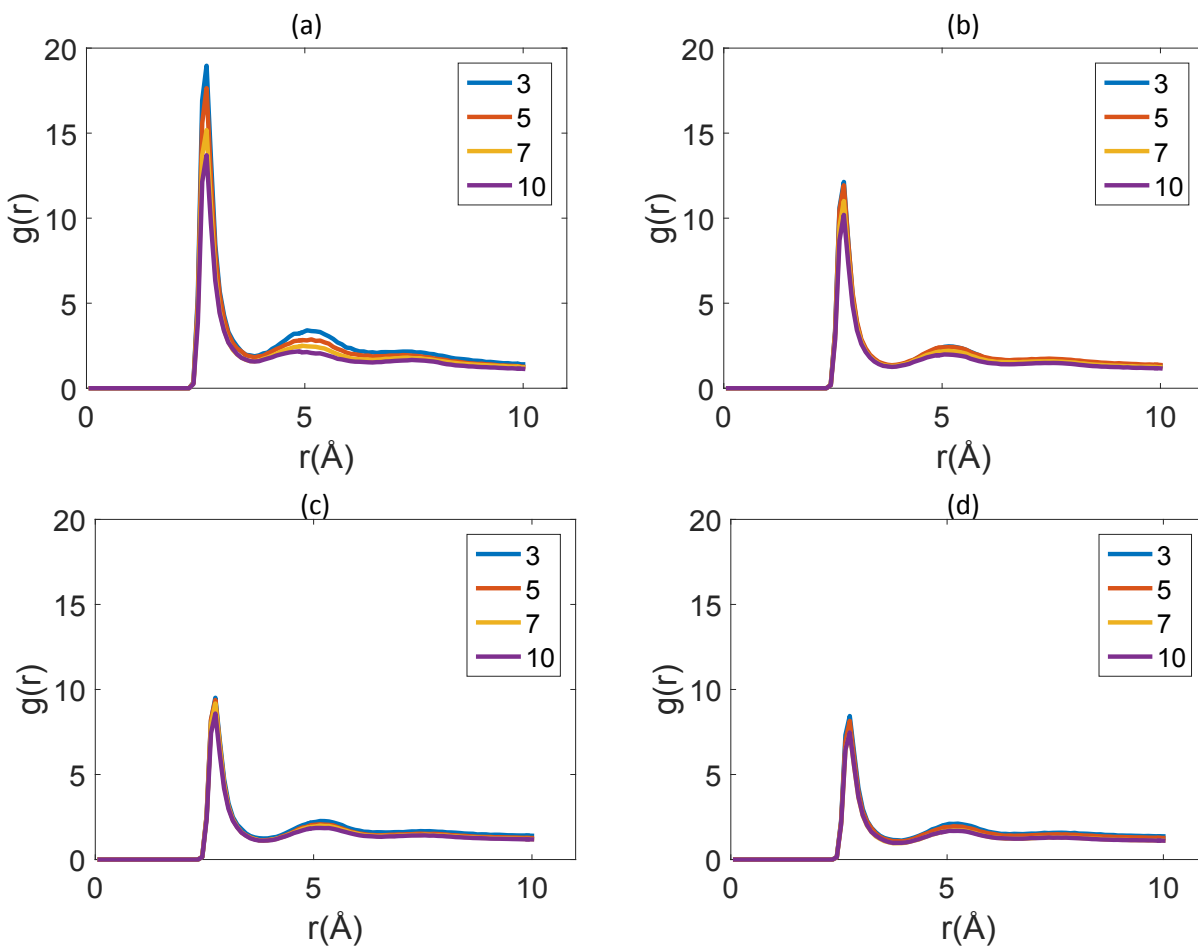


Figure S4. Ow-Ow (Oxygen (hydronium) - Oxygen (water)) radial distribution functions for DDP= 3, 5, 7, 10 for (a) $\lambda = 5$ (b) $\lambda = 10$ (c) $\lambda = 15$ (d) $\lambda = 20$

VI. Water Phase Structure Factors

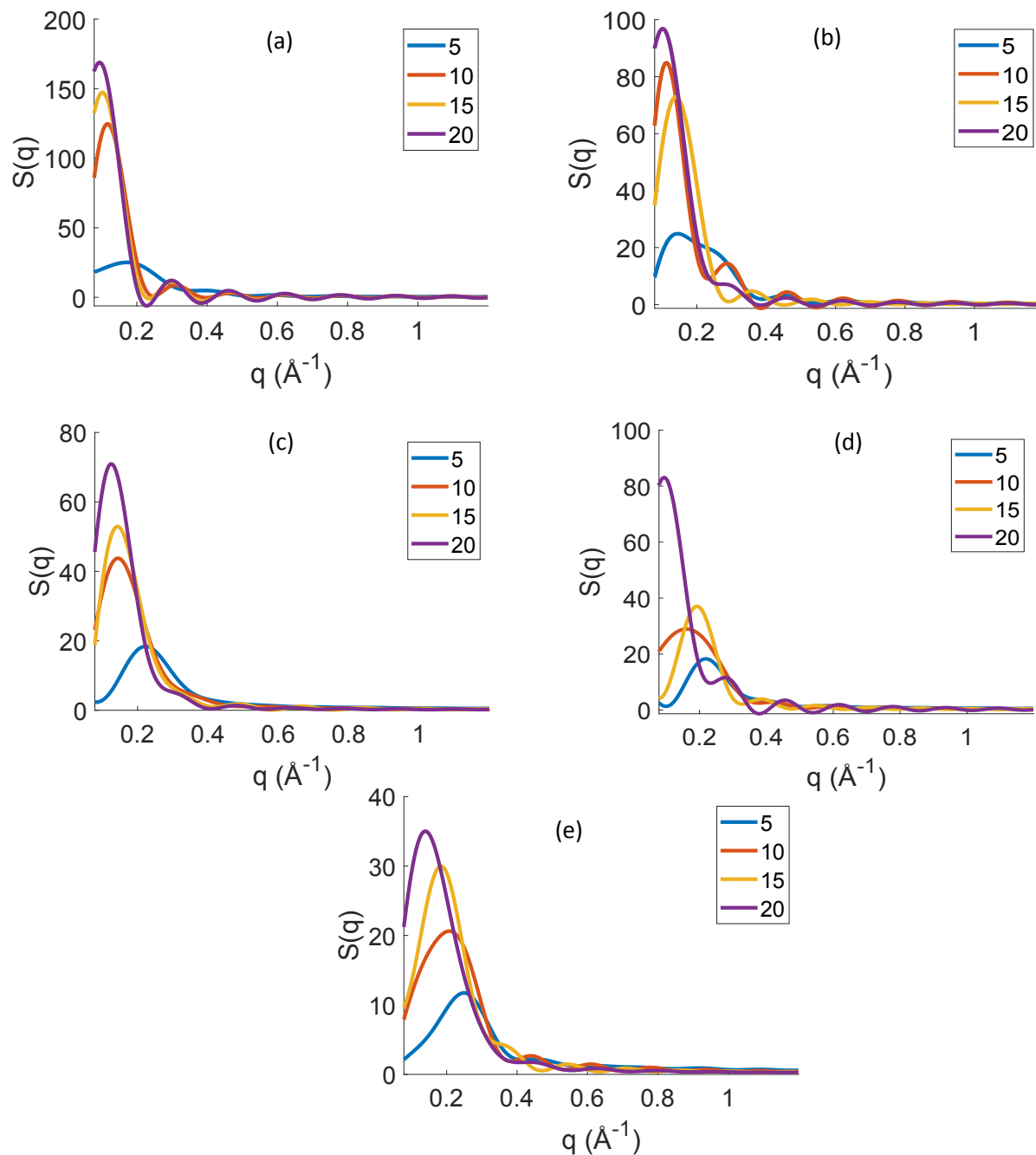


Figure S5. Water phase structure factors for $\lambda = 5, 10, 15, 20$ at (a) DDP = 0 (b) DDP = 3 (c) DDP = 5 (d) DDP = 7 (e) DDP = 10

The structure factors have been computed by the Fourier transform, Equation 1 of the main text, of the radial distribution functions (RDFs) of the oxygen (water and hydronium) – oxygen (water and hydronium). These RDFs are very similar to oxygen (water) – oxygen (water) RDFs (Figure S3). The wave numbers corresponding to the peak locations are very close to the experimental values⁶. Also, the peaks, on average, shift towards smaller wave numbers with increasing hydration level (λ), at all DDP levels, due to the increasing water domain sizes with increasing hydration.

VII. Water Cluster Distribution

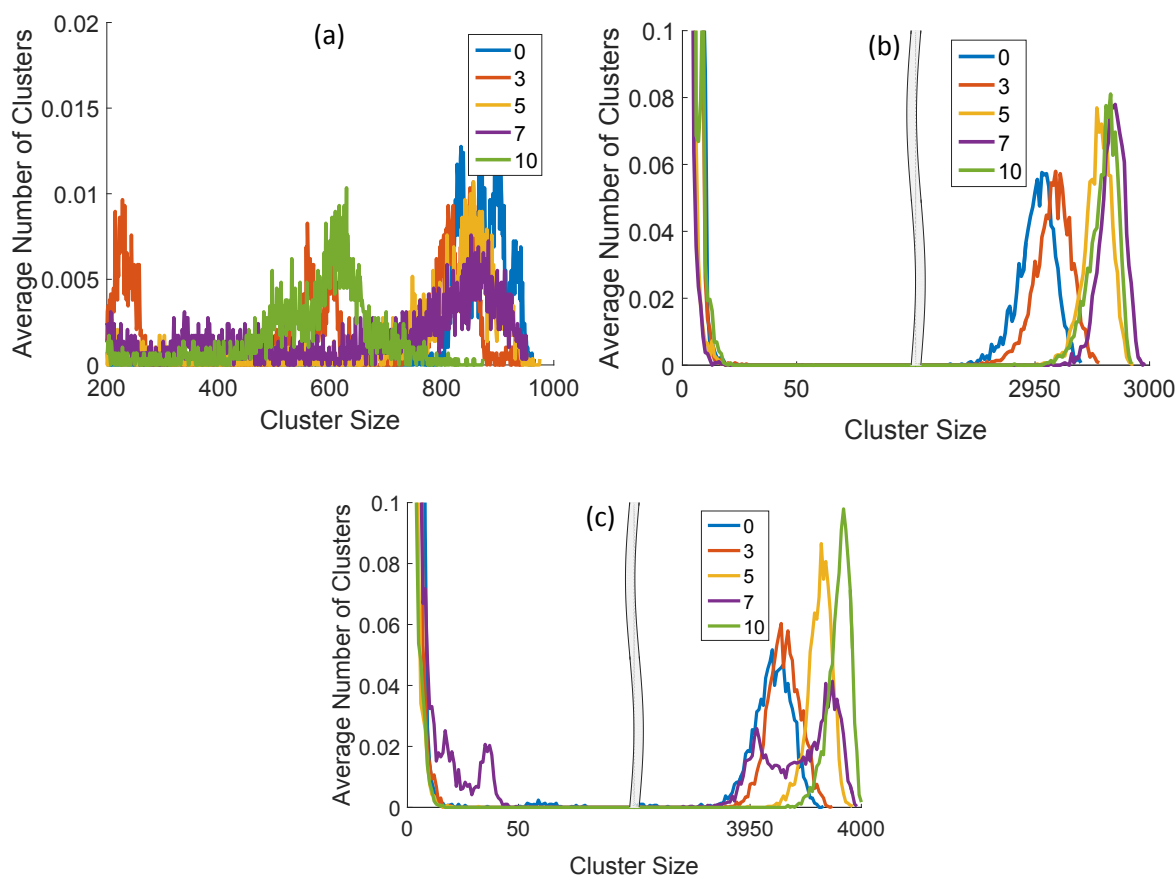


Figure S6. Hydrophilic/water phase cluster distributions for DDP=0, 3, 5, 7, 10 for (a) $\lambda = 5$ (b) $\lambda = 15$ (c) $\lambda = 20$. The average number of clusters for cluster sizes < 10 in parts (a), (b) and (c) are well beyond the vertical scales. Average number of clusters is directly proportional to the occurrence frequency of a particular cluster size in the averaging interval of 3 ns. Hydrophilic/water phase contains both water molecules and hydronium ions.

VIII. Hydrogen Bond Count

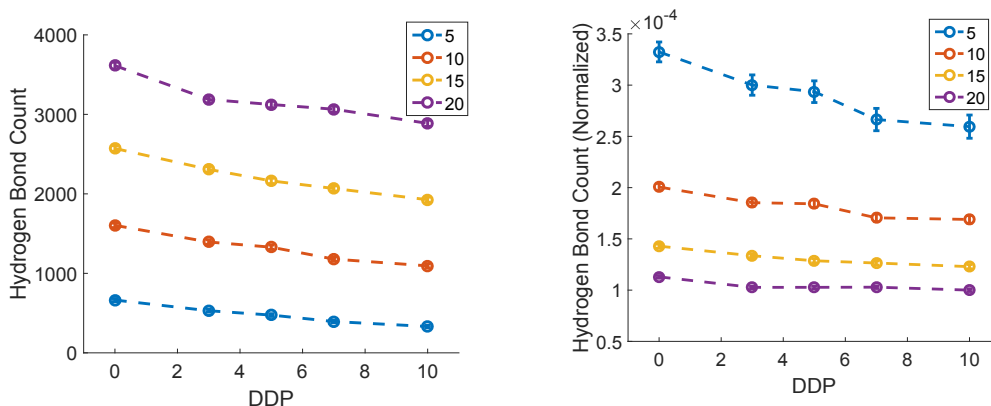


Figure S7. Hydrogen bond count for DDP = 0, 3, 5, 7, 10 at $\lambda = 5, 10, 15, 20$ (a) water-water hydrogen bonds (b) normalized count for water-water hydrogen bonds

IX. Mean Square Displacements (Overall) of water and hydronium

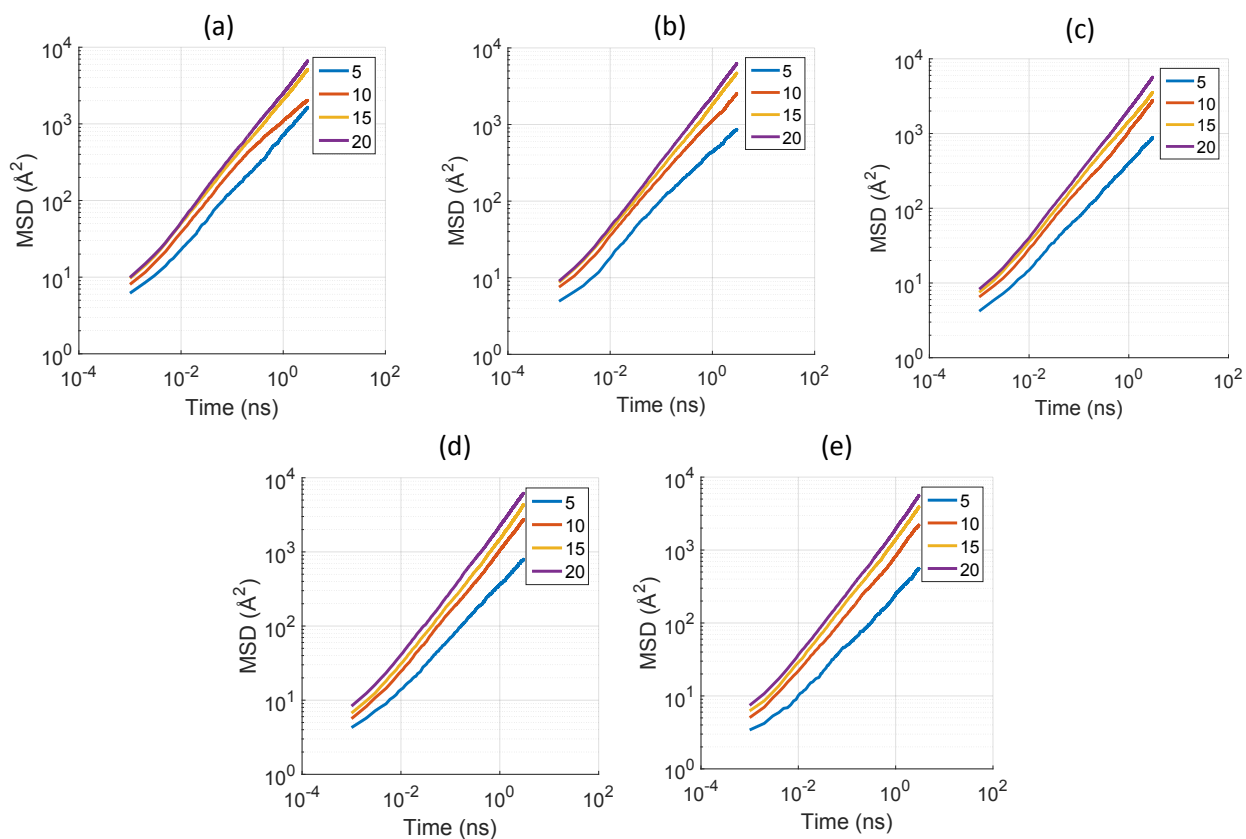


Figure S8. MSD for water molecule center of mass for $\lambda = 5, 10, 15, 20$ for (a) DDP= 0 (b) DDP= 3 (c) DDP= 5 (d) DDP= 7 (e) DDP= 10

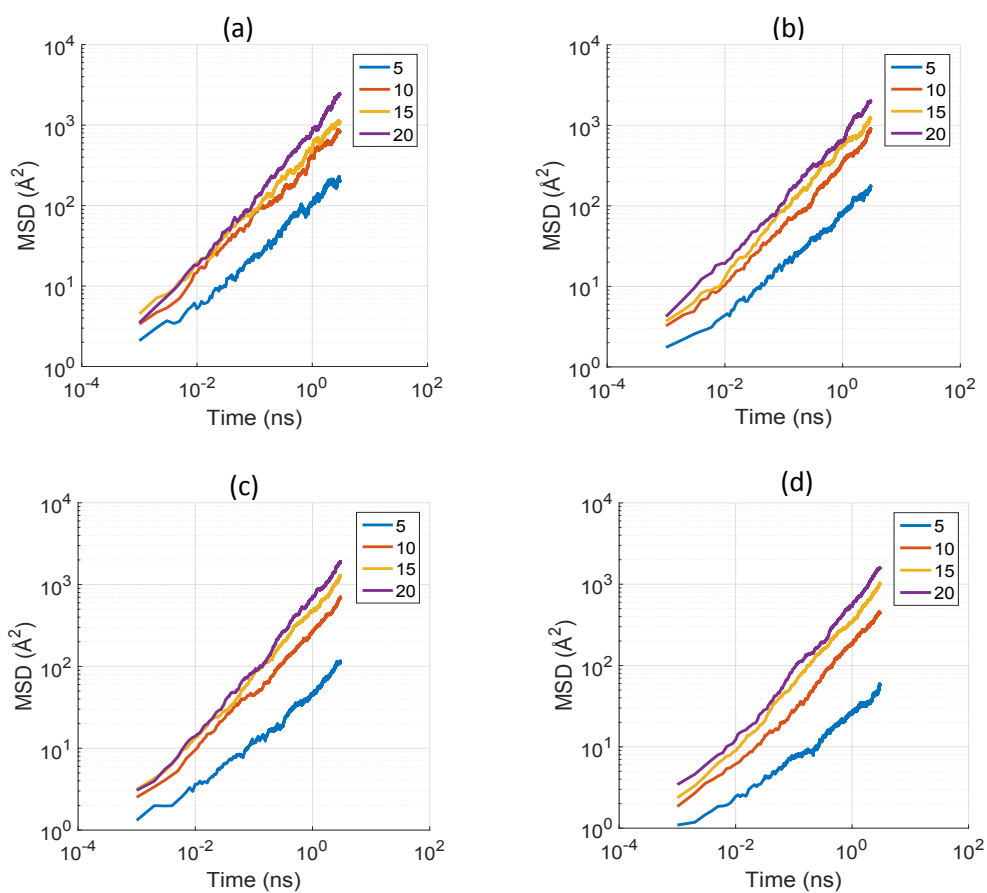


Figure S9. MSD for hydronium ion center of mass for $\lambda = 5, 10, 15, 20$ for (a) DDP=3 (b) DDP=5 (c) DDP=7 (d) DDP=10

X. Mean Square Displacement (within 4.2 Å of sulfur) of water and hydronium

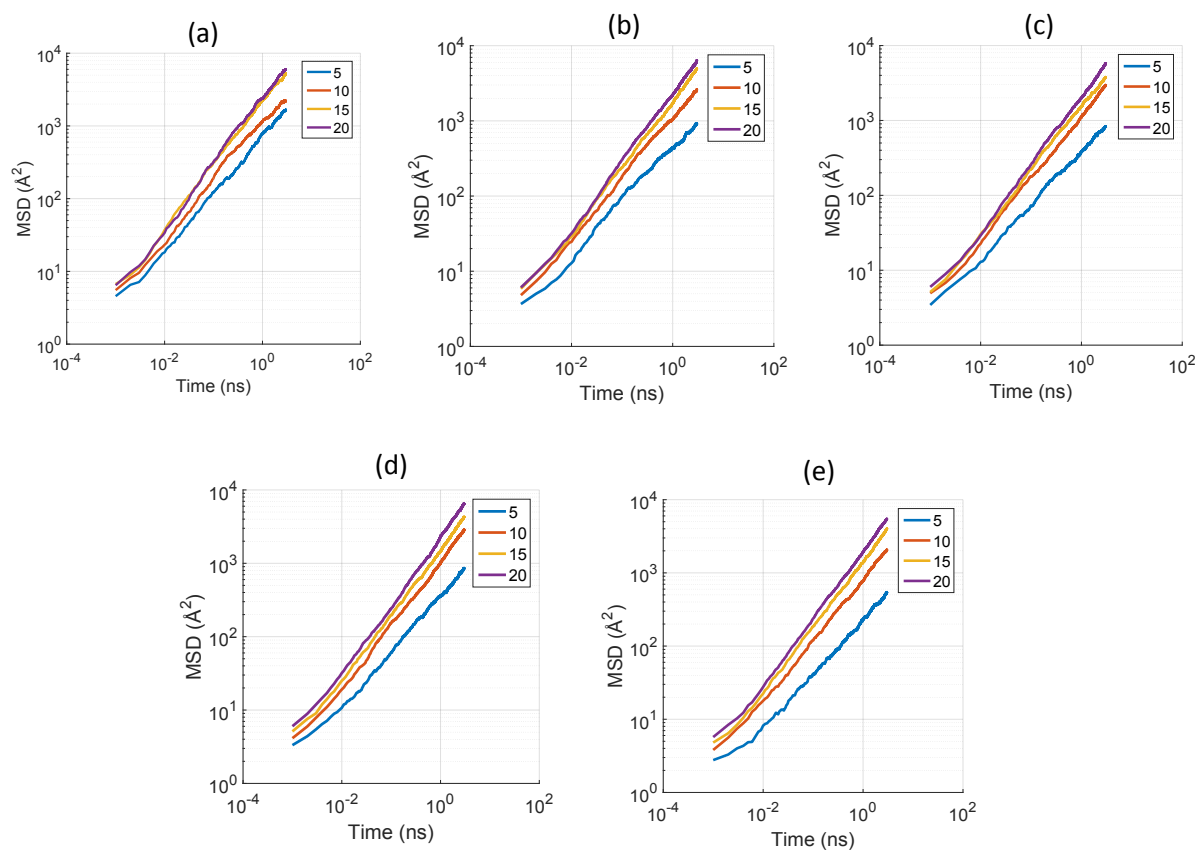


Figure S10. MSD for water molecule center of mass for $\lambda = 5, 10, 15, 20$ for (a) DDP= 0 (b) DDP= 3(c) DDP= 5 (d) DDP= 7 (e) DDP= 10 within 4.2 Å of sulfur atoms of the sulfonic acid groups

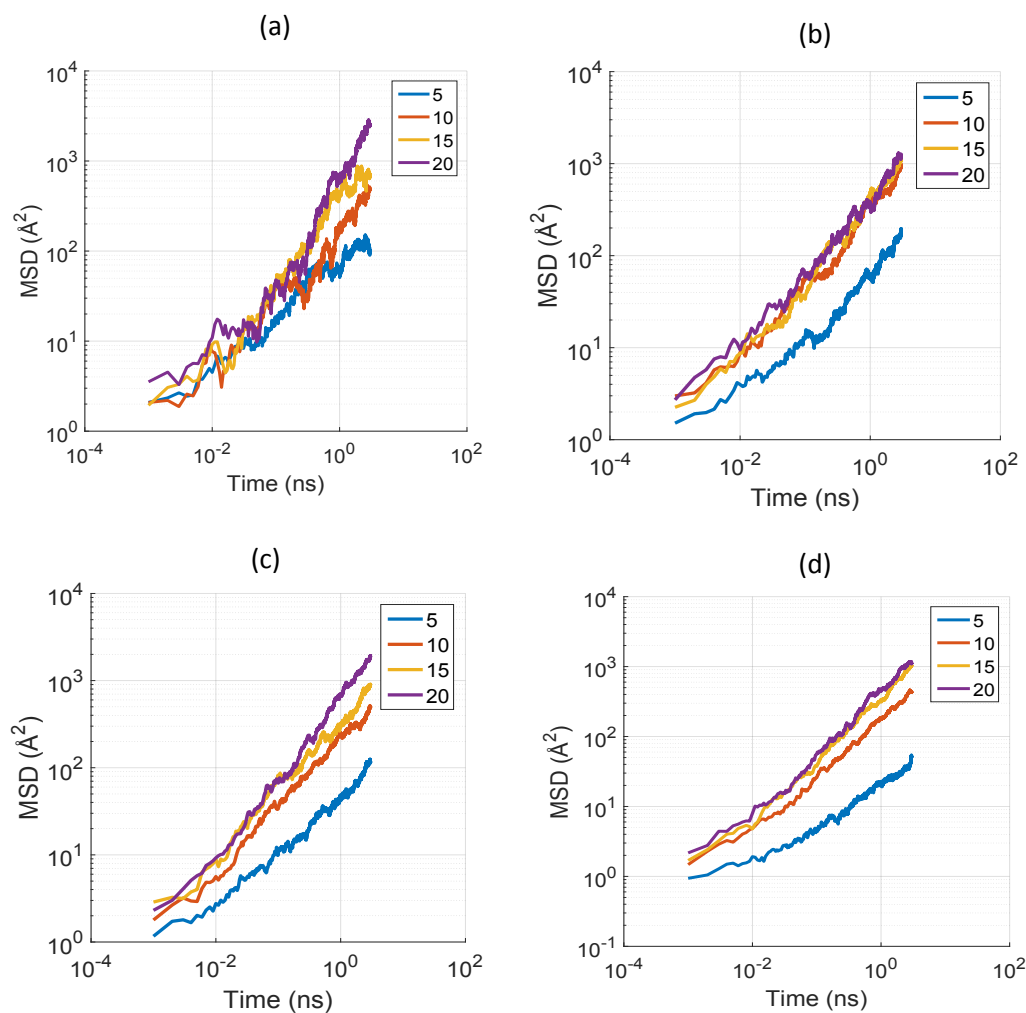


Figure S11. MSD for hydronium ion center of mass for $\lambda = 5, 10, 15, 20$ for (a) DDP= 3 (b) DDP= 5 (c) DDP= 7 (d) DDP= 10 within 4.2 \AA of sulfur atoms of the sulfonic acid groups

XI. Diffusion coefficients (within 4.2 \AA of sulfur) of water and hydronium

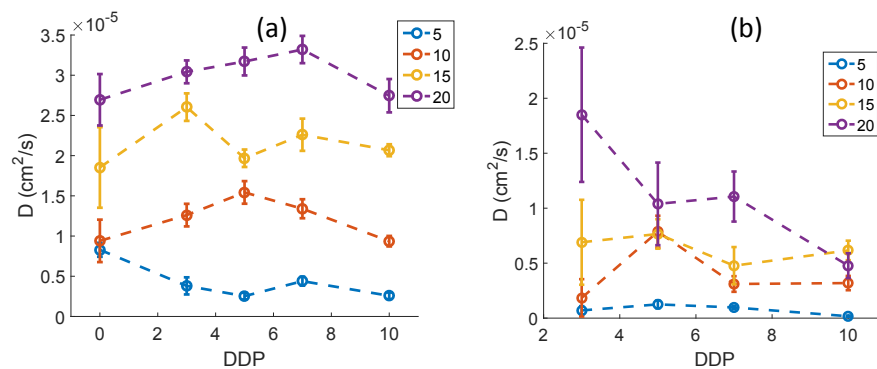


Figure S12. Diffusion coefficients for DDP= 0, 3, 5, 7, 10 at $\lambda = 5, 10, 15, 20$ of center of mass of (a) water molecules (b) hydronium ions whose oxygen atoms are within 4.2 \AA of sulfur atoms of sulfonic acid groups

XII. Residence Time and β coefficient of water and hydronium

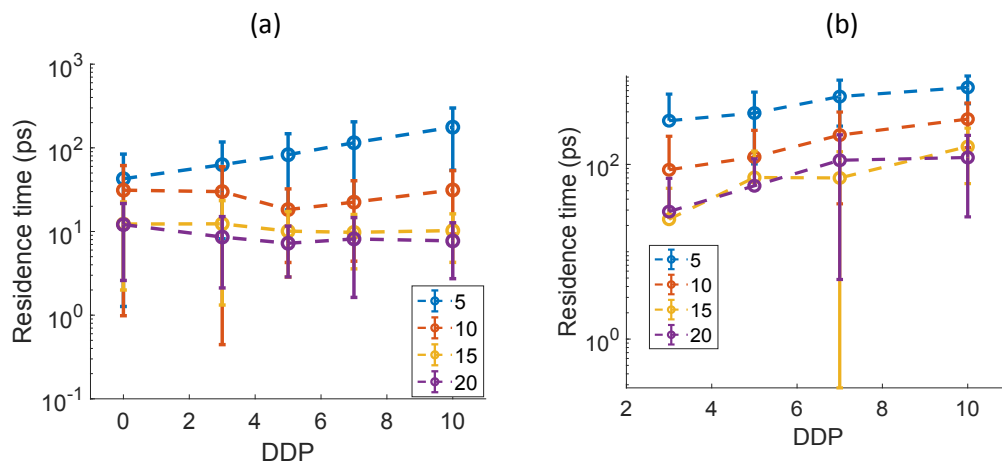


Figure S13. Residence time extracted using exponential fit (Equation S1), for DDP= 0, 3, 5, 7, 10 at $\lambda = 5, 10, 15, 20$ (a) of oxygen (water molecules) and (b) oxygen (hydronium ions)

Exponential fit

In addition to the stretched exponential fit, an exponential fit of the correlation function $C(t)$

$$C(t) = a * \exp\left(-\left(\frac{t}{\tau}\right)\right) \dots \dots \dots S1$$

was also used to get the residence times. Here $C(t)$ is described in Equation 2 of the main text and τ is the residence time

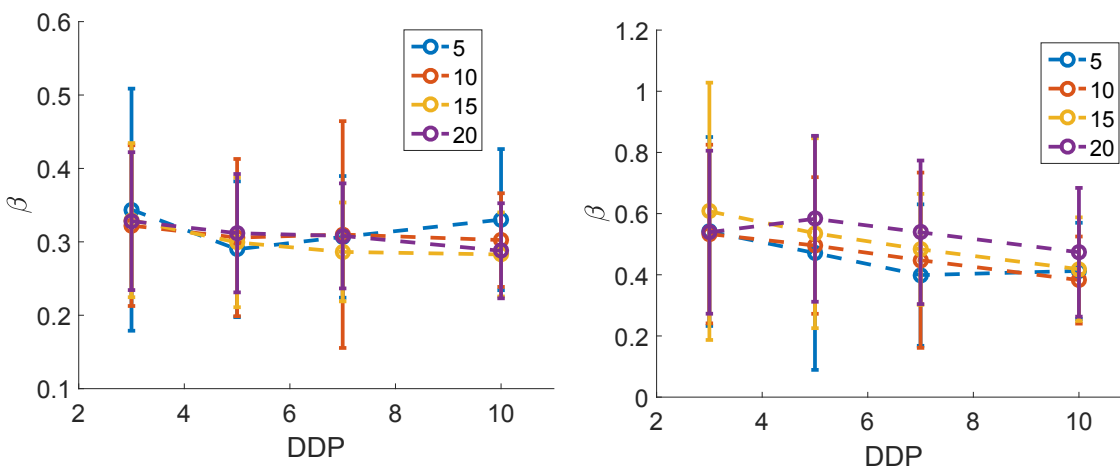


Figure S14. β coefficient value extracted from the stretched exponential fit, Equation 3 of the main text, of the correlation function, Equation 2 of the main text, for different DDP= 0, 3, 5, 7, 10 at $\lambda = 5, 10, 15, 20$ for (a) oxygen (water molecules) (b) oxygen (hydronium ions)

REFERENCES

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- (4) Shinoda, W.; Shiga, M.; Mikami, M. Rapid Estimation of Elastic Properties by Molecular Dynamics under Constant Stress. *Phys. Rev. B* **2004**, *69* (2004), 134103.
- (5) Verlet, L. Computer “Experiments” on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules. *Phys. Rev.* **1967**, *159* (1), 98–103.
- (6) Perrin, J. C.; Lyonnard, S.; Volino, F. Quasielastic Neutron Scattering Study of Water Dynamics in Hydrated Nafion Membranes. *J. Phys. Chem. C* **2007**, *111* (8), 3393–3404.