Supporting Information

Optimizing Water Transport through Graphene-Based Membranes: Insights from Nonequilibrium Molecular Dynamics

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1 Movie of water flow through membrane

The movie shows the flow of water through a membrane consisting of two graphene sheets. The simulations were performed at T=300K in a simulation box of size $(L_x, L_y, L_z) =$ (18.4, 23.0, 100.0)Å. A force of $F = 1.0\epsilon/\sigma$ was applied to the oxygen sites in a slab encompassing the first 10Å in the z direction. The slit width in both sheets is 6Å where the second slit is offset by $0.5L_y$. The sheets are separated by 6Å. The simulation covers a time of 3ns.

The movie highlights the trajectory of a randomly chosen water molecule. It enters the membrane, remaining there for a significant time whilst moving up and down the channel in between the two sheets. The observed path taken by water molecules through the membrane is at odds with the proposition of a rapid diffusion by means of a single, fully bonded monolayer.

2 Effect of periodicity

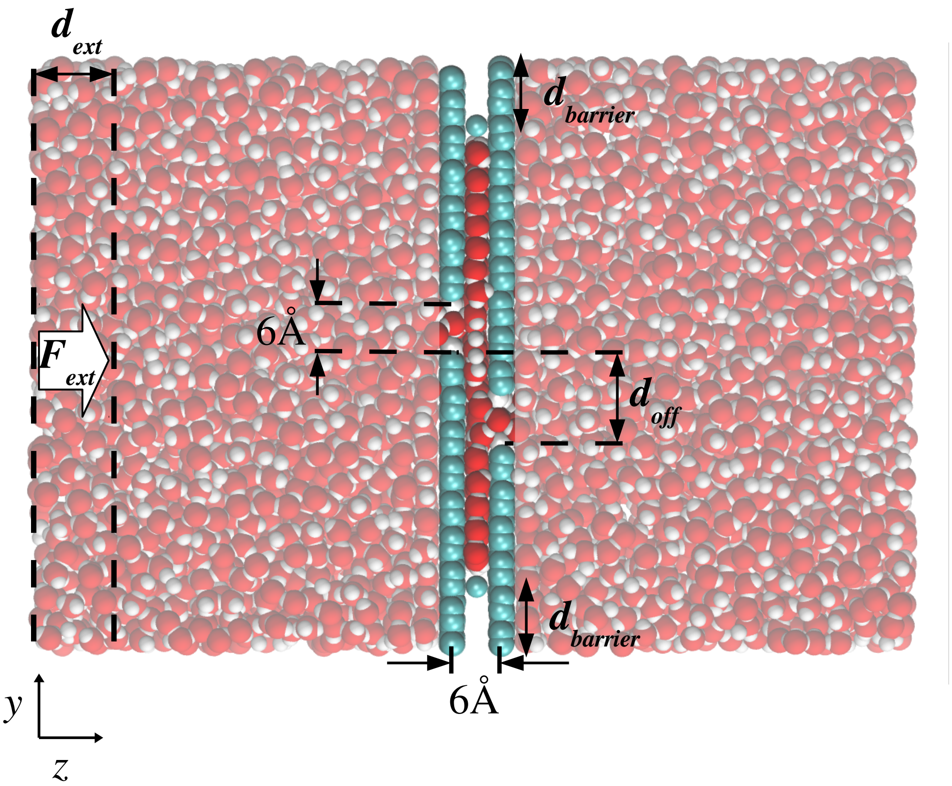


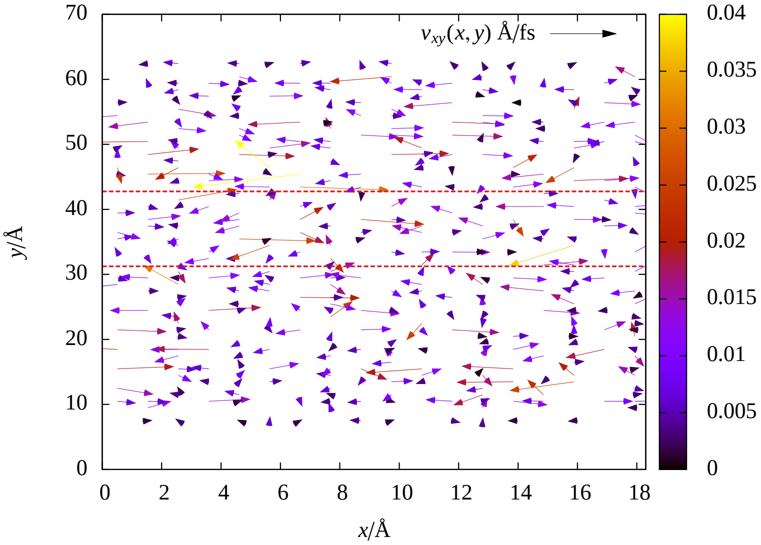
Figure 1: The system setup now includes barrier particles placed at a distace $d_{\text{barrier}} = 0.1 \times L_y$ from each end in the carbon sheet along the x-axis. The offset between the sheets is the same distance as in the $c = 0.5$ simulations presented in the main text. However, the system cell has been elongated in the y direction.

In order to support the conclusions presented in the main text concerning the lack of a plug-like flow an additional simulation was performed with a modified membrane setup such that molecules are only allowed to take one path through the membrane (i.e. the periodicity is effectively removed between the carbon sheets).

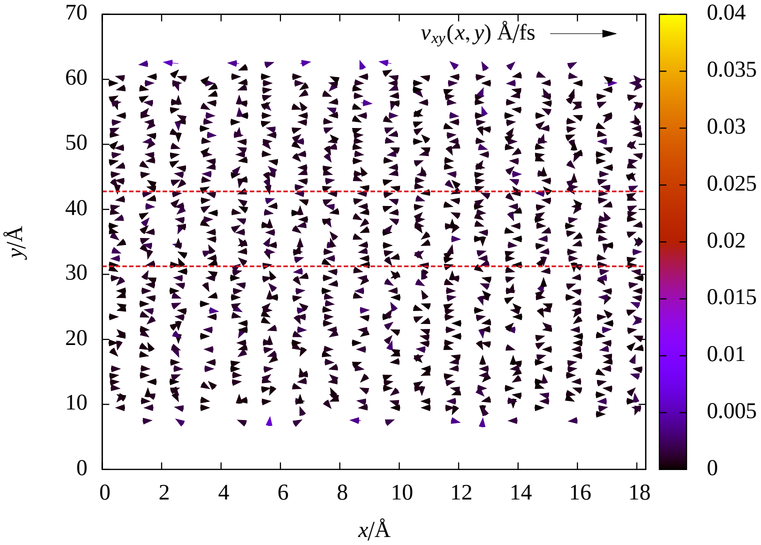
A schematic of the setup can be found in figure 1. Carbon atoms have been placed between the sheets at a distance $0.1 \times L_y$ away from the edges of the simulation box to prevent the water molecules from traversing the periodic boundary. The additional carbon atoms have the same interaction parameters as the carbon atoms in the sheet but their equations of motion are not integrated and thus remain stationary. The box size was changed to $(L_x, L_y, L_z) = (18.4,\ 69.9,\ 105.0)$Å to ensure that the newly introduced carbon edges do not influence the motion of water through the sheet. The offset between the entrance and exit slits is the same distance as in the $c = 0.5$ case from the main text and the applied force has $A = 1.0$.

Figure 2 shows the 2D vector field of the x and y velocity components of water molecules in the xy plane between the sheets. If a steady, plug-like flow is present, then the velocity vectors between the openings would have a net alignment and a non-diminishing magnitude. The instantaneous velocity field indicates no preferential direction for the flow. When the time average is taken, the averaged magnitude of the velocity vectors diminishes to zero, indicating no prefered flow direction at longer timescales. Therefore even in the absence of multiple flow paths, there is no evidence of a plug-like flow of water molecules.

The residence time distribution was calculated to further support the assertion that plug-like flow is not the dominant transport mechanism even when only a single path through the membrane is permitted. Figure 3 shows the residence time distribution for the system presented above as well as the system presented in the main text characterised by a sheet offset of $c = 0.5$. It can be seen that the distribution follows the same trend as for the $c = 0.5$ case, i.e. a peak at short times followed by a slowly decaying tail. Again this is in contrast to the hydrogen bond lifetime distribution, which decays at a faster rate. The average residence time for this setup is $\tau_{\mathrm{res}} = 22.2 \pm 2.0$ps.



(a)



(b)

Figure 2: Instantaneous (panel (a)) and time averaged (panel (b)) velocity fields for molecules in the membrane for the single path system. Dashed lines indicate the position of the openings

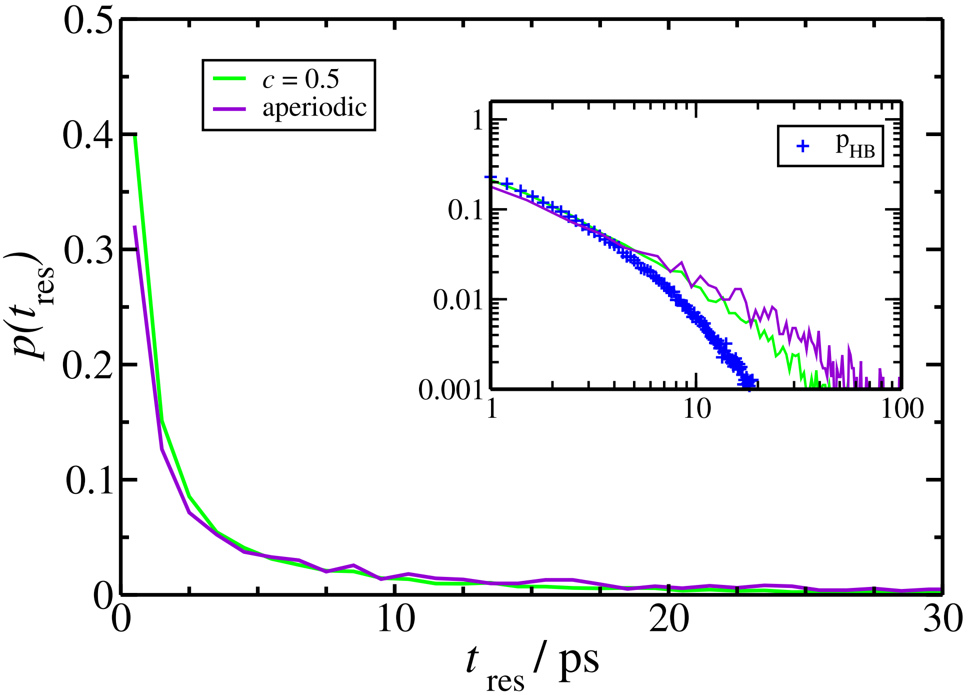


Figure 3: Residence time histogram for the $c = 0.5$ case as presented in the main text (green line), as well for the aperiodic membrane (purple line). The inset plot shows the log-log plot of the same data compared to the hydrogen bond lifetime distribution (blue crosses).