

Supplementary information

Asymmetric transport and desalination in graphene channels

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In our early work, we used time step of 2 fs but subsequently we found that the simulation systems can be also very steady for 2.5 fs time step and the results are also similar. Thus, to save the MD running time we used 2.5 fs time step in our recent work. Nonetheless, to test the effect of time step for the present model, we have conducted additional MD simulations for 1 fs time step and moderate channel size $D = 1.70$ nm. Fig. S1 shows the comparison for the 1 fs and 2.5 fs time step, where the flux values are very close to each other. Thus, the 2.5 fs time step can also produce reliable results.

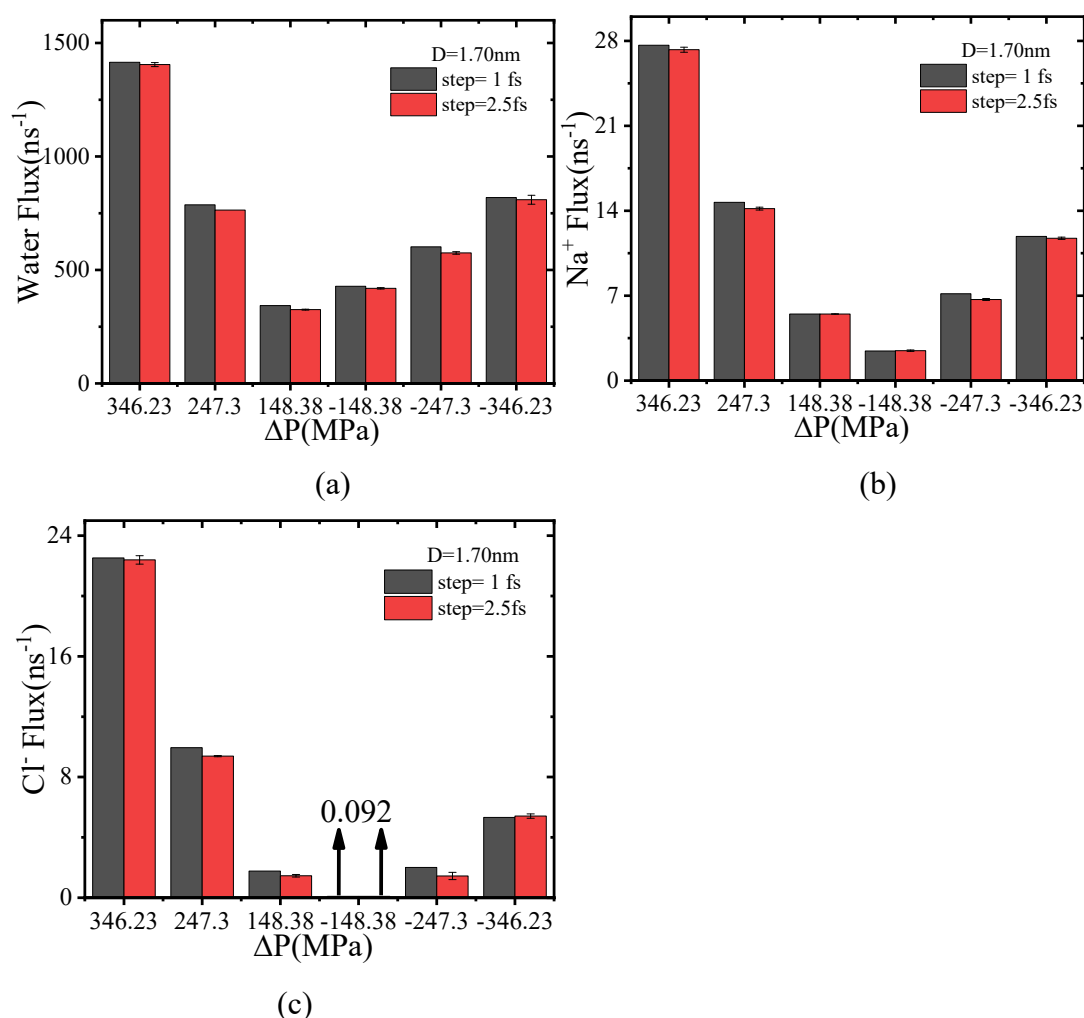
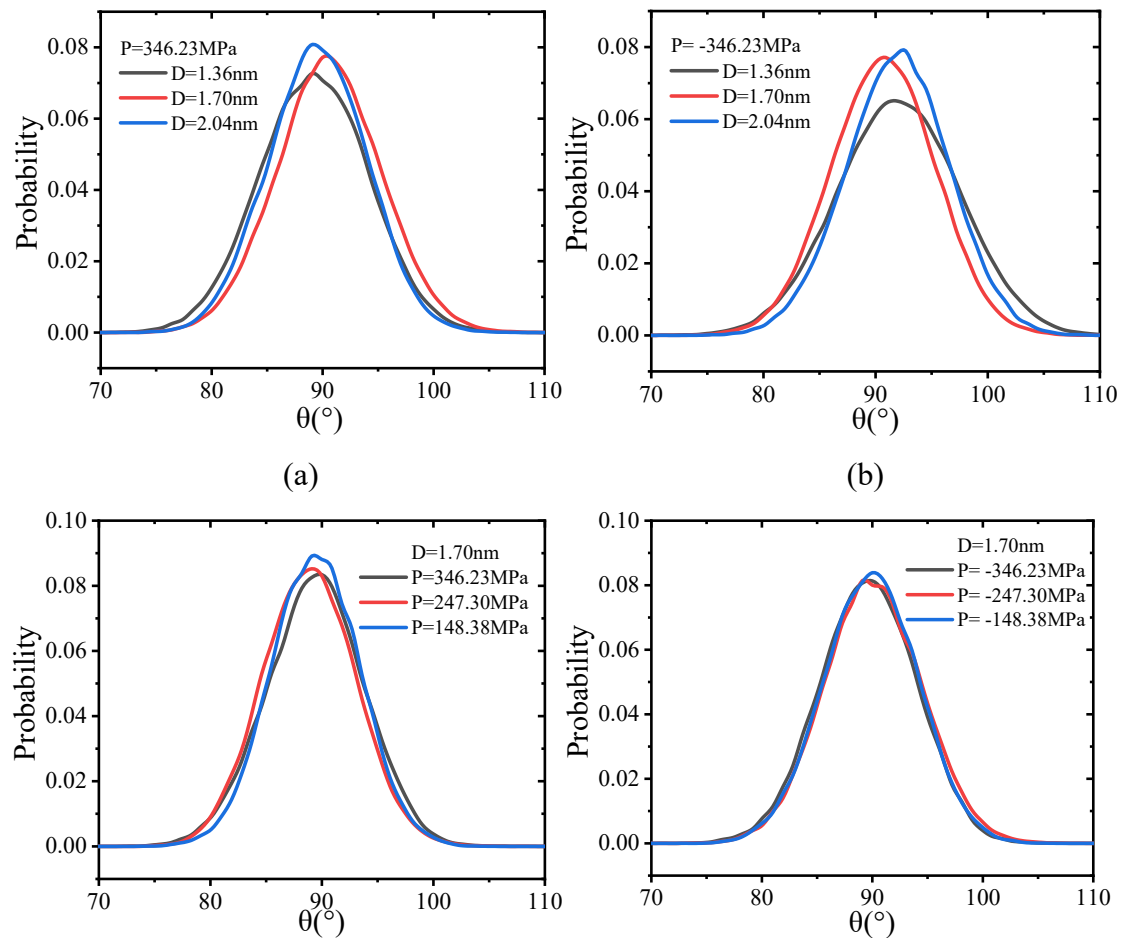


Fig. S1 Comparison for 2.5 fs and 1 fs time step for $D=1.70$ nm and different pressures.

Fig. S2 shows the probability distribution of water dipole orientation inside the channel. θ denotes the dipole angle between water molecules and +z direction, and the

average is taken over all the water molecules inside the channel. As seen in Fig. S2a, the dipole angle in the convergent direction exhibits a single peak distribution that weakly depends on D . Interestingly, the peak locations are all around 90° , indicating that the water molecules tend to flip and reorient frequently. This is actually a random dipole distribution. For $\Delta P = -346.23$ MPa in Fig. S2b, the dipole orientation exhibits similar distributions that also weakly depend on D . For a given channel size, the dipole distribution is insensitive to the pressure values, shown in Fig. S2c and S2d. On the whole, the water dipole orientation is not sensitive to the ΔP and D , but will strongly depend on the electric field [S1]. In fact, the present water model is rigid and the dipole momentum will be not changed. The dipole orientation and distribution could be different for flexible water models. It is believed if not under strong electric field the vibration of O-H bonds and H-O-H angles should be very limited, and thus the dipole orientation for rigid and flexible waters should be similar. We actually made some tests on this point many years ago, where the transport dynamics and dipole orientation for rigid and flexible waters are close to each other.

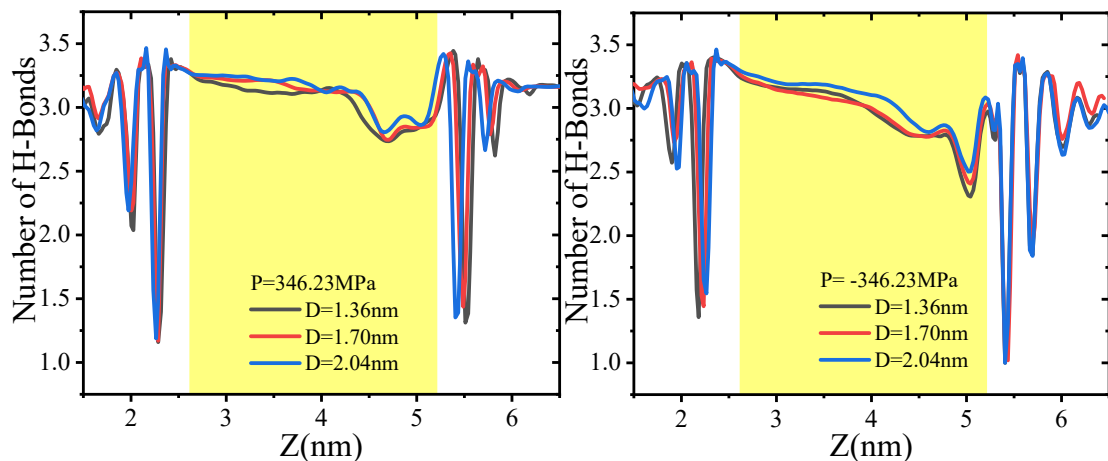


(c)

(d)

Fig. S2 The probability distribution of water dipole angle for (a) $\Delta P = 346.23$ MPa with different D, (b) $\Delta P = -346.23$ MPa with different D, (c) $D = 1.70$ nm with different positive pressures and (d) $D = 1.70$ nm with different negative pressures.

Fig. S3 shows the variation of hydrogen bonds (H-Bonds) as a function of water position along z-axis. As seen in Fig. S3a, from the reservoir to base the H-Bond number displays fluctuations with a sudden drop and jump because of the deformation of bulk water structure when entering a confined space. Inside the channel, the H-Bond number decreases smoothly and has a drop due to the reduced channel space. After moving out of the tip, the H-Bond number exhibits similar fluctuations. It is noteworthy that unlike the carbon nanotubes in which the H-Bond number is sensitive to the channel size [S2,S3], there is only a slight fluctuation in the H-Bonds number as the D varies. This is because in the present two-dimensional graphene channel, the water molecules can also have enough space to form more H-bonds. As shown in Fig. S3b, the overall H-Bond distribution for $\Delta P = -346.23$ MPa is similar to $\Delta P = 346.23$ MPa, but the valleys near the tip have smaller values. This is because when water enters the tip directly, the H-Bond network will be subjected to a sudden destruction. As seen in Fig. S3c and S3d, inside the channel and particularly near the channel tip, the H-bond number increases with the increase of $+\Delta P$ but inversely increases with the decrease of $-\Delta P$. This opposite behavior is mainly attributed to the perturbation of ions in the channel. Apparently, with the increase of $+\Delta P$, the ion occupancy decreases and this promotes the reformation of H-bond; while with the increase of $-\Delta P$, the ion occupancy increases that hinders the H-bond formation.



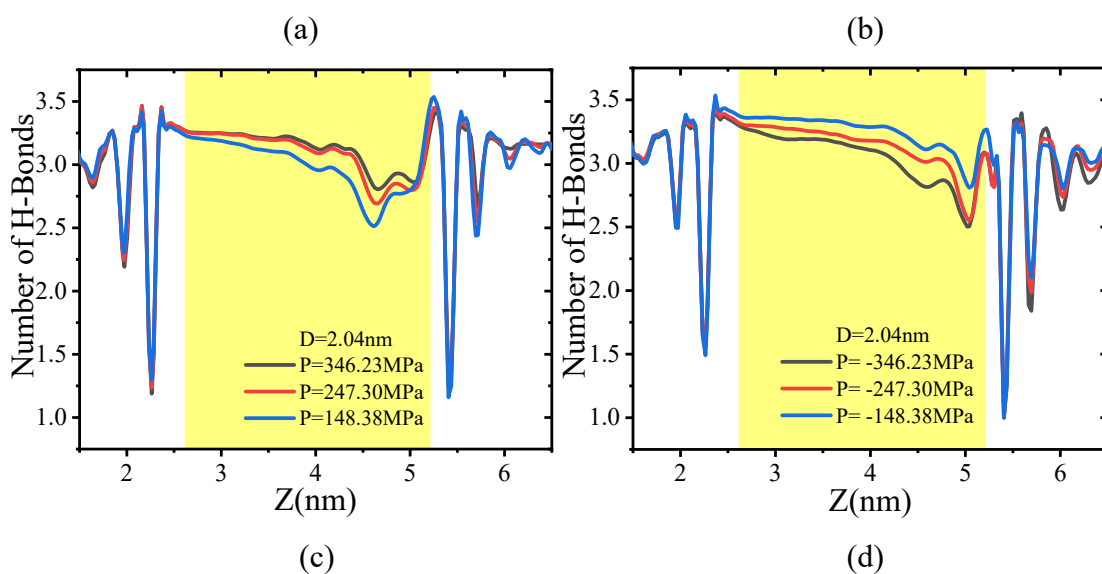


Fig. S3 The average hydrogen bonds (H-Bonds) as a function of water position for of channel under (a) $\Delta P = 346.23$ MPa with different D, (b) $\Delta P = -346.23$ MPa with different D, (c) $D = 2.04$ nm with different positive pressures and (d) $D = 2.04$ nm with different negative pressures.

References

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