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Enhancement of water flow across a carbon nanotube

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It is important to investigate how to enhance the flow rate of single-file water molecules across nanochannels. To our knowledge, all the existing methods are based on pressure gradients, external point charges or uniform/graded electric fields. Accordingly, these methods are all based on exogenous tools, and thus bring challenges for both energy-saving and miniaturisation. In contrast, here we manage to reveal an endogenously determined mechanism of flow enhancement. On the basis of molecular dynamics simulations, we investigate water permeation across a single-walled carbon nanotube (SWCNT A) in the presence of another SWCNT (SWCNT B). We find that the flow rate of the single-file water molecules across SWCNT A is enhanced for the case of unblocked SWCNT B compared with the rate for the case of blocked SWCNT B, and that this flow rate is determined by the separation between the two SWCNTs and the diameter of SWCNT B.

Keywords: carbon nanotube; water molecules; enhancement

1. Introduction

The study on water flow across nanochannels or microchannels exhibits great potential applications. For example, it plays an important role in understanding biological activities [1–4] and in designing nanodevices or nanomachines.[5,6] Nowadays, it is widely accepted that the ability to produce clean water is one of the key technological, social and economical challenges. As a consequence, there is a large interest in seeking for the low-cost methods of obtaining clean water. Luckily, a previous research has shown that the measured water flow rate across nanotubes is higher than predicted.[7] Later, this high fluid velocity is attributed to an almost frictionless resistance.[8] Therefore, these nanodevices are especially efficient in seawater desalination or water purification.[9,10] Meanwhile, it is also found that the properties of water molecules in a carbon nanotube, such as single-file arrangement, wavelike density distribution, wet-dry phase transition and gating, are similar in those inside biological water channels.[11–14] As a result, carbon nanotubes are often used to mimic the function of nanochannels to explore some phenomena efficiently.

To our knowledge, many methods are approached to control water permeation through membranes.[15,16] However, these methods are mainly based on exogenous tools such as pressure gradients, external point charges or uniform/graded electric fields.[6,9,12,14,17–21] Thus, on one hand, these methods usually cost much energy and bring challenges for both energy-saving and miniaturisation. On the other hand, the systems discussed above are mainly with only one nanochannel driven by exogenous factors [6,12,14,17–19] and the systems with many channels have not been fully understood. In practice, the density of channels varies by several orders magnitude, from hundreds of channels per square micrometers to areas lack of channels.[22] For instance, the estimated density of single K^+ channels is about 600 per cell.[23] The effect of a nanochannel on the water permeation across another nanochannel is still not very clear.

In order to explore some basic influence among the water nanochannels and reveal an endogenously determined mechanism of flow enhancement, we design a system containing only two single-walled carbon nanotubes (SWCNTs), A and B. Here, we use all atom molecular dynamics simulations to investigate water transport through SWCNT A under the influence of SWCNT B. Amazingly, the water transfer rate is determined by the separation between the two SWCNTs and the diameter of SWCNT B. These findings show the complex influence between water channel systems at the nanoscale, which may have applications in biology.

2. Methodology and simulation details

The molecular dynamics package GROMACS version 3.3.1 is used in our article, which has also been used widely for studying the properties of water dynamics in a confined system (SWCNTs).[24–26] The simulation framework with two parallel plates immersed in a water box (4.652 nm × 9.967 nm × 4.880 nm) is shown in Figure 1. The plates are joined perpendicularly by two *Z*-directed, uncapped SWCNTs with a separation of 2.380 nm. For clarity and simplicity, the SWCNT with upper *Y* direction is marked as SWCNT A, while the other

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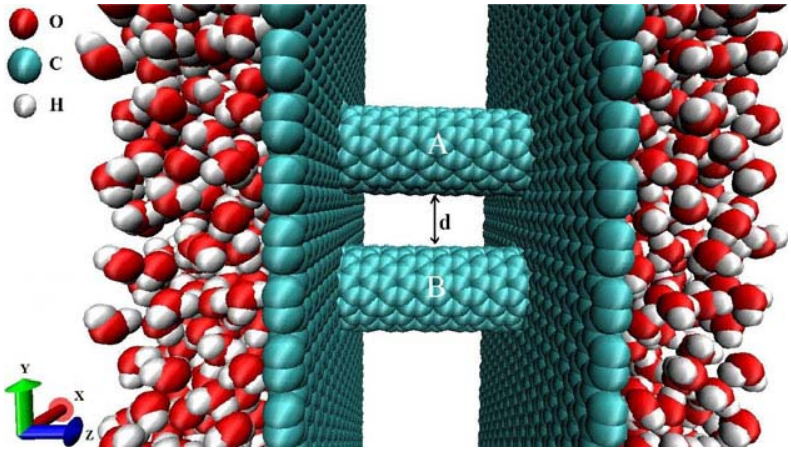

Figure 1. (Colour online) Snapshot of the simulation system with two *Z*-directed uncapped SWCNTs perpendicularly joining the centres of two graphite sheets. The system is filled with water molecules (H_2O), and the two SWCNTs are labelled as A and B, respectively. *d* is the surface distance between SWCNT A and SWCNT B.

SWCNT is marked as SWCNT B. The diameter of SWCNT A is set to be 0.772 nm, while the diameter of SWCNT B is set to be 0.772, 0.849, 0.926, 1.003, 1.081 and 1.158 nm in each case accordingly. Here, the separation between SWCNT A and SWCNT B is defined as the nearest surface distance, and marked as d (see Figure 1) for simplicity. First, we test whether blocked or unblocked SWCNT B will affect the water transfer properties of SWCNT A. So, we design two different systems with the same separation, $d = 0.4$ nm. One system with unblocked SWCNT B and the other system with blocked SWCNT B are designed. For blocked SWCNT B, each entrance of SWCNT B is blocked by one carbon atom. Meanwhile, there are no water molecules in blocked SWCNT B. Second, we change d from 0.6 to 2.3 nm. Lastly, we change the diameters of SWCNT B from 0.849 to 1.158 nm. At the same time we keep the diameter of SWCNT A as 0.772 nm and the centre distance between SWCNT A and SWCNT B as a constant distance, 1.122 nm. Here, the diameter ratio, R_a, equals the diameter of SWCNT B divided by the diameter of SWCNT A.

The Lennard-Jones diameter and well depth of carbon atom are $\sigma_{CC} = 0.34$ nm and $\varepsilon_{CC} = 0.3612\,\mathrm{KJ\,mol^{-1}}$. These parameters of carbon atom are the same with the model used in the previous work,[13] while the water molecule model is the TIP3P water model.[27] The system contains 3008 water molecules. In addition, we freeze all the carbon atoms to their original lattices in the simulations. The NVT ensemble is maintained at 300 K using the thermostat of Nosé–Hoover [28,29]. No additional pressure is applied in our system. Thus, water molecules can transport across SWCNT A either from right side to left side or from left side to right side. Periodic boundary conditions are also applied to all three directions of the simulations boxes. The time step is set to 2 fs, and the total simulation time is 50 ns (the first 5 ns is used for system equilibration and the remaining 45 ns is collected for statistics). Here, the transfer rate of water molecules across SWCNT A, V_f, is calculated according to the following equation:

$$V_f = \frac{N(t)}{t}, \tag{1}$$

where $t = 5$ ns and $N(t) = (1/9)\sum_{k=1}^{9} N_k(t)$. Here, $N_k(t)$ is the number of water molecules transported across SWCNT A either from right to left or from left to right within the statistic time, $t = 5$ ns. Because the total statistical time is 45 ns, $N_k(t)$ have nine values. The method of particle-mesh Ewald (PME) [30] is used for the long-range electrostatic interaction and the cut-off distance for Lennard-Jones forces is set to be 1.4 nm.

3. Results and discussion

Figure 2 shows the number of water molecules, N_f, flowing across SWCNT A as a function of time for two different conditions (SWCNT B is blocked or unblocked). Here, N_f is the number of water molecules transported across SWCNT A either from right to left or from left to right within the time for statistics. In the system, the diameter of either SWCNT A or SWCNT B is 0.772 nm, while the surface distance between SWCNT A and SWCNT B is 0.4 nm. Surprisingly, the results show that the existence of SWCNT B has an effect on the flowing properties of water molecules in SWCNT A. Clearly, 201 water molecules transfer across SWCNT A within 45 ns if the entrance of SWCNT B is blocked. However, N_f, increases to 291 water molecules within the same time if the entrance of SWCNT B is unblocked. So, the flow rate of the single-file water

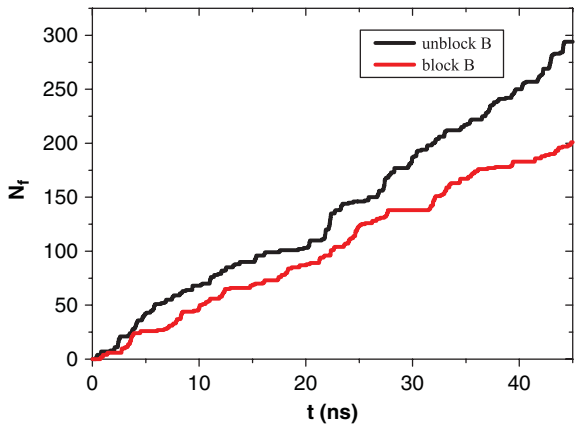

Figure 2. (Colour online) The number of water molecules, N_f, flowing across SWCNT A without pressure difference as a function of time, t. 'B unblocked' means SWCNT B is unblocked (the black line), while 'B blocked' means SWCNT B is blocked (the red line).

molecules across the SWCNT A is enhanced up to 44.8% within 45 ns for the case of unblocked SWCNT B compared with the rate for the case of blocked SWCNT B. Thus, we infer that the existence of unblocked SWCNT B will increase the transfer rate of water molecules across SWCNT A in the NVT ensemble.

Because the separation between two channels varies greatly, it is still not clear how the separation affects water permeation. The unexpected result shown in Figure 2 encourages us to engage more fully with the research. Thus, we change the separation between SWCNT A and SWCNT B from 0.6 to 2.3 nm. The results are shown in Figure 3. The result shows that V_f tends to increase when d decreases. V_f is 4.378 water molecules per nanosecond when d reaches 2.3 nm, which is close to the water transfer rate when SWCNT B is blocked (see the dotted-and-dashed line in Figure 3). However, V_f increases to 7 water molecules per nanosecond when d decreases to 0.6 nm, which means V_f increases by 59.89%. Obviously, the results indicate that SWCNT B almost has no effect on the water transfer rate across SWCNT A if d is long enough, while SWCNT B will increase the water transfer rate across SWCNT A if d is appropriately short. According to the simulation results, the tendency of water transfer across SWCNT B is similar to water transfer across SWCNT A.

For convenience, the diameters of SWCNT A and SWCNT B we choose are the same in Figure 3. What will happen if the diameters of SWCNT A and SWCNT B are different? Thus, we change the diameter of SWCNT B from 0.849 to 1.158 nm. Meanwhile, we keep the diameter of SWCNT A as 0.772 nm and the centre distance between SWCNT A and SWCNT B as a constant distance, 1.122 nm. As shown in Figure 4, we find that the water transfer rate of SWCNT A, V_f, increases from 5.356 water molecules per nanosecond to 8.171 water molecules per nanosecond, namely a growth rate of 52.86 % when R_a increases from 1.1 to 1.5. Notably, V_f is larger than the water transfer rate when SWCNT B is blocked (see the dotted-and-dashed line in Figure 4) as well.

We interest in why water molecules are more easily to be transported across the SWCNT A when d is smaller or

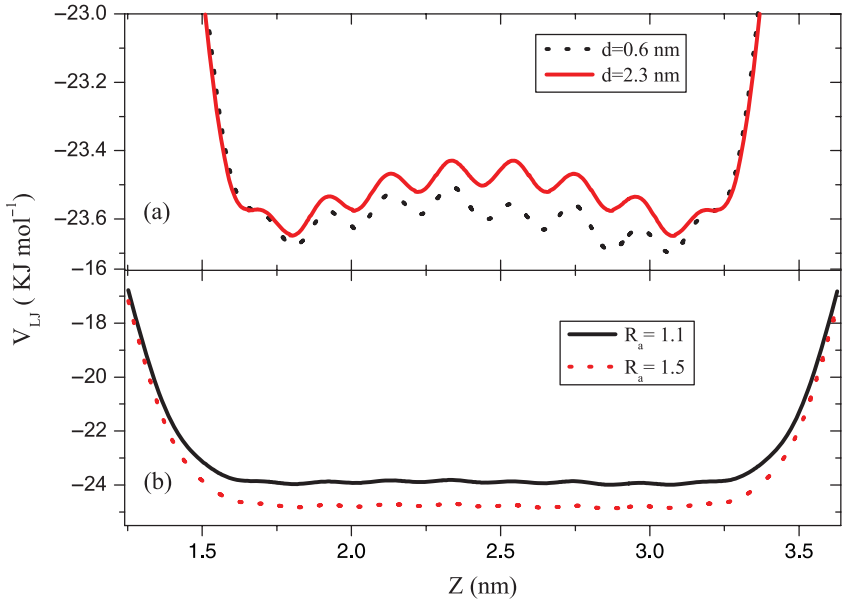

Figure 3. (Colour online) The transfer rate of water molecules flowing across SWCNT A, V_f, as a function of the distance between SWCNT A and SWCNT B, d (the surface-to-surface distance). The red dotted-and-dashed line means the transfer rate of water molecules across SWCNT A when SWCNT B is blocked and serves as a constant to the eye.

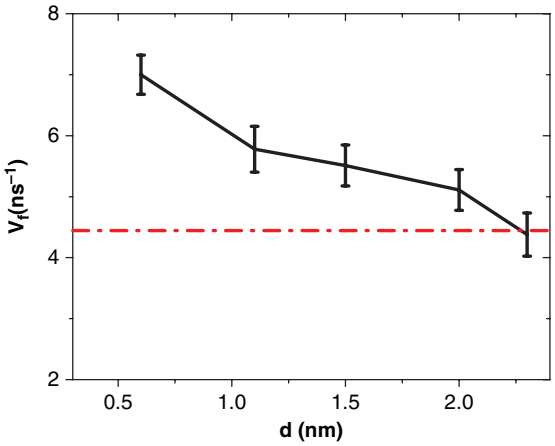

Figure 4. (Colour online) The transfer rate of water molecules flowing across SWCNT A, V_f, as a function of diameter ratio, R_a. The red dotted-and-dashed line means the transfer rate of water molecules across SWCNT A when SWCNT B is blocked and serves as a constant to the eye. The definition of R_a is given in the main text. Error bars are included.

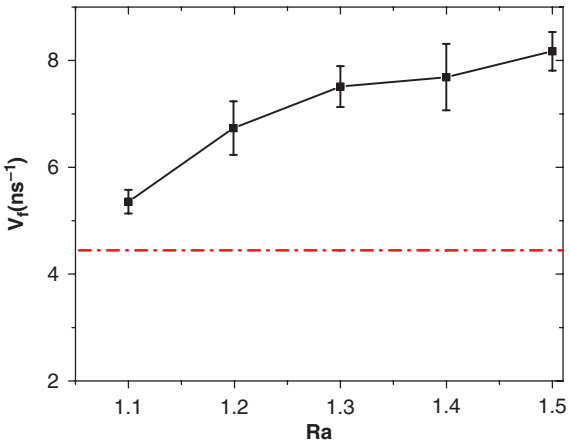

Figure 5. (Colour online) (a) Comparations of van der Waals interaction, V_{LJ}, between water molecules in SWCNT A and the SWCNTs for $d = 0.6$ nm and $d = 2.3$ nm. (b) Comparations of van der Waals interaction, V_{LJ}, between water molecules in SWCNT A and the SWCNTs for $R_a = 1.1$ and $R_a = 1.5$.

R_a is larger. In order to understand those different behaviours, as Li et al. [31] pointed out that the van der Walls interaction is much stronger than the electrostatic interaction energy. Thus, we calculate the interactions potential of van der Waals between water molecules in SWCNT A and the carbon atoms along the centre of SWCNT A axes. The interaction potential, V_{LJ}, is calculated according to

$$V_{LJ} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]. \quad (2)$$

Here, ε_{ij} and σ_{ij} are empirical parameters of the Lennard-Jones potential for the interaction between atom i and atom j with separation r_{ij}. The calculation results are shown in Figure 5. Here, we find that the van der Waals interaction between water molecules in SWCNT A and all the carbon atoms varies with different d or R_a. For clarity and simplicity, we just display two comparations, $d = 0.6$ nm and $d = 2.3$ nm, $R_a = 1.1$ and $R_a = 1.5$. For $d = 0.6$ nm, we find that v_{LJ} distribution inside SWCNT A are quite inhomogeneous. Notably, compared with $d = 2.3$ nm, V_{LJ} are always stronger when $d = 0.6$ nm (see Figure 5(a)). This explains the reason why water molecules can be transported across SWCNT A faster when d decreases. As Figure 5(b) shows, For $R_a = 1.1$, we find that V_{LJ} distribution inside the SWCNT A are also quite inhomogeneous. Compared with $R_a = 1.1$, V_{LJ} are always stronger when $R_a = 1.5$ (see Figure 5(b)). This explains the reason why water molecules can be transported across SWCNT A faster when R_a increases. It is worth noting that the van der Waals interaction between water in SWCNT A and all the carbon atoms is too weak to reduce the water transfer rate of SWCNT A.

4. Conclusion

On the basis of molecular dynamics simulations, we have investigated water permeation across an SWCNT A in the presence of another SWCNT B. We find that the flow rate of the single-file water molecules across SWCNT A is enhanced up to 44.8% within 45 ns for the case of unblocked SWCNT B compared with the rate for the case of blocked SWCNT B, and that this flow rate is determined by the separation between the two SWCNTs and the diameter of SWCNT B. We observe the flow rate of water molecules across SWCNT A is enhanced up to 59.89% and 52.86% by changing the separation and diameter ratio, respectively. The flow enhancement originates from the stronger van der Waals interactions between water molecules and the SWCNTs when the effective separation between the two SWCNTs is closer. This work may help to design high-flux nanochannels for transporting water molecules, and also to understand the water flow through nanochannels in biological membranes.

Disclosure statement

No potential conflict of interest was reported by the authors.

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References

[1] Murata K, Mitsuoka K, Hirai T, Walz T, Agre P, Heymann JB, Engel A, Fujiyoshi Y. Structural determinants of water permeation through aquaporin-1. Nature. 2000;407(6804):599–605. doi:10.1038/35036519.

[2] Miyazawa A, Fujiyoshi Y, Unwin N. Structure and gating mechanism of the acetylcholine receptor pore. Nature. 2003;423(6943):949–955. doi:10.1038/nature01748.

[3] Sui HX, Han BG, Lee JK, Walian P, Jap BK. Structural basis of water-specific transport through the AQP1 water channel. Nature. 2001;414(6866):872–878. doi:10.1038/414872a.

[4] Zhou M, Morais-Cabral JH, Mann S, Mackinnon R. Potassium channel receptor site for the inactivation gate and quaternary amine inhibitors. Nature. 2001;411(6838):657–661. doi:10.1038/35079500.

[5] Gong XJ, Li JY, Zhang H, Wan RZ, Lu HJ, Wang S, Fang HP. Enhancement of water permeation across a nanochannel by the structure outside the channel. Phys Rev Lett. 2008;101(25):257801. doi:10.1103/PhysRevLett.101.257801.

[6] Wan RZ, Li JY, Lu HJ, Fang HP. Controllable water channel gating of nanometer dimensions. J Am Chem Soc. 2005;127(19):7166–7170. doi:10.1021/ja050044d.

[7] Holt JK, Park HG, Wang YM, Stadermann M, Artyukhin AB, Grigoropoulos CP, Noy A, Bakajin A. Fast mass transport through sub-2-nanometer carbon nanotubes. Science. 2006;312(5776):1034–1037. doi:10.1126/science.1126298.

[8] Joseph S, Aluru NR. Why are carbon nanotubes fast transporters of water? Nano Lett. 2008;8(2):452–458. doi:10.1021/nl072385q.

[9] Service RF. Desalination freshens up. Science. 2006;313(5790):1088–1090. doi:10.1126/science.313.5790.1088.

[10] Nasrabadi AT, Foroutan M. Ion-separation and water-purification using single-walled carbon nanotube electrodes. Desalination. 2011;277(1–3):236–243. doi:10.1016/j.desal.2011.04.028.

[11] Cambré S, Schoeters B, Luyckx S, Goovaerts E, Wenseleers W. Experimental observation of single-file water filling of thin single-wall carbon nanotubes down to chiral index (5,3). Phys Rev Lett. 2010;104(20):207401. doi:10.1103/PhysRevLett.104.207401.

[12] Su JY, Guo HX. Control of unidirectional transport of single-file water molecules through carbon nanotubes in an electric field. ACS Nano. 2011;5(1):351–359. doi:10.1021/nn1014616.

[13] Hummer G, Rasaiah JC, Noworyta JP. Water conduction through the hydrophobic channel of a carbon nanotube. Nature. 2001;414(6860):188–190. doi:10.1038/35102535.

[14] Meng XW, Wang Y, Zhao YJ, Huang JP. Gating of a water nanochannel driven by dipolar molecules. J Phys Chem B. 2011;115(16):4768–4773. doi:10.1021/jp2025297.

[15] Ito Y, Park YS, Imanishi Y. Nanometer-sized channel gating by a self-assembled polypeptide brush. Langmuir. 2000;16(12):5376–5381. doi:10.1021/la991102+

[16] Yoshimi Y, Arai R, Nakayama S. Influence of the solvent on nature of gate effect in molecularly imprinted membrane. Anal Chim Acta. 2010;682(1–2):110–116. doi:10.1016/j.aca.2010.09.050.

[17] Li JY, Gong XJ, Lu HJ, Li D, Fang HP, Zhou RH. Electrostatic gating of a nanometer water channel. Proc Natl Acad Sci USA. 2007;104(10):3687–3692. doi:10.1073/pnas.0604541104.

[18] Qiao R, Aluru NR. Atypical dependence of electroosmotic transport on surface charge in a single-wall carbon nanotube. Nano Lett. 2003;3(8):1013–1017. doi:10.1021/nl034236n.

[19] Wang Y, Zhao YJ, Huang JP. Giant pumping of single-file water molecules in a carbon nanotube. J Phys Chem B. 2011;115(45):13275–13279. doi:10.1021/jp2069557.

[20] Reale R, English NJ, Marracino P, Liberti M, Apollonio F. Translational and rotational diffusive motion in liquid water in square-wave time-varying electric fields. Chem Phys Lett. 2013;582:60–65. doi:10.1016/j.cplett.2013.07.030.

[21] Figueras L, Faraudo J. Competition between hydrogen bonding and electric field in single-file transport of water in carbon nanotubes. Mol Simul. 2012;38(1):23–25. doi:10.1080/08927022.2011.599032.

[22] Morris CE. Mechanosensitive ion channels. J Membr Biol. 1990;113(2):93–107. doi:10.1007/BF01872883.

[23] Ganfornina MD, Lopez-Barneo J. Single K^+ channels in membrane patches of arterial chemoreceptor cells are modulated by O_2 tension. Proc Natl Acad Sci USA. 1991;88(7):2927–2930. doi:10.1073/pnas.88.7.2927.

[24] Van der Spoel D, Lindahl E, Hess B, Groenhof G, Mark AE, Berendsen HJC. Gromacs: fast, flexible, and free. J Comput Chem. 2005;26(16):1701–1718. doi:10.1002/jcc.20291.

[25] Nicholls WD, Borg MK, Lockerby DA, Reese JM. Water transport through carbon nanotubes with defects. Mol Simul. 2012;38(10):781–785. doi:10.1080/08927022.2011.654205.

[26] Haan M, Gwan JF, Baumgaertner A. Correlated movements of ions and water in a nanochannel. Mol Simul. 2009;35(1–2):13–23. doi:10.1080/08927020802433160.

[27] Jorgensen WL, Chandrasekhar J, Madura JD, Impey RW, Klein ML. Comparison of simple potential functions for simulating liquid water. J Chem Phys. 1983;79(2):926–935. doi:10.1063/1.445869.

[28] Nose' S. A unified formulation of the constant temperature molecular dynamics methods. J Chem Phys. 1984;81(1):511–519. doi:10.1063/1.447334.

[29] Hoover WG. Canonical dynamics: equilibrium phase-space distributions. Phys Rev A. 1985;31(3):1695–1697. doi:10.1103/PhysRevA.31.1695.

[30] Darden TA, York DM, Pedersen LG. Particle mesh Ewald: an $N \cdot \log(N)$ method for Ewald sums in large systems. J Chem Phys. 1993;98(12):10089–10092. doi:10.1063/1.464397.

[31] Li XY, Shi YC, Yang YL, Du HL, Zhou RH, Zhao YL. How does water–nanotube interaction influence water flow through the nanochannel? J Chem Phys. 2012;136(17):175101. doi:10.1063/1.4707346.