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

Supporting information for: Phonon coupling induced thermophoresis of water confined in a carbon nanotube

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Simulation Protocol

The computational set-up and simulation details are presented in this section. We considered a 30 nm long CNT with a diameter 0.94 nm and chirality vector (12,0) for this study, where the density profile of water is unknown and placed the CNT in a box of 45 nm x 5 nm x 5 nm with water molecules. The system is shown in Figure S1. We conducted the simulations in the canonical ensemble at 300 K for 5 ns and subsequently for 10 ns in the NVE ensemble. Then, the water molecules outside the CNT were removed at the end of 10 ns and this water-filled CNT was used in all our simulations. The present simulations are conducted in two stages; first the system is equilibrated at 300 K by implementing canonical and micro-canonical ensemble and then non-equilibrium MD simulations are conducted by imposing thermal gradient along the length of the CNT. The Nosé-Hoover thermostat is used to maintain the temperature of hot and cold zones of the CNT, while the rest of the CNT and water is kept at micro-canonical ensemble. We conducted the non-equilibrium simulation for

100 ns to obtain a steady flow rate and reduced thermal noise.

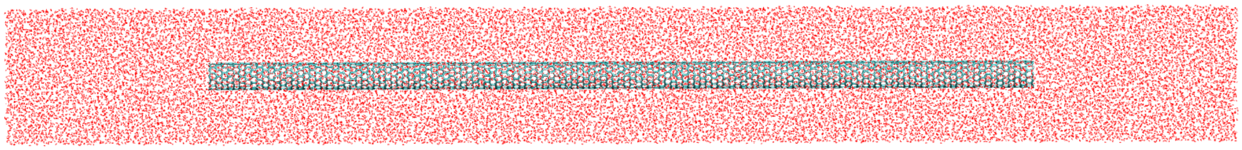

Figure S1: This system is created to fill the water naturally to the CNT (12,0) studied in this work.

Simulated Cases

The system consists of water-filled CNT, as shown in Figure S2. We simulated water-filled and empty CNT, then a water-filled CNT by arresting the degree-of-freedom (dof) of the center of CNT by fixing few carbon atoms at center similar to Oyarzua *et al.*.[1] For all these systems we imposed the thermal gradients of 0.0, 0.5, 1.5 and 2.6 K/nm along the axis of the CNT, by keeping the temperature at (hot and cold zone) 310-310 K, 330-310 K, 350-290 K and 370-270 K.

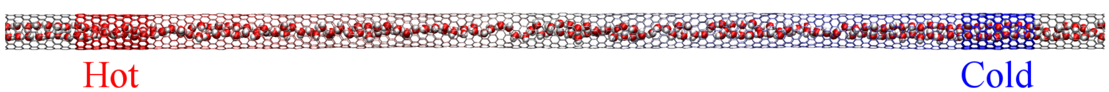

Figure S2: Schematic of the water-CNT system. The red and blue zone represent the high and cold temperature sections, respectively. The CNT is 30 nm long with both ends fixed.

Vibrational Analysis

In order to describe the importance of vibrations of the carbon atoms of the CNT in thermophoresis, we computed the amplitude and frequencies of carbon atoms when subjected to various thermal gradients. We used the same procedure followed in earlier reports[1,2] to perform vibrational mode separation by extracting the amplitude and frequencies of CNT.

First, the computational domain is divided into bins of size 0.5 nm along the length of the CNT to compute the centre-of-mass of the carbon atoms in each bin. Subsequently, FFT analysis is performed on the centre-of-mass of the CNT to separate the vibrational modes. The center of mass signal from the central bin of the CNT while subjected to 3.2 K/nm is giving a waveform similar to that of sinusoidal oscillations. This is shown in Figure S3. The corresponding FFT spectrum of the centre-of-mass signal is shown in Figure S4, where the three vibrational modes can be easily recognized. This FFT analysis is performed for all the bins to obtain the amplitude and frequencies of vibrational modes along the entire length of the CNT.

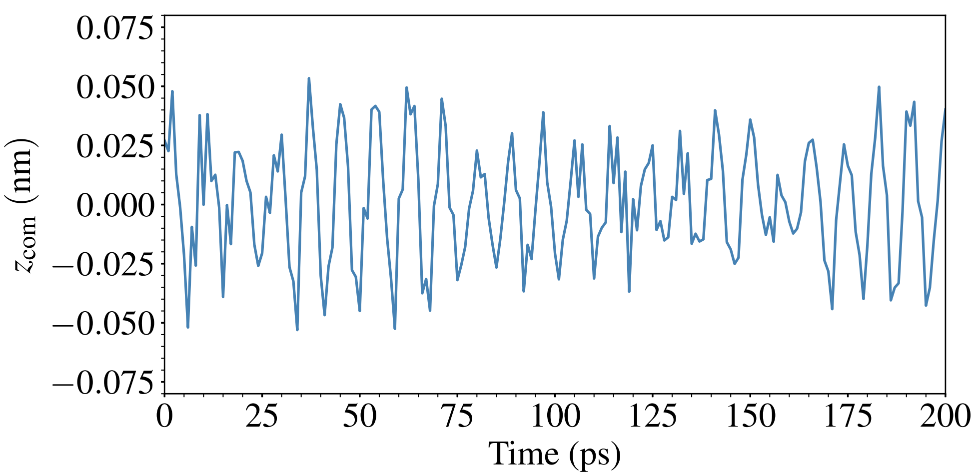

Figure S3: The temporal oscillation signal at center of the water-filled CNT.

Furthermore, we have compared the solution obtained through the FFT of the signal and the original centre-of-mass signal for cross-verification. The FFT signal obtained by using the entire frequency range and the FFT solution obtained from using only the three dominant vibrational modes are shown along with the original centre-of-mass data in Figure S5. Then, we have compared the FFT of three dominant vibrational modes of the empty and water-filled CNTs as shown in Figure S6. In the case of the FFT spectrum of the water-filled CNT, we identified that for all imposed thermal gradients, the peaks of vibrational modes undergo a frequency shift with thermal gradient. Also, all vibrational modes were found suppressed

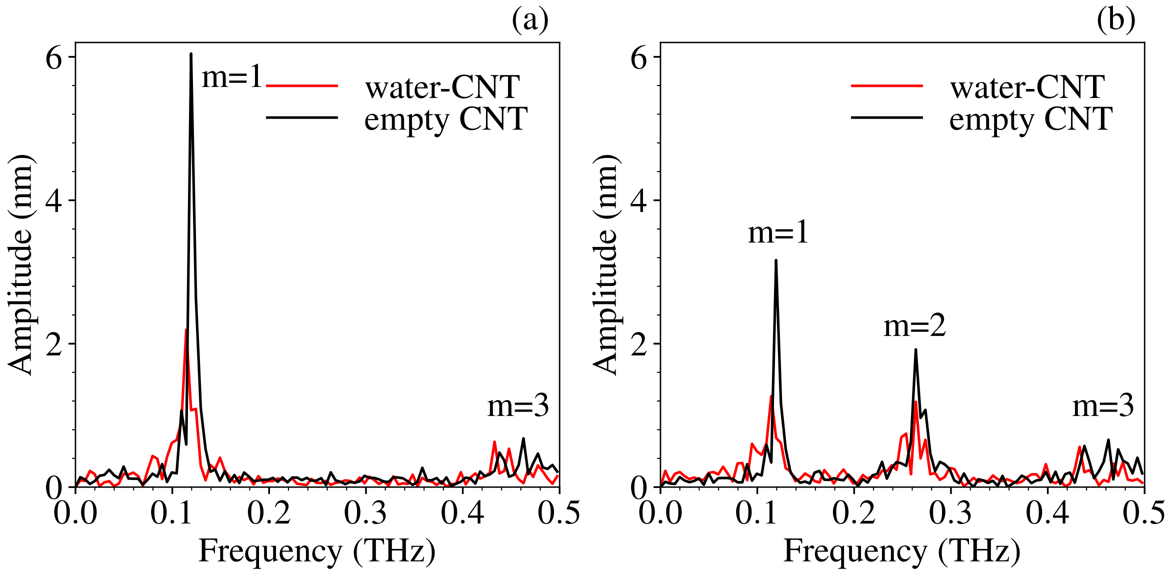

Figure S4: The FFT spectrum at (a) center and (b) quarter of the CNT along the axial direction for water-filled and empty CNTs. The highest dominant vibrational mode is found at the centre of the CNT and next dominant modes were found at one fourth the length of the CNT from both the ends.

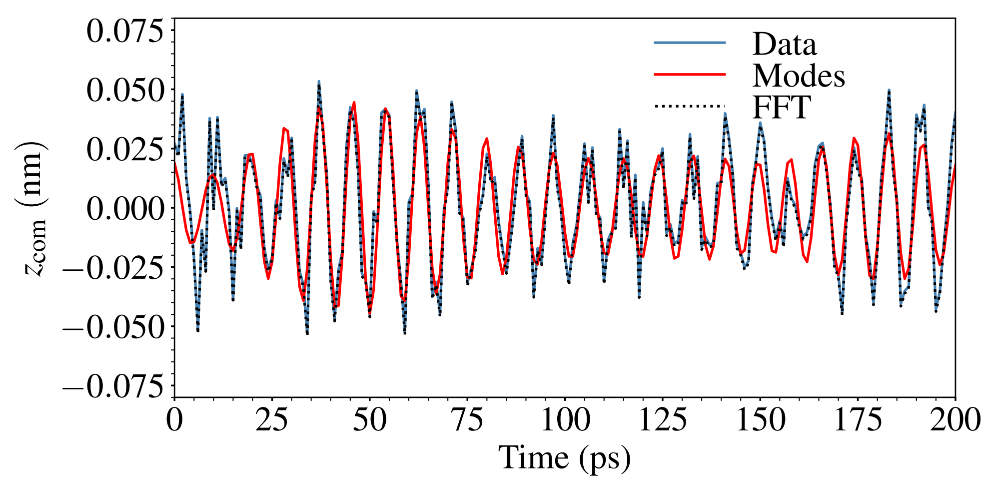

Figure S5: Oscillation signals at the center of the water-filled CNT. The blue line shows the data extracted from the simulations (Figure S3), the dashed black line is the FFT signal over the entire frequency range, and the red line depicts the FFT signal when using the frequencies and amplitudes of only the three dominant vibrational modes.

due to the presence of water.

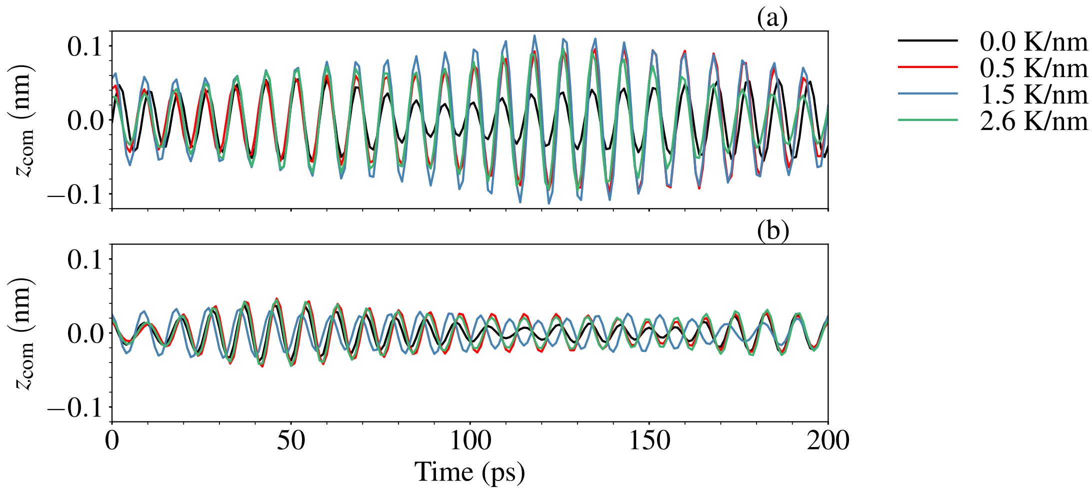

Figure S6: The comparison of FFT solution signal of three dominant vibrational modes of the (a) empty and (b) water-filled CNTs.

We carefully repeated the same procedure for the water-filled CNT system with central-fixed, to study the effect of fixing the center of the CNT on thermophoretic transport of water. The amplitude of the FFT curve for the dominant vibrational modes is shown in Figure S7, as a function of the length of the CNT subjected to the various thermal gradient. We observed the maximum amplitude at the hot side of the CNT, which is consistent with the results of Oyarzua *et al.*.[1] The amplitude of vibrations in the hot side of the CNT remained unchanged even after the thermal gradient imposed on the CNT is changed. Oyarzua *et al. etal.*[1] reported a decrease in the amplitude of vibrations of the CNT with a decrease in the thermal gradient with negligible amplitude of vibrations observed at equilibrium condition (0.0 K/nm). In our study we found that CNTs do have vibrations at any finite system temperature even while they are not subjected to any thermal gradient. Also, the amplitude of vibrations are not dependent on the imposed thermal gradient, instead it does depend on the average temperature of the system.

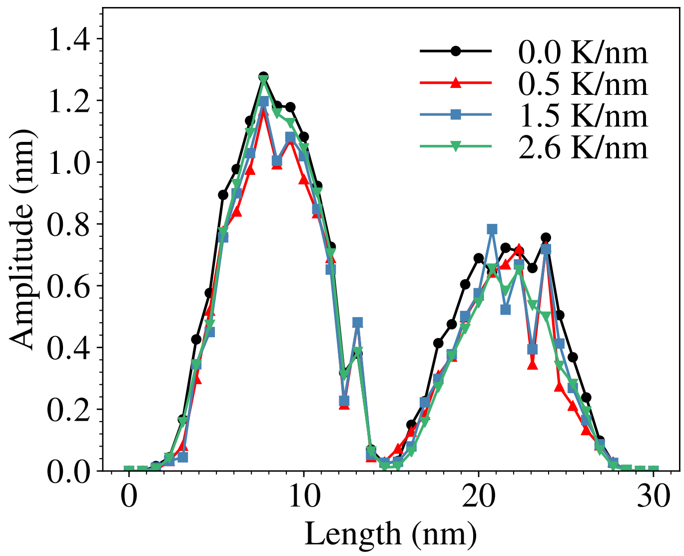

Figure S7: The amplitude of FFT for the dominant vibrational modes of the CNT with restricted dof as a function of the length of the CNT subjected to various thermal gradient, similar to Oyarzua *et al.* *et al.*[1]

The average axial velocity of water increases linearly with the applied thermal gradient in the water-filled CNT. The results are compared with a previous study,[1] as shown in Fig. S8. The rate of increase of velocity for the various thermal gradient of our system is 37% higher than the similar system reported by Oyarzua *et al.*.[1] We have obtained a continuous flow of water in the preferential direction without any restrictions on dof of CNT, similar to many previous studies[3,4]. The restriction on the dof of the CNT is believed to have no significance in the thermophoretic transport of water through CNT. The study of the center of mass oscillations of the CNT and the difference in the amplitude of the vibrational modes on both side of the fixed points[1] is found to be insufficient to explain the origin of the thermophoretic force. This necessitated a detailed study on the effect of surface and radial vibrational modes of the CNT on the thermophoretic transport of water. Further discussions are included in the main paper.

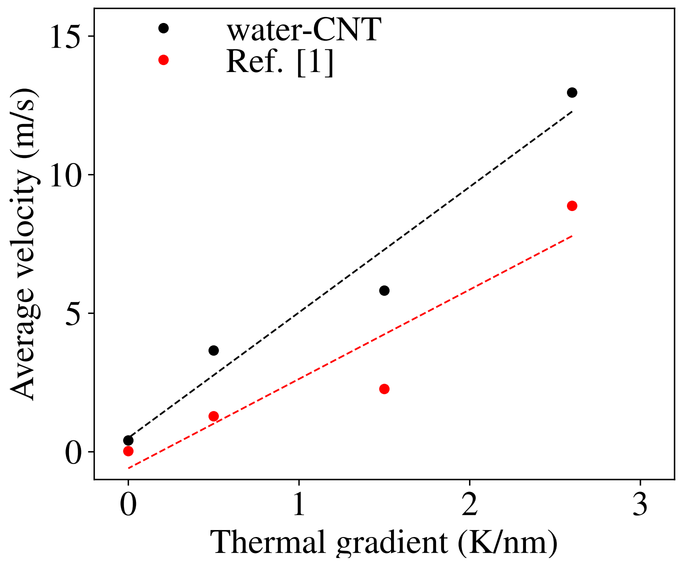

Figure S8: The average velocity of water in this study (water-filled CNT system) and in the study by Oyarzua *et al.*[1] for various thermal gradients.

Distribution of water density inside the CNT

Figure S9 shows the radial density distribution of water inside the CNT at equilibrium condition. The distribution of oxygen and hydrogen atoms of water molecules are studied to asses the molecular orientation inside the CNT. From Figure S9, oxygen atoms are arranged in a cylindrical structure at a distance of 0.15 nm from the axis of the CNT. The water structure corresponds to tilted pentagonal rings inside the CNT with a maximum number of oxygen atoms arranged at 0.15 nm from the axis. They are unaffected by the flow and this distribution is consistent with the previous MD studies.[5]

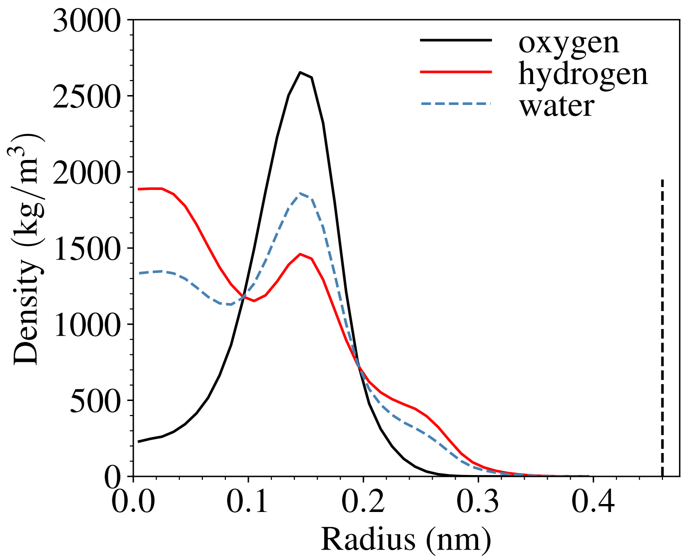

Figure S9: The radial density distribution of water inside the CNT measured at equilibrium condition. The dashed line is drawn to indicate the position of the CNT surface.

Diffusion enhancement of water with an increase in the thermal gradient

To demonstrate the increase in diffusion enhancement of water in CNT, the mean square displacement(MSD) and diffusion coefficients are demonstrated in S10

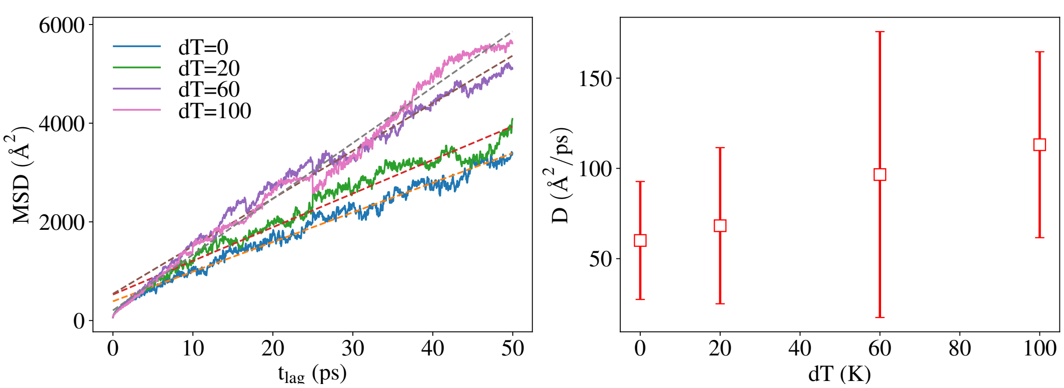

Figure S10: (a) The variation of the Mean Square Displacement (MSD) with time and (b) The increase in diffusion coefficient with increase in temperature gradient for the water molecules.

Flow rate of water in CNT with the temperature gradient

The flow rate of water with a thermal gradient is given as it is a direct manifestation of diffusion transport. This is demonstrated in Figure S11

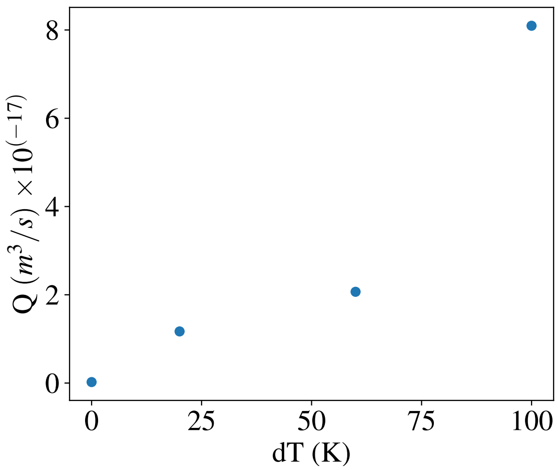

Figure S11: The enhancement in flow rate of water with increase in the thermal gradient

References

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