Supporting information for: Water thermophoresis in Carbon Nanotubes: The interplay between the thermophoretic and friction forces

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Simulation protocol

In this section the setup and details of the conducted Molecular Dynamics (MD) simulations are explained. As stated in the main article, water droplets of 400, 600 and 800 water molecules and a CNT(17,17) of chirality is used. For all the cases, we perform the simulations in three stages. First, each system is equilibrated in the NVT ensemble at 300 K during 0.5 ns with the Berendsen thermostat. Subsequently, the cases are conducted in the NVE ensemble for 1.5 ns. And third, the constrained or unconstrained simulation are conducted for 3 ns.

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The constrained velocity simulation are MD simulations that allows the study of the dynamics of a motile particle at constant velocity. The technique consists of computing the center of mass velocity (v_{com}) at the end of every time step, then, this v_{com} is subtracted to the velocity of each water molecule in the droplet, and then, the target velocity or constrained velocity (v_{const}) value is added. Thereby, we are forcing the droplet to move with a target velocity value v_{const}, without affecting the velocity distribution of the molecules in the droplet. Therefore, in the constrained simulations during each time step, the velocity of the droplet center of mass is stored, and the difference between the computed v_{com} and the constrained velocity v_{const} over the time step determines the force acting on the droplet, as defined in Eq. (1),

$$F_N = m \cdot a = m \cdot \frac{dv}{dt} = m \cdot \frac{(v_{com} - v_{const})}{dt} \tag{1}$$

Where m is the total mass of the droplet and dt is the time step of the simulations (2 fs). In the cases with no applied thermal gradient (constant temperature) the acting force corresponds to the friction force ($F_N = F_F$), and in the cases with imposed thermal gradient, the force acting on the droplet is a combination of the thermophoretic force and the friction force, as described in Eq. 1 of the main manuscript ($F_N = F_T - F_F$).

It is important to note that the relation between the friction force (F_F) and the constrained velocity (v_{const}) is possible due to the very high slippage in the water-CNT interface,[S1–S3] assuming an equivalent value between the slip velocity v_s and the center of mass velocity v_{com}, in line with Falk et al.[S4] Moreover, due to this very high slippage of water in CNTs, the viscous dissipation in the fluid is negligible. In fact, previous investigations[S1–S3] reported water slip length over 75 nm for a CNT of 2 nm in diameter, leading to a plug-like velocity profile for water confined in CNTs.[S5,S6] Furthermore, Chen et al.[S7] found that water spontaneously slip inside CNTs due to thermal fluctuations at room temperature.

Finally, recall that the unconstrained simulations are non equilibrium molecular dynamic simulations with an imposed thermal gradient in the CNT and free motion of the droplet.

Thermal gradient

In order to impose a thermal gradient along the CNT, two different temperatures are applied at the ends of the nanotube (see Figure 1.a of the main article). These two temperatures produce a temperature profile along the CNT as shown in Figure S1. The thermal gradient is represented by the slope of the linear fit made at the center of the CNT. For the example of the Figure S1, for imposed temperatures of 370 K and 280 K the obtained thermal gradient is 0.70 K/nm. In Table S1 the applied temperatures and the resulting thermal gradients are presented. The mean temperature in all cases is 325 K.

Due to the trend of the temperature profiles (Figure S1), force computation is made between the 20 nm and 60 nm in the axial direction of the CNT.

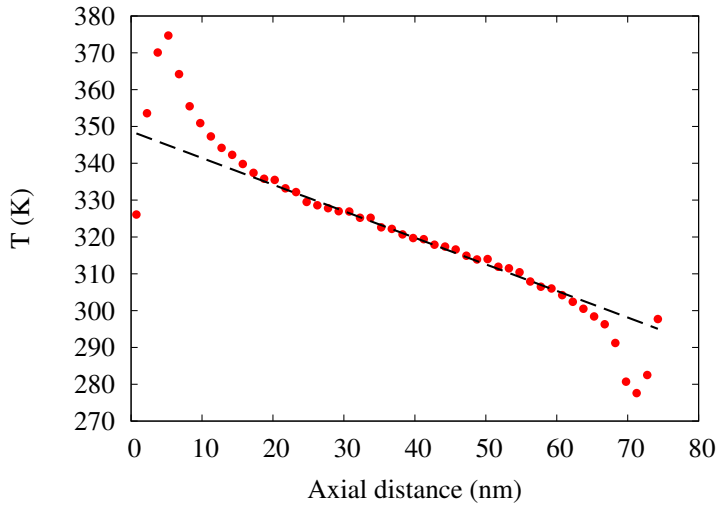

Figure S1: Temperature profile along the carbon nanotube. The applied temperatures are 370 K and 280 K. The resulting slope represents the thermal gradient of 0.70 K/nm.

Table S1: Thermal gradient obtained from the applied temperatures.

Temperatures (K)	Thermal gradient (K/nm)
340 - 310	0.20
360 - 290	0.50
370 - 280	0.70

Friction Force

As discussed in the main article, the friction force acting on the motion of the droplet has a dependency on the contact area between the droplet and the CNT. The contact area of each droplet is calculated as,

$$A = 2\pi r_{eff} L \tag{2}$$

where r_{eff} is the effective radius defined as,

$$r_{eff} = R - \frac{1}{2}\sigma_{CO} \tag{3}$$

where R is the radius of the CNT and σ_{CO} is the Lennard Jones C-O parameter. The L in equation (1) is the length of the droplet in contact with the CNT. To measure this length, a track on the droplet is made, as shown in Figure S2. Here, all the farthest water molecules in the liquid-vapor interface in the direction of the radius is saved, and from all these molecules, the one closest to the center is plotted, for both meniscus (back and front). From equation 2 and 3, the resulting contact area for the 400, 600 and 800 molecules are $24.3\,\mathrm{nm}^2$, $36.8\,\mathrm{nm}^2$ and $48.7\,\mathrm{nm}^2$ respectively. The ratio between the friction force and the respective contact area as a function of the velocity of the center of mass is depicted in Figure S3, which is a zoom of the inset in Figure 2.a of the main article.

In Figure S3 The slope between F_F/A and velocity v,[S4] corresponds to the friction coefficient of the CNT(17,17) and water. This friction coefficient is 3631.3 $\pm$ 89.7 Ns/m^3.

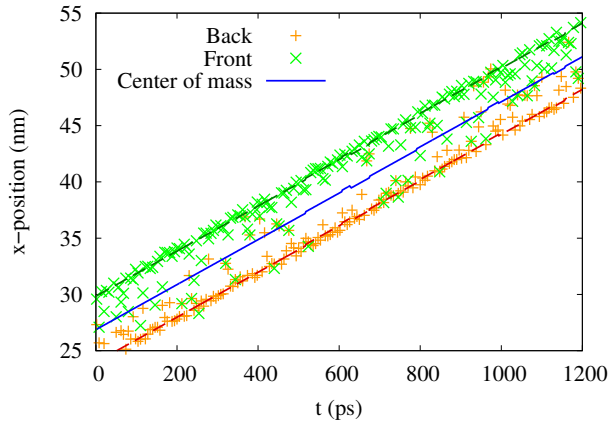

Figure S2: Tracking of the 600 water molecule droplet. The average length is 5.88 nm.

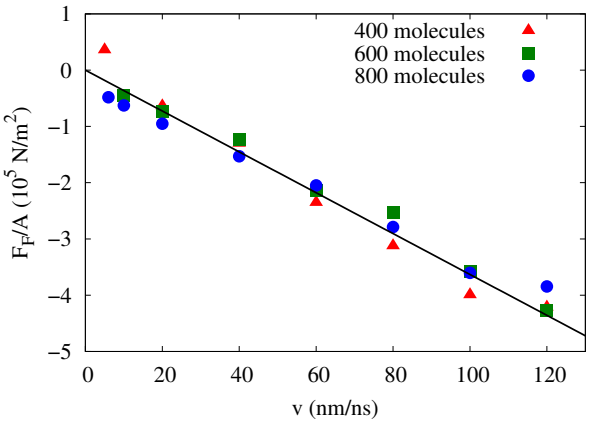

Figure S3: Friction Force divided by the solid-liquid contact area as a function of the mean velocity. The solid black line is a linear fit of the data and the slope corresponds to the friction coefficient.

Acceleration of the droplet

As discussed in the main text (Fig 3.a), a decreasing net force F_N is observed as the velocity of the droplet is increasing. This result indicate that in the first regime of increasing velocity, while the thermophoretic force is constant and the friction force is increasing with velocity, the net motion of the droplet is with a decreasing acceleration. Since $F_N = m \cdot a$, the acceleration as a function of the velocity can be computed. This is shown in Figure S4 for thermal gradients of 0.50 K/nm (Fig S4.a) and 0.70 K/nm (Fig S4.b)

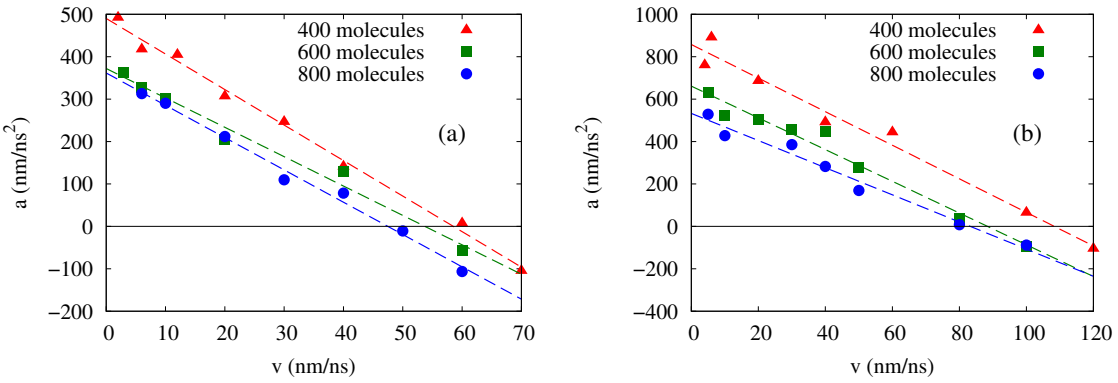

Figure S4: Acceleration of the droplet obtained from the computed net force (F_N). The solid line is a guide for $a = 0$ and the dashed lines are fits to the data. (a) Acceleration as a function of the velocity of the center of mass (v_{com}) under a thermal gradient of 0.50 K/nm (b) Acceleration as a function of the velocity of the center of mass (v_{com}) under a thermal gradient of 0.70 K/nm.

Net force for different droplet sizes

How the net force F_N decrease in magnitude as the velocity of the center of mass is increasing while the size of the droplet is changed is discussed in the main text (Figure 4.a). In Figure 4.a of the main text, the slopes of the linear fits for each droplet size corresponds to the respective value of the slope of friction force, which is the friction coefficient times the solid-liquid contact area. This change in the slopes is observed also for a thermal gradient of 0.70 K/nm, as depicted in Figure S5 .

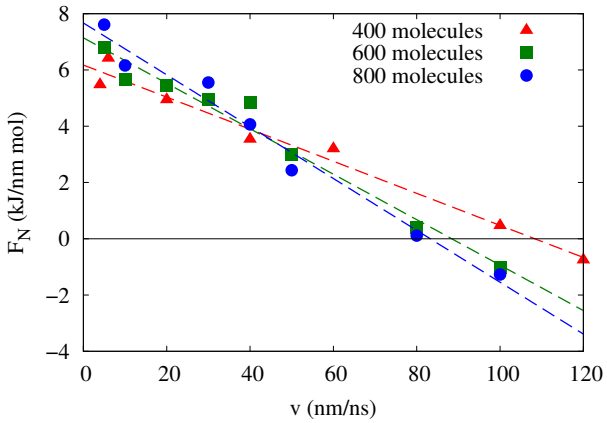

Figure S5: Net Force computed from the simulations as a function of the velocity of the center of mass. The applied thermal gradient is 0.70 K/nm. The solid line is a guide for $F_N = 0$ and the dashed lines are fits to the data.

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