

On phonons and water flow enhancement in carbon nanotubes

To the Editor — The intriguing physics of water transport through carbon nanotubes (CNTs) has motivated numerous studies, reporting flow rates higher than those estimated by continuum models¹. The quantification of water transport in CNTs remains unresolved, however, with flow rates reported by different experiments and simulations having discrepancies of over three orders of magnitude. Reports of ultrafast^{2–5} and more modest rates^{6–9} conflict with each other. Molecular dynamics (MD) simulations have been used to resolve this puzzle by helping to decipher how the CNT walls interact with water molecules

In a recent MD study, harnessing impressive computational resources, Ma *et al.*¹⁰ stated that phonon modes of CNTs enhance water diffusion by 300%. They studied double-walled CNTs filled with water in a periodic domain, with an axial length of 20 nm and with chiral indices of (20,20) and (25,25) for the inner and outer (rigid) CNT, respectively (Fig. 1a). Ma *et al.* examined two different settings for the inner-CNT atoms: phonon-active and phonon-free cases (the MD details are described in Supplementary Section 1). In the phonon-active case, CNT vibrations are defined by bonding potentials. In the phonon-free case, the phonon-modes are eliminated by removing bonding terms, and the CNT vibrations are determined through harmonic constraints. The authors carried out 5 million MD simulations of force-driven flow in double-walled CNTs, using the all-atom TIP4P/2005 water model¹¹ and applying a force of 0.012 pN to the water molecules. Ma *et al.* reported oscillatory patterns for the axial centre-of-mass water velocity (v) and shear stress (τ). The frequency of these oscillations correlates well with the axial centre-of-mass velocity of the CNT (V_{CNT}), confirming that τ oscillations stem from axial CNT phonon modes. Thus, the question arises: how much do those oscillations affect the water flow inside the CNT?

To answer this question, Ma *et al.* carried out a second set of simulations with no force-driven water flow, using the coarse-grained monatomic water (mW)

model¹². They postulated the water self-diffusion coefficient (D) as the quantity of interest, computed from the mean squared displacement (MSD):

$$D = \frac{1}{2N_{\text{D}}t} \text{MSD}(t) \quad (1)$$

$$= \frac{1}{2N_{\text{D}}t} \frac{1}{N} \sum_{i=1}^N [r_i(t) - r_i(0)]^2$$

where N_{D} is the dimensionality of the system and $r_i(t)$ is the position at time t . The MSD is computed from the axial position of the centre of mass of the entire fluid; thus, i and N_{D} are equal to 1. Ma *et al.* observed a 300% increment in D for the phonon-active compared with the phonon-free CNT case. This enhancement was attributed to the oscillating shear stress τ and therefore to the CNT phonons.

Here, we re-examine the effects of the CNT phonons on water transport. We find that phonon CNT-oscillations induce a constant-frequency oscillation of water velocity, consistent with the findings of Ma and colleagues. But our results show only a small effect of phonon modes on water flow rates. We find that the use of a coarse-grained water model, the estimate of the diffusion coefficient from MSD from the centre-of-mass position of water and the high friction of the phonon-free CNT used as reference can lead to high estimates of flow enhancement. In turn, we estimate an order-of-magnitude lower diffusion enhancement that is also independent of phonon modes.

We perform a set of short, force-driven flow simulations in double-walled CNTs, using the TIP4P-Ew water model¹³ and a MD protocol similar to that of Ma and colleagues. For phonon-active systems, we recover the oscillations in τ and v with a sample of 500,000 MD simulations (see Supplementary Section 3). Moreover, we include an extra system with fixed CNTs. As expected, the oscillatory pattern of v disappears for the latter case; however, the overall water accelerations for phonon-active and fixed CNTs are equal (see Supplementary Section 2), indicating a small effect of phonon modes on water flow.

We also perform a second set of simulations that are not force-driven, for which we continue to use the TIP4P-Ew water model; we do not switch to a coarse-grained water model as in the work by Ma and colleagues. We evaluate phonon-active, phonon-free and fixed CNTs. Three spring constants are examined in phonon-free CNTs: the value used in Ma *et al.*, defined here as 1κ , as well as values of 2κ and 10κ . We evaluated the diffusion coefficient from two different MSD slopes: MSD of the centre of mass of water is denoted as MSD_{COM} and results in D , as calculated by Ma *et al.*, whereas MSD of oxygen positions is denoted as MSD_{O} (i runs over oxygen atoms and N_{D} is equal to 3 in equation (1)), which results in D_{O} .

We find that estimates of the diffusion coefficient are sensitive to the choice of the MSD for the calculation (Fig. 1b and Supplementary Section 4). The diffusion coefficient values are ordered according to the root-mean-square fluctuations of the carbon atoms, which quantifies the CNT mobility. First, we find an enhancement of about 150% in D for the phonon-active over the phonon-free 1κ CNTs, about half of the 300% reported by Ma *et al.* (Fig. 1b, grey line). This discrepancy is attributed to the use of an atomistic rather than a coarse-grained water model. We note that the diffusion estimate for bulk water using the mW model is particularly high ($6.5 \text{ nm}^2 \text{ ns}^{-1}$ at 298 K; ref. 12) and about three times as high as diffusion values estimated using TIP4P-Ew (ref. 13), TIP4P/2005 (ref. 11) and experimental values¹⁴. This is consistent with the fact that coarse-grained models result in higher diffusion than atomistic models, owing to softer intermolecular interactions. Specifically, the parametrization of the mW model was focused on reproducing thermodynamics, while compromising kinetics. Second, we compute D_{O} and report a 45% increase for the phonon-active over the phonon-free 1κ (Fig. 1b, black line), a value that is much lower than the 150% from our own D calculations and the 300% D reported by Ma and colleagues. We remark that diffusion estimates for the phonon-free 10κ , which does not consider phonon modes, are similar to

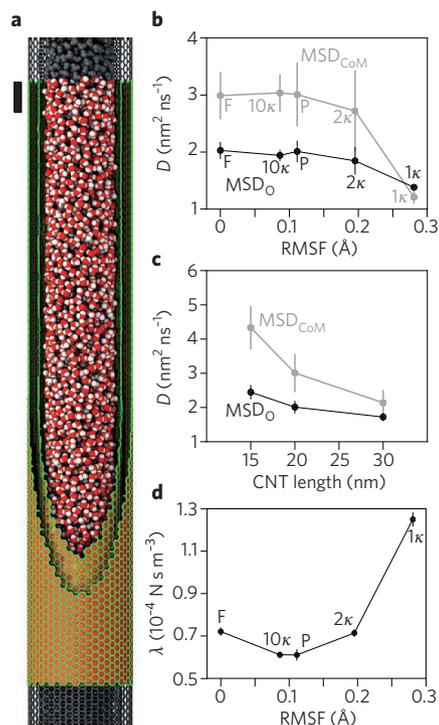


Figure 1 | Water transport through vibrating CNTs in a periodic domain. **a**, All-atom MD model of a CNT filled with water. Water molecules are pictured as red and white beads, CNT atoms are represented as hexagons in green lines. Inner and outer CNTs have (n,m) chiralities of (20,20) and (25,25), respectively. CNT atoms are removed from the surface to reveal the confined water. The coloured system is periodic in the axial direction; the periodic images are shown in grey tones. Scale bar (top left), 1 nm. **b**, D values computed from MSD_{CoM} (grey) and MSD_{O} (black) as a function of root-mean-square fluctuations (RMSF). F and P labels indicate fixed and phonon-active cases, respectively. 1κ , 2κ and 10κ labels refer to phonon-free cases with different spring constants (see Supplementary Section 1). CNT cases are ordered according to the RMSF of the inner CNT atoms. **c**, Comparison of values of D computed from three phonon-active CNTs of lengths 15, 20 and 30 nm. Note that D is over-estimated in **b** and **c** when using MSD_{CoM} . **d**, Friction coefficient (λ) for all cases. Error bars in **b–d** are standard error of the mean.

the phonon-active case. Consequently, our results show only a moderate effect of phonon modes on water diffusion. It is possible that enhancement due to phonon modes is greater for CNTs with smaller diameters, where bulk water behaviour is absent at the CNT centre.

The variation of diffusion from MSD_{O} and MSD_{CoM} is further examined with two additional phonon-active CNTs of lengths 15 nm and 30 nm. We find that values of

the diffusion coefficient from MSD_{CoM} are sensitive and inversely proportional to the considered water mass (Fig. 1c). On the other hand, the diffusion coefficient values from MSD_{O} show some variation with the CNT length, which is attributed to the oscillation of the entire fluid mass.

We also carried out a set of MD simulations using open systems of water and CNTs (Supplementary Section 9), from which we directly calculate the flow rate; this set-up allows a direct comparison to experimental devices⁹. The resulting enhancement of water flow rate for phonon-active relative to phonon-free 1κ CNTs is 20%.

Finally, we supplement our MD findings with fluctuating hydrodynamics calculations (Supplementary Sections 5 and 6). We derive an analytical expression for the MSD_{CoM} of a water-slab in a uniformly oscillating CNT and identify two contributions to it, one due to the oscillating CNT and the other attributed to thermal fluctuations. These calculations confirm that the CNT oscillations do not contribute to the diffusion of the centre of mass.

The 45% diffusion enhancement using MSD_{O} is attributed to a surface friction effect related to the CNT mobility. To clarify this point, we compute the friction coefficient, λ (ref. 15):

$$\lambda = \frac{1}{Ak_{\text{B}}T} \int_0^{\infty} \langle \mathbf{F}(t) \cdot \mathbf{F}(0) \rangle dt \quad (2)$$

where $\mathbf{F}(t)$ is the total axial force between water and CNT (Supplementary Section 8). For the phonon-free 1κ case, λ shows an increment of about 110% compared with the phonon-active CNT case (Fig. 1d). Hence, the magnitude of diffusion enhancement is subject to the choice of the reference point; Ma *et al.* used a reference CNT with no active phonons and with high surface friction that hinders diffusion, thus resulting in a relatively high diffusion enhancement in the phonon-active case.

The present findings, as well as those from the study by Ma *et al.*¹⁰ and other groups^{1,16}, highlight the need for developing a standard reference system for the study of water transport in CNTs and other nanoporous membranes, in order to quantify experimental and computational uncertainties that influence the estimates of flow rates. □

Data availability

The data that support the plots within this paper and all other findings of this study are available from the corresponding author upon reasonable request.

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Author contributions

E.R.C.C., E.P., J.H.W. and P.K. designed the MD studies. E.P., E.R.C.C. and G.L. performed MD simulations. E.P., E.R.C.C., J.H.W. and P.K. performed the analysis of the MD results. A.P. and M.P. introduced the fluctuating hydrodynamics framework and A.P. performed continuum fluid dynamics simulations. P.K. coordinated the project and the analysis of the results. All authors contributed to writing and editing of the manuscript.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available at www.nature.com/reprints. Correspondence and requests for materials should be addressed to P.K.

Competing financial interests

The authors declare no competing financial interests.

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Reply to 'On phonons and water flow enhancement in carbon nanotubes'

Ma *et al.* reply — We are glad to see that Cruz-Chú *et al.*¹ followed our work showing the importance of coupling between the motion of water molecules confined in double-walled carbon nanotubes and the longitudinal phonon modes of the nanotubes. In agreement with our simulations, they found an enhancement of diffusion of confined water and oscillation in the shear stress induced by the coupling with phonons. However, using a different model for water, they observed a smaller enhancement of the diffusion coefficient of the water slab than that predicted in our work. In addition, they showed that the magnitude of enhancement depends on the choice of reference phonon-free system.

In our original work², the diffusion coefficient of the centre of mass of water confined in double-walled carbon nanotubes was calculated using two models of water, the coarse-grained model (mW) and the all-atom model (TIP4P/2005), with the same methodology as in the correspondence by Cruz-Chú *et al.* It should be noted that the TIP4P/2005 model reproduces water properties no worse than the TIP4P-Ew model used by Cruz-Chú *et al.*, as demonstrated in ref. 3. Our simulations show that both models predict similar enhancement of the diffusion coefficient D_{ac} for the phonon-active over the phonon-free nanotube (Fig. 1).

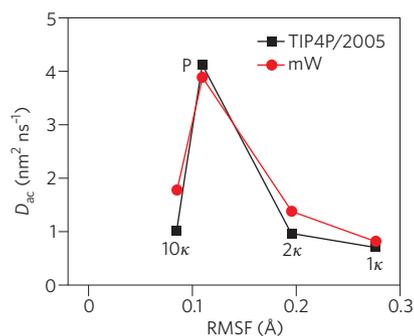


Figure 1 | Diffusion coefficient of water slab.

Black squares and red filled circles correspond to coefficients calculated using the TIP4P/2005 and mW water models, respectively. The P label refers to phonon-active cases, and 1κ, 2κ and 10κ labels refer to phonon-free cases with different spring constants. The double-walled carbon nanotubes are ordered according to the root-mean-square fluctuations (RMSF) of the atoms of the inner nanotube.

There is a slight dependence of the diffusion coefficient calculated for the reference phonon-free system on the choice of the stiffness of the spring connecting the carbon atoms with their equilibrium positions. However, for all values of parameters, we found more than 200% enhancement of the diffusion coefficients.

The coupling between the phonon modes and water can be understood by considering the effect of surface oscillations on interfacial friction². This conclusion has been supported by the calculations of friction coefficient carried out by Cruz-Chú *et al.*, which demonstrated a reduction of interfacial friction due to surface oscillation. This is consistent with our previous predictions of oscillation-induced reduction of interfacial friction and corresponding enhancement of diffusion, which have been done within a generalized Prandtl–Tomlinson model for the interfacial dynamics⁴. We would like to emphasize that both effects have the same physical origin rather than being mutually exclusive.

Besides calculating the diffusion coefficient of the centre of mass of confined water, D_{ac} , which was discussed in our work², Cruz-Chú *et al.* also considered the diffusion coefficients of oxygen atoms, D_o , and the effect of coupling with phonons on this quantity. This is an interesting characteristic of the confined fluid, which we did not study. But its relation to D_{ac} is not straightforward. In particular, D_{ac} is determined not only by diffusion of individual water molecules but also by correlations between the motion of different molecules. This can be clearly inferred by expanding (equation (1) in the work of Cruz-Chú *et al.*) for both D_{ac} and D_o , and setting N_D to be 1, that is, only studying the diffusion along the axial direction. As a result, the coupling of water motion with phonons may have a different effect on D_{ac} and D_o , as found by Cruz-Chú and colleagues.

Our simulations show that the predicted enhancement of diffusion of confined water due to the coupling with the longitudinal phonon modes of the nanotubes depends only marginally on the model of water and on the choice of the phonon-free reference system. The enhancement of diffusion is directly related to phonon-induced reduction of friction: these are two facets of the same phenomenon. □

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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Additional information

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Competing financial interests

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