Comment on "Pumping of Confined Water in Carbon Nanotubes by Rotation-Translation Coupling"

Carbon nanotubes (CNT) allow easy entrance and passage of water [1] and are thus of interest for microfluidics. In electro-osmosis, charged double layers are set into motion by external electric fields. In recent simulations, electro-osmosis of water inside a CNT in the absence of free charges was observed and rationalized by invoking an electric-field-driven torque-vorticity conversion at oriented interfacial water molecules [2]. Though exciting at first sight, this result seems at odds with both Onsager's reciprocal theorem (since an externally applied pressure drop cannot cause a steady electric current due to the absence of free charges) and thermodynamics (since the electric field performs no work in the steady state). In this Comment, we present evidence that results presented in [2] strongly depend on the cutoff scheme implementation in GROMACS.

We concentrate on (16, 0) CNTs for which a pronounced dependence of the water flux on the electric field strength was demonstrated [2]. In the thinner (10, 0) CNTs, a long-lived nonzero flux is also obtained without electric field, showing that the simulations do not converge well enough to yield the true steady state [2,3]. We perform molecular dynamics simulations of SPC/E water in a 9.8 nm long (16, 0) CNT connected to a reservoir ($4.0 \times 3.6 \times 2.0$ nm) in the presence of an axial electric field using GROMACS [4]. We use a Nosé-Hoover thermostat, an anisotrotropic Parrinello-Rahman barostat, periodic boundary conditions, and particle mesh Ewald summation for the electrostatics. For the Lennard-Jones interaction we compare the simple cutoff scheme, which sets the force to zero beyond r_c and thus creates a force discontinuity at $r = r_c$, as employed in [2], with the shifted cutoff scheme, where the force decays to zero [4]. We simulate for 5 ns and collect the last 3 ns for analysis, for $r_c = 1.0$ nm we extend the simulation time by 40 ns. In the inset of Fig. 1 we show the cumulative flux of water molecules through the cross section of the CNT at one end (open symbols) versus time for both cutoff schemes. We also show the conditional cumulative flux (filled symbols), according to [2] defined as the number of molecules exiting the tube on one end that have previously entered on the other end. Except the lag time in the conditional flux of about 8 ns, caused by the time it takes a water molecule to traverse the CNT, the results for the two flux definitions are similar and show a striking yet unphysical difference between the cutoff schemes: For the simple cutoff we find an average flux (obtained from a linear fit to the cumulative flux) of 22 ± 8 ns^{-1}, comparable to 34.0 ± 5.2 ns^{-1} from [2], while the shifted cutoff exhibits vanishing flux. In Fig. 1 we plot the average flux versus r_c. In the limit $r_c \to \infty$, the spurious difference between the cutoff schemes disappears and the water flux vanishes, in accord with basic thermodynamics and generalized hydrodynamic theory [5]. Using the alternative simulation package LAMMPS [6] the flux vanishes, even for small r_c, regardless of the cutoff scheme (see Fig. 1). The mean water orientation does not depend on the cutoff scheme and thus is unrelated to the flux [3]. We conclude that electric-field-induced steady flow of pure water in a CNT is a simulation artifact related to the implementation of the simple cutoff in GROMACS.

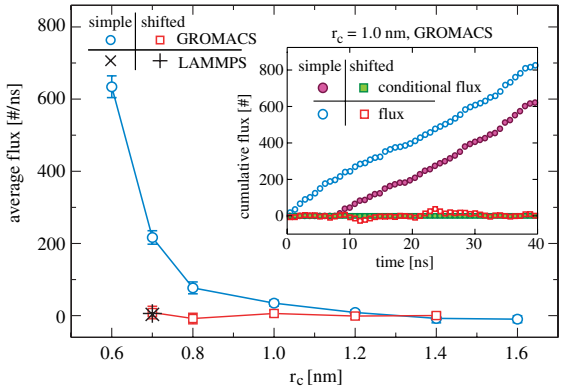

FIG. 1 (color online). Axial average flux (water molecules per ns) through a (16, 0) CNT for electric field $E_z = 1.0$ V nm^{-1} versus cutoff length r_c for simple and shifted cutoff schemes in GROMACS and LAMMPS. The inset shows the conditional (as defined in [2]) and the unconditional cumulative flux for $r_c = 1.0$ nm in GROMACS as a function of time.

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