Dragging of Polarizable Nanodroplets by Distantly Solvated Ions

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We show by molecular dynamics simulations that ions intercalated in carbon and boron-nitride nanotubes can be *solvated at distance* in polarizable nanodroplets adsorbed on their surfaces. When the ions are driven in the nanotubes by electric fields, the adsorbed droplets are dragged together with them. We illustrate this phenomenon by dragging assemblies of 20–10 000 water molecules by individual Na^+ and Cl^- ions. This ion-facilitated dragging could be applied in molecular delivery, separation, and desalination.

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Recent studies have demonstrated efficient dragging of molecules adsorbed on carbon nanotubes (CNT) by their Coulombic scattering with electrons passing through the nanotubes [1–3]. Detection of molecular flows around CNTs by related means has also been proposed [4], tested [5–7], and applied in nanofluidic devices [8,9]. It is of a fundamental and practical interest to design techniques that could also manipulate large molecules and molecular assemblies [10,11].

To follow this goal, we investigate if ions intercalated inside carbon or boron-nitride nanotubes (BNT) can be ''solvated at distance'' in polarizable droplets adsorbed on their surfaces [12]. The strength and long-range order of the Coulombic coupling between an ion and a highly polar solvent is significant even if the two are separated by nanometer distances. The coupling could be preserved at room temperatures, if this space is filled by a dielectric material with a relatively small dielectric constant, such as nanotubes with large band gaps. Therefore, polarizable nanodroplets on the surfaces of such nanotubes might get locked to the intercalated ions and dragged by them in the presence of electric fields.

We first calculate *ab initio* the electrostatic potential φ generated above a (4,3) CNT (band gap of 1.28 eV) [13] by a Li^+ ion located in its center and φ generated above a (5,5) BNT (band gap of 5.5 eV) [14] by a Na^+ ion. In the calculations, the 5 nm long tubes are kept neutral and frozen, since their structure is rather rigid. The potentials φ are obtained from natural bond orbital atomic charges, using the Becke three-parameter Lee-Yang-Parr hybrid functional (B3LYP) and the 3–21g basis set in GAUSSIAN03 [15]. The potential φ of Li^+ is decreased by $\approx$25% due to screening, while that of Na^+ is decreased by $\approx$10%. The same results are obtained in the presence of the electric field of $\mathcal{E} = 0.1$ V/nm applied along the tube axis. When the ions are shifted along the axis by a small distance d, the total energy of both systems changes by $\approx \mathcal{E}d$, as if the nanotubes are absent. These results show that the screening of the ionic field is small in selected CNTs and BNTs. In these tubes, the ion can be also driven by electric fields. With this in mind, we model for simplicity the ion-droplet dynamics in some typical nanotubes and consider them to be nonpolarizable.

In Fig. 1, we display a Na^+ ion intercalated inside an unpolarized (10,0) CNT that is distantly solvated in $N_w = 400$ water molecules adsorbed on the CNT surface. The system is relaxed in the box of $\approx$1000 nm^3, fitting the coexistence of gas and liquid phases at the temperature of $T = 300$ K. The water droplet is spontaneously formed on the CNT even in the absence of the ion, similarly like on other fibers [16].

We study this hybrid system by molecular dynamics simulations with the NAMD package [17], based on the CHARMM27 force field [18]. We estimate parameters of atoms in aliphatic groups and the nanotube from similar atom types or calculate them *ab initio* [15], and add them to the force field. The systems are equilibrated as an NVT (constant number of molecules, volume, and temperature) ensemble with periodic boundary conditions, where the long-range electrostatic forces are computed by the

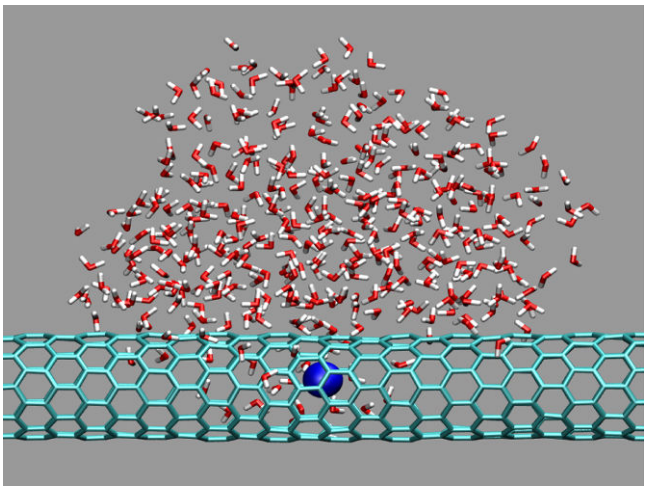


FIG. 1 (color online). Nanodroplet with $N_w = 400$ water molecules dragged on the surface of unpolarized (10,0) CNT by a single intercalated Na^+ cation. The ion is driven by the electric field of $\mathcal{E} = 0.1$ V/nm applied along the tube z axis.

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particle-mesh Ewald method [19]. The time step is 1 fs, and a small Langevin damping coefficient of 0.01 ps^{-1} is chosen to minimize the unphysical loss of momenta to the reservoirs [20]. The tube is aligned along the z axis, it is blocked from shifting and left free to vibrate.

We start by exploring the strength of the ion coupling to the distant solvent, characterized by the ion-droplet binding energy E_b. In Fig. 2, we show the obtained E_b that is averaged over 10 000 frames, separated by 500 fs intervals. For nanodroplets with $N_w = 100$–800 waters, the binding energies E_b of the Na^+ and Cl^- ions saturate to values that are several times smaller than their solvation energies in bulk water, $E_{solv} = 7.92$ and 6.91 eV [12], respectively. For nanodroplets with $N_w < 100$, the binding energies are smaller, and at $N_w \approx 5$–15 they become comparable to kT.

We can also estimate the coupling energy E_b analytically by assuming that the ion is located at a distance of $d \approx 0.35$ nm above a flat surface of water with the dielectric constant $\varepsilon_w \approx 80$. This gives $E_b \approx -\frac{e^2}{4d}\left(\frac{\varepsilon_w - 1}{\varepsilon_w + 1}\right) \approx -1$ eV, in good agreement with Fig. 2. The fact that in the simulations the Na^+ ion binds twice as strongly to the nanodroplet than the Cl^- ion is caused by the character of the water polarization: the Na^+ ion attracts from each water the O atom that is twice as charged as the H atoms, while Cl^- attracts just one of these two H atoms. The large difference between E_b and the bulk solvation energies is caused by the fact that ions solvated in bulk water are surrounded by 2–3 times more water molecules that are about twice as close to them. These binding energies are proportionally decreased if the nanotube polarization is included, as discussed above.

In the inset of Fig. 2, we also show two snapshots of the 1D electrostatic potential generated by the water droplet ($N_w = 400$) along the axis of the nanotube with the intercalated Na^+ ion. The 1 eV deep well with a potential gradient of 0.5–1 V/nm should be large enough to block the moving ion from leaving the droplet even in the presence of electric fields of $\mathcal{E} \approx 0.1$–0.2 V/nm.

We continue our study by dragging the droplets with the ions in the presence of electric fields, aligned along the nanotubes (see the movie [21]). The field acts on the whole system, except on the nanotube that is treated as nonpolarizable. In Fig. 3 (left axis), we show the velocity v_w of the nanodroplets with N_w water molecules. The data are calculated from 50 ns simulations ($\approx$50 rounds along the CNT) at $\mathcal{E}_0 = 0.1$ V/nm and $T = 300$ K. This statistical averaging is fully sufficient for the presentation of the results [20]. The obtained velocity v_w is proportional to the electric field and it strongly depends on the droplet size. It has practically the same value if the Na^+ or Cl^- ions are used for the dragging. In order to test the scalability of this dragging phenomenon, we also model a droplet with $N_w = 10\,000$, located between two parallel (10,0) CNTs separated by a 5 nm distance. If one Na^+ ion is placed in each nanotube, and both ions are driven by the field of $\mathcal{E}_0 = 0.1$ V/nm, the droplet moves together with the ion pair at a high velocity of $v_w = 6.6$ nm/ns, due to a small contact with the CNTs (movie).

The character of the nanodroplet motion on the nanotubes might be closer to sliding [22] than rolling [23], due to partial wetting of the CNT surface with a large van der Waals binding. In macroscopic systems, the droplet velocity for both mechanisms of motion is controlled by the momentum and energy dissipation of water layers sliding inside the droplet [22]. Both mechanisms give the qualitative dependence of the droplet velocity $v_w \propto e\mathcal{E}/(r\eta)$, where the droplet radius is $r \propto N_w^{1/3}$ and the water viscosity is $\eta \propto 1/T$ [24]. The results in Fig. 3 roughly

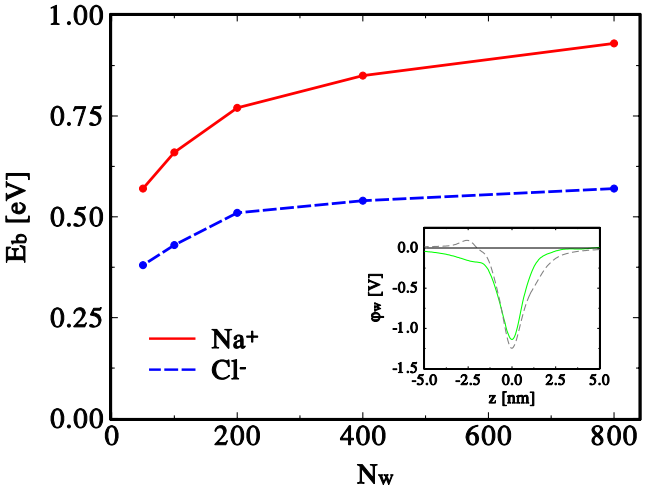


FIG. 2 (color online). Binding energy E_b between the Na^+ and Cl^- ions and water nanodroplets with N_w molecules (molecules that left to the gas phase are neglected). (inset) Typical snapshots of the electrostatic potential φ_w generated by the water molecules along the axis of the CNT with the intercalated Na^+ ion.

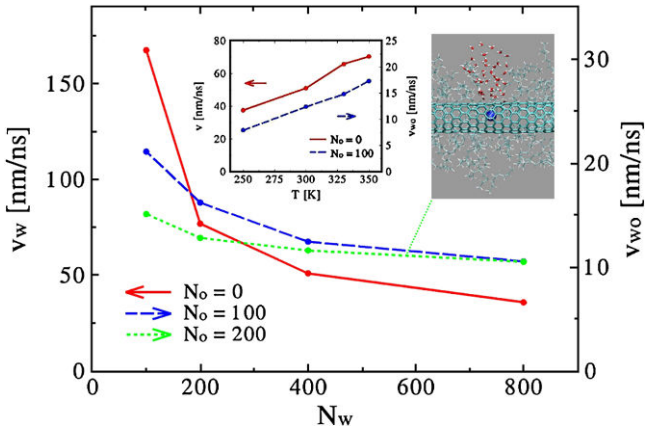


FIG. 3 (color online). Dependence of the nanodroplet velocity on the number of its water molecules N_w. Dragging of the droplet in the presence of octane molecules is considered as well. (right inset) Visualization of the nanodroplet with $N_w = 50$ in $N_o = 200$ oil molecules. (left inset) Temperature dependence of the droplet velocity for $N_w = 400$.

confirm this dependence even for the motion of nanoscale droplets, but the driving velocity scales more steeply with the number of water molecules, $v_w \propto 1/N_w^{2/3}$. In the inset, we also show for $N_w = 400$ that the temperature dependence is almost linear, $v_w \propto T$, as expected. To clarify more the motion of the nanodroplet, we test its dragging by a Na^+ ion that is *directly* solvated in it. The obtained velocity of the droplet is about 20% larger than when the ion is inside the tube. This is most likely caused by the tendency of the droplet to roll, since the dragging force acts close to its center rather then on its periphery at the nanotube surface.

The character of the nanodroplet motion could be dramatically altered, if a monolayer of oil is adsorbed on the nanotube surface. In Fig. 3 (right axis), we show that the presence of N_o octane molecules decreases the droplet velocity v_{wo} by an order of magnitude, due to friction between water and oil. Smaller droplets, $N_w < 100$, are attached to the ion by a narrow "neck" passing through the oil layer (see inset in Fig. 3). Larger droplets, $100 < N_w < 200$, are more or less spherical, significantly submerged inside the oil, and they share a very small surface area with the CNT. In analogy to a water droplet inside bulk oil, their driving could be described by the Stokes law that is largely valid at the nanoscale [25,26]. Here, it gives $F = -6\pi r \eta v_{wo}$, where $F = e\mathcal{E}_0 = 16$ pN is the drag force acting on the droplet, r is the droplet radius, and $\eta \approx 0.54$ mPa s is the viscosity of octane at $T = 300$ K. For $N_w = 100$, we find $r \approx 3.5$ Å, so $v_{wo} = 4.5$ m/s. This value is 3–4 times smaller than that obtained in the simulations, due to the incomplete coverage of the nanodroplet by oil.

If the nanotube is fully submerged in water instead of oil, then the dynamics of the field-driven ion becomes very different [27]. We simulate this situation in a (10,0) CNT, placed in the periodic water box of $3 \times 3 \times 6.8$ nm^3, for the driving field of $\mathcal{E} = 0.1$ V/nm. The results, presented in Table I, show that the velocities of the ions are 4–5 times larger than those of the ions dragging the water droplet. This is because water molecules around the submerged nanotube just rearrange fast locally when they react to the field-driven ion. At higher temperatures, the ions move faster, since their binding to the water molecules is less stable [28]. The velocities of the Cl^- ion are smaller than those of the Na^+ ion, because Cl^- easily attracts the light H atoms that are not bound (frustrated) in water molecules at the nanotube surface.

We also discuss the *dynamical stability* of the coupled ion-droplet pair. In larger electric fields or when the nanodroplet is small, the ion might get released, and, in the model with periodic boundary conditions, it might get later recaught by the nanodroplet. In Fig. 4, we plot for $\mathcal{E} = 0.02$ V/nm the trajectory of the ion that left the droplet of $N_w = 20$ and was recaught in the next run around it. The ion's trajectory is shown by the dark line, and the time-frame separation on the vertical axis is 100 fs. The electric field along the CNT axis created by the ion-polarized droplet is plotted by contours. The positive and negative regions that lock the ion are obtained from the derivative taken at the sides of the potential well (see inset of Fig. 2).

The ion released from the droplet goes once around the tube and reapproaches the droplet with the velocity of $v_{\text{ini}} \approx 1,400$ m/s (bottom). After it gets closer to the droplet, the water molecules become fast polarized (inset at $z = -1.3$ nm, $t = 7$ ps). The ion first passes around the droplet, just to be attracted back by several chained molecules protruding from the droplet ($z = 1.7$ nm, $t = 10.0$ ps). This is possible, since a chain of 5 hydrogen-bonded and aligned water molecules generate at the distance of 1 nm the field of ≈ 0.17 V/nm, which is opposite to and almost an order of magnitude larger than the external field. The deceleration of the ion by this large induced field causes the coupled system to gain high Coulombic potential energy. Thus the ion position oscillates 3–4 times, before it is fully seized back by the droplet ($z = 2$ nm, $t = 18$ ps). The two start to move together at a much smaller velocity $v_{\text{end}} \approx 130$ m/s, while the waters are already interconnected. If the droplet does not catch the ion

TABLE I. Velocities of the Na^+ and Cl^- ions inside the (10,0) CNT submerged in water and at $\mathcal{E} = 0.1$ V/nm.

Ion	240 K	270 K	300 K
Na^+	464.7 m/s	622.5 m/s	733.7 m/s
Cl^-	284.5 m/s	401.6 m/s	547.9 m/s

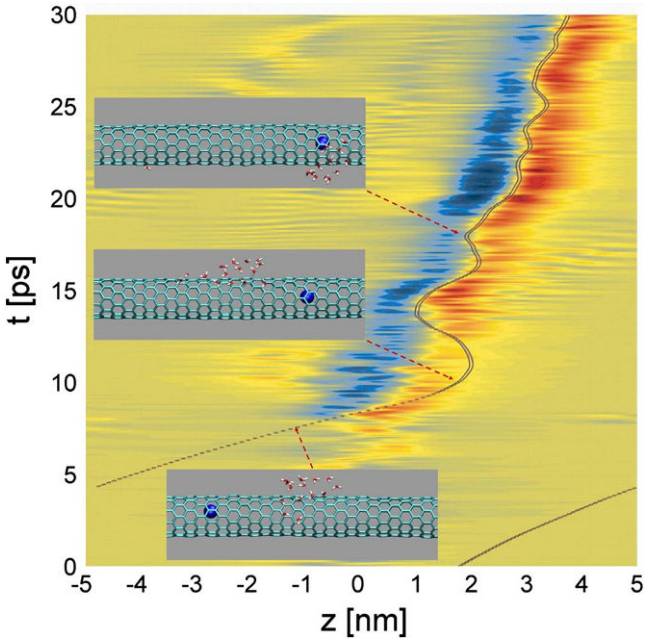


FIG. 4 (color online). The trajectory of the Na^+ ion that is recaught by a water nanodroplet with $N_w = 20$. The axial position and the time of the ion motion are shown on the horizontal and vertical axis, respectively. The electric field generated by the water molecules along the CNT axis is plotted by contours.

within several of its runs around the periodic system, the ion might heat and temporally evaporate the droplet. The transient oscillations observed in this ion catching closely resemble quasiparticle formation in condensed matter systems [29].

Finally, we check if boron-nitride nanotubes could be potentially used for the ion-droplet dragging. The BNTs screen electric fields very little, but it is not clear if their large surface polarity does not prevent this dragging. In order to test this possibility, we briefly simulate dragging of droplets with $N_w = 100$ and 400 waters on the (5,5) BNT. The atomic charges of the B and N atoms are calculated *ab initio* [15], and approximated by the values of $1.0e$ and $-1.0e$ [30,31]. This BNT is highly polar, but little polarizable (neglected). In the simulations, one Na^+ ion is driven inside the tube by the electric field of $\mathcal{E} = 0.1$ V/nm, and $T = 300$ K. The molecules of the droplets with $N_w = 100$ and 400 waters form on the (5,5) BNT an open and closed *ring*, respectively, formed by 1–2 water layers. These droplets move with an average velocity of $v_w = 0.28$ and 1.29 nm/ns, respectively (movie). The droplet with $N_w = 400$ waters moves about 40 times slower on the BNT than on the CNTs due to strong coupling to the highly polar BNT surface. We also obtain that $v_w \propto 1/N_w$, showing a stronger dependence on N_w than on CNTs. This can be understood by the fact that the driving of the flattened nanodroplets is close to sliding, where the friction is proportional to the contact area, or N_w.

The presence of large screening in metallic SWNTs does *not* imply that molecular dragging by individual ions or ionic solutions is negligible. This is because two ions separated by the wall of a metallic SWNT can still "see each other" via their screening charges that interact in the monolayer. Our recent *ab initio* calculations have shown that the coupling of two such ions is only reduced by $\approx 70\%$, due to this imperfect screening. The dragging of assemblies of polar molecules on the surfaces of nanotubes by ions moving through them complements the passive transport of gases [32,33] and liquids [34–37] through CNTs. The described drag phenomena might be used in a number of important nanofluidic applications, such as molecular delivery, separation, desalination, and manipulation of nanoparticles at the nanoscale. The methodology might also be integrated into modern lab-on-a-chip techniques [38].

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