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Coulombic Dragging of Molecules on Surfaces Induced by Separately Flowing Liquids

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Nanosystems provide a rich spectrum of fascinating drag phenomena. Several years ago, we predicted that atoms and molecules intercalated inside carbon nanotubes or adsorbed at their surfaces could be pumped like in a nanopen by electrons passing through the tubes.[1] The experiments that followed[2,3] have confirmed that this effect exists and could be used for efficient transportation of materials at the nanoscale. We have also speculated that nanotube electrons, highly exposed to external stimuli, could be driven by fluids passing around them.[4] This effect was also found and studied in several modifications[5−7] with rich potential applications. These phenomena were highlighted by the discovery that water can enter and pass through carbon nanotubes (CNTs),[8] due to strong van der Waals binding. The unusually "low friction" conditions in CNTs also allow fast passage of gases[9] and easy mutual slipping of the multiwall carbon nanotubes.[10]

In this communication, we would like to enrich the above family by a new class of molecular drag phenomena. In particular, we use molecular dynamics (MD) simulations to show that polar molecules adsorbed on the surfaces of CNTs can be driven along them by polar liquids flowing inside the tubes. This effect is very close in origin to the above suggested and observed electron molecule drag phenomena.[1−7] The broader goal of our studies is to control positions, configurations, and numerous activities of molecules on material surfaces.[11]

In Figure 1, we show the selected zwitterion molecule $NH_3^+(CH{=}CH)_3CH_2(CH{=}CH)_6CO_2^-$ driven along the surface of the (14,0) CNT by water molecules passing inside;[12] driving of the $CH_2{=}CH{-}CH{=}CHNH_3^+$ and $CH_2{=}CH{-}CH{=}CHCH_2O^-$ ions is studied as well. These molecules are relatively mobile on the tube surface but stay attached to it, due to moderate van der Waals binding. We consider a 98 Å long CNT, aligned along the z-axis in a periodic box of $48 \times 48 \times 99.4$ Å, with the $(x,y,z) = (0,0,0)$ point located at its center.

The water flow inside the CNT is induced by applying the force of 0.001 kcal mol^{-1} Å^{-1}, oriented along the tube, on the oxygen atom of each water molecule whose z coordinate satisfies $-49.7 < z < -20.0$ Å. Given the number of molecules in this column and the tube diameter, this generates a pressure of $P \approx 70$ atm.[13] Once we apply this pressure, water starts to flow inside the CNT with the average velocity $\langle v_{\mathrm{wat}} \rangle \approx 10{-}20$ m/s, depending on the tube parameters. The ions or polar molecules positioned on the surface of the tube are on average driven in the same direction as the water flow.

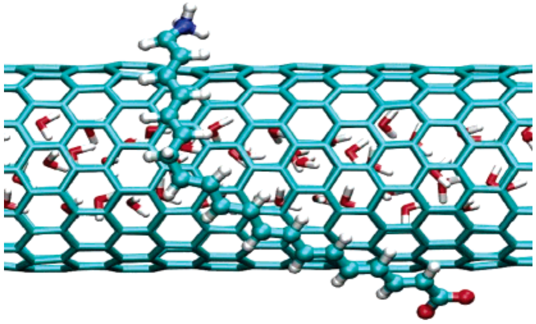

Figure 1. The $NH_3^+(CH{=}CH)_3CH_2(CH{=}CH)_6CO_2^-$ zwitterion molecule adsorbed on the surface of the (14,0) CNT is driven by the flow of water passing inside. The water flow going to the left is realized at $T = 300$ K.

We study the dynamics of this system by MD simulations, performed with the NAMD package.[14−17] In the simulations, we apply Langevin dynamics, at $T = 300$ K, with the damping coefficient of 0.01 ps^{-1}. This is a compromise between the 0.001 ps^{-1} rate, valid for intertube coupling,[18] which could apply also to the neutral part of the molecule, and the 0.1 ps^{-1} damping, which might be correct for polar groups and water. In this way, we can approximately simulate the dragging phenomenon in this system with one damping constant. We model the effect in zigzag CNTs[19] $(n,0)$, with $n = 11$, 14, and 17, which should damp the adsorbed molecules less than metallic CNTs, due to the absence of free-electron dynamical screening. They also allow easier penetration of the electric field through the tube wall since its dielectric constant[20] only effectively reduces the coupling strength by a factor of 2−4. In classical MD simulations, all of these effects are absent, but we retain the correct CNT sizes. The tube is left free to vibrate, except for a few fixed atoms that hold it in place. Therefore, besides the Langevin damping, the dragged molecule is also directly relaxed by collisions with the tube.

The Coulombic potential energy E_C between the molecule adsorbed on the nanotube and all the water molecules flowing inside the tube is

$$E_{\mathrm{C}} = \sum_i q_i \varphi(r_i), \qquad \varphi(r) = \frac{1}{4\pi\epsilon} \sum_j \frac{Q_j}{|r - r_j|}. \qquad (1)$$

Here, q_i and Q_j are the charges of the ith atom in the adsorbed molecule and jth atom in the water chain (O or H), respectively, with the coordinates r_i and r_j. In E_C, the charges q_i or Q_j are effectively reduced by the size of the dielectric constant ϵ of the (semiconducting) nanotube and water. We model this effect by scaling the charges q_i, instead of using the unknown ϵ.

The adsorbed molecule diffuses on the CNT surface, but when it is enough polar, its random motion is determined more by the fluctuating and slowly "shifting" Coulombic potential, $\varphi(r)$, generated by the flowing polar liquid,[4] rather than by the lattice-modulated van der Waals interactions with the CNT. Therefore, the center of mass of its diffusion trajectory tends to slowly shift with the fluctuating relief of $\varphi(r)$. The more polar the molecule is, the smaller diffusion constant it has since it becomes more *locked* (localized) in the potential wells of the fluctuating potential $\varphi(r)$, generated around the string of flowing polar molecules.[21] As a result, the molecular dynamics gains a more deterministic character, resembling motion on an "elastic transportation belt".

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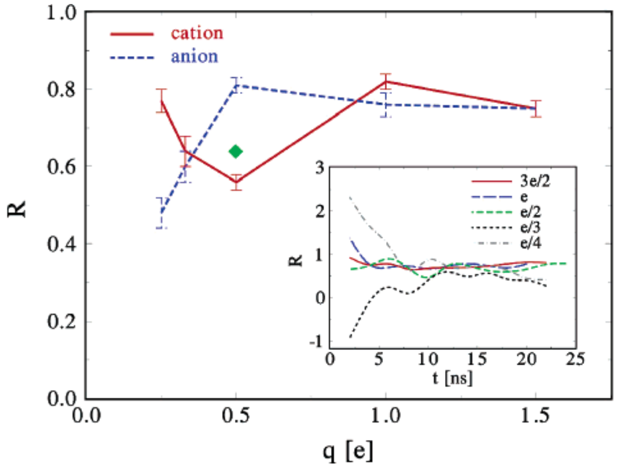

Figure 2. The ratio *R* of the distances traveled by the adsorbed ions $CH_2{=}CH{-}CH{=}CH{-}NH_3^+$ and $CH_2{=}CH{-}CH{=}CH{-}CH_2O^-$, with different effective total charges *q*, and water inside the (14,0) CNT. The small rectangle at $q \approx 0.5$e applies to the $NH_3^+(CH{=}CH)_3CH_2(CH{=}CH)_6CO_2^-$ zwitterion molecule with correct (unscaled) charges. (Inset) The ratio between the average speed of the $CH_2{=}CH{-}CH{=}CH{-}CH_2O^-$ anion and the flowing water plotted with the time of driving (averaging). For shorter averaging times *t*, the ratio *R* significantly deviates from the converged values, especially in ions with small charges that diffuse faster on the fluctuating potential $\varphi(r)$ of the moving water column.

In Figure 2, we present the ratio *R* between the total distances traversed by the attached ions (molecule) on the surface of the CNT and the water flowing inside the tube. The last is calculated via the number of water molecules passing through the tube entrance in one direction minus those passing in the opposite direction, divided by their linear density. The results are obtained from dragging the systems for $t \approx 100$ ns. We show the ratios *R* for different effective total charges *q* of the $CH_2{=}CH{-}CH{=}CHNH_3^+$ and $CH_2{=}CH{-}CH{=}CHCH_2O^-$ driven ions, in order to reflect the effect of the dielectric constant ϵ in eq 1. The charges of all their atoms are scaled by the same amount, with respect to their approximate values in the isolated molecules, found by ab initio methods and CHARMM force field (see Supporting Information). Small changes of the charges in the molecule, when it is at the surface, are not supposed to significantly change the results.

We can see that the ratios are $R \approx 0.6{-}0.8$, except for small effective total charges *q*, where the dragging is rather different for the two ions. We also show by the small rectangle at $q \approx 0.5$e the obtained ratio $R \approx 0.65$ for the above zwitterion molecule, driven under the same conditions as the ions. This value falls between *R* for the two ions when their effective charges are about the same as the charged groups in the zwitterion molecule. In the inset, we also show for illustration the time dependence of the ratio *R* for the $CH_2{=}CH{-}CH{=}CH{-}CH_2O^-$ anion. The ratio *R* is stabilized faster if the charge of the ion is bigger since the motion is determined more by dragging than by diffusion. Note that the water column in narrow tubes can flow in two different orientations.[22] Over the time, it switches from one orientation to the other, but this switching does not take part very often (10−100 ns). The results presented in Figure 2 are averaged over the two orientations of water columns. The reason the ions have different driving ratios *R* is most likely associated with the large asymmetry of the water dipoles that drive the attached ions. Localization of the ions can be induced more by the heavy oxygen atoms of water than by its hydrogens. This could explain the larger driving ratio *R* of cations at smaller total charges *q*.

Table 1. The Dependence of the Ratio *R* for the Two Ions with *q* = e on the Tube Radius and Number of Water Molecules Inside the CNT

nanotube – H_2O	(11,0) – 64	(14,0) – 156	(17,0) – 232
cation	0.82 ± 0.04	0.82 ± 0.02	1.00 ± 0.01
anion	1.00 ± 0.01	0.77 ± 0.03	0.71 ± 0.02

The ion motion also depends on the radius of the CNTs, as shown in Table 1. As we go from the (11,0) to the (17,0) tube, the ratio *R* grows for the cation and drops for the anion. This is yet another manifestation of the different driving for the two ions shown in Figure 2. This effect could be associated with stronger localization of the cations by the heavy oxygens in thicker water columns, where hydrogens, on the contrary, drag molecules less effectively, due to their light mass and more available space.

The discussed molecular dragging phenomena are robust and should allow transportation of materials at the nanoscale in analogy to molecular transportation in biological cells.[23] Molecular dragging can be realized in two basic ways, where the dragging medium (polar gas or liquid) is either inside or outside the tube, and the dragged medium is on the other side. These novel phenomena complement other molecular transportation methods, such as current-induced dragging of molecules[1−3] or their mechanical rolling.[24]

Supporting Information Available: Partial charges and force field parameters for the molecules, water and CNTs, complete ref 16. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Král, P.; Tománek, D. *Phys. Rev. Lett.* **1999**, *82*, 5373−5376.
(2) Regan, B. C.; Aloni, S.; Ritchie, R. O.; Dahmen, U.; Zettl, A. *Nature* **2004**, *428*, 924−927.
(3) Svensson, K.; Olin, H.; Olsson, E. *Phys. Rev. Lett.* **2004**, *93*, 145901.
(4) Král, P; Shapiro, M. *Phys. Rev. Lett.* **2001**, *86*, 131−134.
(5) Ghosh, S.; Sood, A. K.; Kumar, N. *Science* **2003**, *299*, 1042−1044 (pending U.S. Patent No. 6718834 B1).
(6) Sood, A. K.; Ghosh, S. *Phys. Rev. Lett.* **2004**, *93*, 086601.
(7) Subramaniam, C.; Pradeep, T; Chakrabarti, J. *Phys. Rev. Lett.* **2005**, *95*, 164501.
(8) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. *Nature* **2001**, *414*, 188−190.
(9) Holt, J. K.; Park, H. G.; Wang, Y. M.; Stadermann, M.; Artyukhin, A. B.; Grigoropoulos, C. P.; Noy, A.; Bakajin, O. *Science* **2006**, *312*, 1034−1037.
(10) Cummings, J.; Zettl, A. *Science* **2000**, *289*, 602−604.
(11) Wang, B.; Král, P; Thanopulos, I. *Nano Lett.* **2006**, *6*, 1918−1921.
(12) Majumder, M.; Chopra, N.; Andrews, R.; Hinds, B. J. *Nature* **2005**, *438*, 44.
(13) Zhu, F.; Tajkhorshid, E.; Schulten, K. *Biophys. J.* **2002**, *83*, 154−160.
(14) MD simulations are performed by the NAMD molecular dynamics package,[15] based on the CHARMM27 force field.[16] We estimate parameters of atoms in aliphatic groups and the nanotube from similar atom types and add them to the CHARMM27 force field. The long-range electrostatic forces are computed by the particle-mesh Ewald method.[17] The time step of these long runs is chosen to be 2 fs.
(15) Kalé, L.; Skeel, R.; Bhandarkar, M.; Brunner, R.; Gursoy, A.; Krawetz, N.; Philips, J.; Shinozaki, A.; Varadarajan, K.; Schulten, K. *J. Comput. Phys.* **1999**, *151*, 283−312.
(16) Mackerell, A. D.; et al. *J. Phys. Chem. B* **1998**, *102*, 3586−3616.
(17) Darden, T.; York, D.; Pedersen, L. *J. Chem. Phys.* **1993**, *98*, 10089−0092.
(18) Servantie, J.; Gaspard, P. *Phys. Rev. Lett.* **2003**, *91*, 185503.
(19) Saito, R.; Fujita, M.; Dresselhaus, G.; Dresselhaus, M. S. *Appl. Phys. Lett.* **1992**, *60*, 2204−2206.
(20) Leonard, F.; Tersoff, J. *Appl. Phys. Lett.* **2002**, *81*, 4835−4837.
(21) Laage, D.; Hynes, J. T. *Science* **2006**, *311*, 832−835.
(22) Best, R. B.; Hummer, G. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 6732−6737.
(23) Vale, R. D. *Cell* **2003**, *112*, 467−480.
(24) Shirai, Y.; Osgood, A. J.; Zhao, Y.; Yao, Y.; Saudan, L.; Yang, H.; Yu-Hung, C.; Alemany, L. B.; Sasaki, T.; Morin, J.-F.; Guerrero, J. M.; Kelly, K. F.; Tour, J. M. *J. Am. Chem. Soc.* **2006**, *128*, 4854−4864.

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