Simulation of the flow of aqueous solutions through carbon nanotubes

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Abstract
The flow of aqueous NaCl and NaI solutions through carbon nanotubes is treated by extensive molecular dynamics simulations. The dependence of diverse transport features on the solute specificity, the nanotube geometry, and the various atomic models employed, including polarizability, is addressed in detail. The interpretations are developed in conjunction with the structural details of the solution and the energy barriers the solute components have to overcome.

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Molecular dynamics
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1. Introduction
The development of methods for cutting carbon nanotubes (CNTs) into small open-ended pipes [1] enabled the arrangement of tubes of controllable sizes [2,3] within membranes [4,5]. Single-walled CNTs have thus become promising materials for nanofluidic technology, opening perspectives to applications involving filtration and separation. Unexpectedly high flow rates have been found, mostly independent of the pore length.

Peter and Hummer [6] have studied computationally the Na\(^+\) ion transport through narrow hydrophobic pores in model membranes formed of hexagonally packed armchair type CNTs of chirality \((10, 10)\), evidencing the fact that subnanometer pores pose a huge free-energy barrier to ions. As promising candidates for water desalination by reverse osmosis, CNT membranes have been simulated under hydrostatic pressure and equilibrium conditions by Corry [7]. While ions are not able to pass through narrow pores \((5, 5)\) and \((6, 6)\), due to the formation of stable hydrogen bonds, water faces no such impediment. The considered membranes thus allow under a hydrostatic pressure difference for high degrees of desalination to be achieved.

In addition to many aspects addressed in the literature (relevance of geometrical details, free energy barriers, hydration of ions etc.), several other aspects are being tackled in the present study, as well, among which the detailed electrostatics, ion specificity, and relevance of polarizability, some of them already published [8]. Among the modeling particularities we have opted for, worth mentioning are: (1) single CNTs embedded in explicit membranes are treated, rather than membranes resulted from close packing of CNTs; (2) rigid-body dynamics is employed for the water molecules; (3) large ensembles of initial configurations and significantly longer data collection times are considered, providing substantially better statistics.

2. MD methodology
The reported simulations have been performed entirely by a homemade MD computer code (MDsqad). A central role therein is played by the usage of rigid-body dynamics for the water molecules, assuring high accuracy at large time steps by the intrinsic reduction of the number of degrees of freedom and by the absence of a supplementary “shake”-type algorithm to preserve the equilibrium structure of molecules. Since the Euler angle representation of the rotational equations of motion is singular for particular angles, the quaternion representation has been used instead [9].

A Gaussian thermostat [9], known for conserving the velocity distributions, was implemented for the translational degrees of freedom. The degrees of freedom for the rotation of the water molecules and the translation of the ions have been allowed to relax freely to the equilibrium temperature.

3. Force field
Two molecular representations for water have been implemented: the non-polarizable four-site model TIP4P of Jorgensen
et al. [10,11] and the polarizable five-site model COS/G2 of Yu and van Gunsteren [12], belonging to the category of the so-called charge-on-spring (COS) models.

The COS/G2 model features three fixed atomic sites (on the O and H atoms) and a pair of virtual polarization sites: a fixed site S located on the bisector of the fixed HOH angle and a movable site M, which can be repositioned with respect to the former. The induced dipole of the molecule is determined by the total electric field \( \mathbf{E}_S \) acting on the fixed polarization site and implies the self-consistent relocation of the movable site at a relative position \( \mathbf{r}_{SM} \) from the fixed one:

\[
\mu^{\text{ind}} = \alpha_{\text{pol}} \mathbf{E}_S = \varrho_{\text{pol}} \mathbf{r}_{SM},
\]

where \( \alpha_{\text{pol}} \) is the molecular polarizability.

In addition to periodic boundary conditions, in order to account for the long-range electrostatic interactions, Ewald sum techniques have been applied. The real-space contributions have been evaluated by standard Ewald summation. The corresponding reciprocal-space contributions have been treated according to the \( \text{P}^3\text{M} \) particle–particle/particle–mesh method developed by Hockney and Eastwood [13], as formulated by Deserno and Holm [14], which replaces the real charge distribution with an equivalent mesh-based distribution \( \rho_{\text{M}}(\mathbf{r}_p) \) by using a charge assignment function \( W(\mathbf{r}_p - \mathbf{r}_i) \):

\[
\rho_{\text{M}}(\mathbf{r}_p) = \frac{1}{V_h} \sum_{i=1}^{N} q_i W(\mathbf{r}_p - \mathbf{r}_i). \tag{2}
\]

Here \( \mathbf{r}_p \) are the mesh points and \( V_h = h_x h_y h_z \) is the volume element corresponding to the mesh spacings. Specifically, we considered a regular 32 \( \times \) 32 \( \times \) 128 point grid and a seventh-order charge assignment function.

The role of the standard Coulomb Green's function is taken by the optimal influence function \( G_{\text{opt}}(\mathbf{k}) \), which can be adjusted along with the space-splitting parameter \( \alpha \) for a given geometry, such as to make the result most closely resemble the continuum solution.

The \( k \)-space electrostatic field resulted by solving the Poisson equation for the Fourier-transformed mesh-based charge distribution \( \tilde{\rho}_{\text{M}}(\mathbf{k}) = \mathcal{F}_{\text{FFT}}[\rho_{\text{M}}(\mathbf{r}_p)] \) is transformed back to real space as a mesh-based field:

\[
\Phi^{(k)}(\mathbf{r}_p) = \mathcal{F}_{\text{FFT}}^{-1}[\tilde{\rho}_{\text{M}}(\mathbf{k}) \times G_{\text{opt}}(\mathbf{k})](\mathbf{r}_p),
\]

\[
\mathbf{E}^{(k)}(\mathbf{r}_p) = \mathcal{F}_{\text{FFT}}^{-1}[-i \mathbf{k} \times \tilde{\rho}_{\text{M}}(\mathbf{k}) \times G_{\text{opt}}(\mathbf{k})](\mathbf{r}_p), \tag{3}
\]

where \( i \mathbf{k} \) differentiation in reciprocal space is used to obtain the electric field \( \mathbf{E}^{(k)}(\mathbf{r}_p) \). The mesh-based field is then reprojected onto the real particles by using the charge assignment function to yield the reciprocal space contributions to the total energy and to the electrostatic forces acting on them:

\[
E^{(k)} = \sum_{i=1}^{N} q_i \sum_{\mathbf{r}_p \in M} \Phi^{(k)}(\mathbf{r}_p) W(\mathbf{r}_i - \mathbf{r}_p),
\]

\[
\mathbf{F}_i^{(k)} = q_i \sum_{\mathbf{r}_p \in M} \mathbf{E}^{(k)}(\mathbf{r}_p) W(\mathbf{r}_i - \mathbf{r}_p). \tag{4}
\]

As solute anions, besides the \( \text{Na}^+ \) cation, we have selected two representative halides from the Hofmeister series, i.e. chloride and iodide, which are known to have a different enough behavior to suggest general trends. For consistency reasons, we have treated by a COS-type model also the polarizability of the individual ions. A beneficial side-effect resides in the fact that the overall electrostatics of the system relies solely on point charges. The actual interaction parameters pertaining to water, the solute ions and the carbon atoms composing the nanotubes are summarized in Ref. [8].

The execution speed of the MDSquad code reaches in typical CNT simulations (without polarizability) 2.4 ns/day/core on up-to-date processors.

4. Channel model

The considered channel model consists of a rigid non-polar armchair-type \((n,n)\) CNT of length 60.17 Å, extending symmetrically between two neutral graphene planes, and two reservoirs, formed on either side of the membrane. The five considered chiralities range from (8,8) to (12,12) and, in terms of radius, between 5.42 and 8.12 Å. The size of the simulation cell has been adjusted in all cases such as to correspond to a reference water density of 1 g/cm\(^3\).

The \( \text{NaCl} \) and \( \text{NaI} \) solutions have been modeled by 1000 water molecules and 15 solute ions of each species, resulting in a concentration of approximately 0.83M.

In order to drive the ions through the channel, a homogeneous electric field of 0.02 V/Å (in the range of typical physiological conditions in biological ion channels) has been applied parallel to the channel axis.

5. Trajectory ensembles

The simulations for non-polarizable water and ions have been carried out for each solute type and particular nanotube radius up to a total of 400 ns. With a view to reduce time correlations and improve statistics, the measurements have been actually compiled from 32 trajectories of 12.5 ns, each started from a different random initial configuration. In the case of polarizable models, due to the significantly higher computational effort, the data collection time has been half the above (200 ns from 16 trajectories).

Each particular initial configuration is prepared at first as a cubic arrangement of water molecules, disposed uniformly but oriented randomly on a regular rectangular grid, with the ions placed randomly in the interstices. The cube is then split by a median plane, giving rise to the two reservoirs, and the nanotube is inserted in between. From this particular arrangement, with densely filled reservoirs and completely empty channel, one needs simply to conduct a smooth NVT equilibration to obtain the “final” initial configuration, by allowing the solution to relax freely into the channel.

The main advantage of this protocol is the accurate control of the density through the volume, with the pressure fluctuating statistically about its equilibrium value. Additional PVT equilibration runs at fixed pressure, which may possibly distort the simulation cell and the CNT itself, become thus unnecessary. In addition, the initial flow of the solution into the pore introduces a high degree of microscopic hazard in a natural way.

6. Solution structuring

A snapshot from a typical run for the \((10,10)\) nanotube is depicted in Fig. 1, showing the pronounced water structuring and the appreciable distance of the solution constituents to the hydrophobic nanotube walls.

Qualitatively, the intermediate nanotube \((10,10)\) marks the transition from a flow with scarce ion passages to a “gating” regime, in which cascades of ions of one species, accompanied by rare passages of the other species, are interrupted by cascades in which the ions reverse the roles. In the \((12,12)\) nanopore the anions and cations cross the channel in opposite directions at comparable rates and several ions of both species may be accommodated.
Fig. 1. Snapshot from a typical simulation for the CNT (10, 10). The size of the simulation cell is 29.78 Å × 29.47 Å × 91.70 Å.

Fig. 2. Normalized average radial density profiles for water and ions for the CNTs (8,8), (10,10), and (12,12). The ion profiles are normalized to the maximum density of both ion species. The dashed drop-line in the upper panel shows the position of the carbon wall.

by the pore simultaneously. Quite frequently, cations and anions pair and cover jointly portions of the pore.

Regardless of the pore radius, water forms well-defined boundary layers both inside the channel and near the membrane surfaces. The cylindrical water layers formed inside the channel (Fig. 2) enclose alternating regions of peaking solute ion density, which correspond to most probable paths taken by the transiting ions.

While in the (8,8) nanotube the Na\(^+\) ions occupy the central region, forcing both anion species to pass on average in the vicinity of the water boundary layer, with increasing channel radius, the tendency of the Cl\(^-\) ions to switch positions with the Na\(^+\) ions, passing closer to the axis, becomes apparent. As such, a well defined ordering of the maxima is established for wider channels and replicated towards the interior.

Polarizable models (with dash–dot lines) do not appear to affect the structuring of water and only marginally the positions of the ion peaks. Instead, polarizability influences significantly the relative ion abundances, the I\(^-\) anions showing substantially increased densities in the proximity of the water boundary layers.

The axial profiles of the potential of mean force (Fig. 3), derived from the transversely averaged position probabilities as PMF\(z = -kT \ln\left\langle P(r, z)\right\rangle_z\), evidence the preference of the anions to reside on average within the reservoirs. The inclusion of polarizable models produces hardly distinguishable deviations. The ions can be seen to face an appreciable energy barrier to enter the tube, which significantly increases with decreasing pore radius. The energy barrier increase is, however, less pronounced for the water molecules.

Fig. 3. Axial PMF profiles for the NaCl and NaI solutions in the CNTs (8,8) and (10,10). Black represents water, blue Na\(^+\), green Cl\(^-\), and pink I\(^-\). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Average ion coordinations for the NaCl (continuous lines) and NaI (short-dash lines) solutions without polarizability as functions of the CNT radius.

For the wider CNTs, the ion profiles are more or less flat and practically overlapping inside the pore, indicating an almost frictionless motion. Hence, the conductance of water through these CNTs is largely independent of their length and our simulations for half length CNTs prove this point unambiguously. By contrast, the profiles for the cations and anions in the (8,8) CNT have non-vanishing slopes, making the ion passages more difficult.

Average coordination numbers of the ions within the NaCl and NaI solutions have been calculated as integrals over the major peak of the Na\(^+\)–O, Cl\(^-\)–H and I\(^-\)–H radial distribution functions (Fig. 4). The cation and anions show fairly similar behavior, with significantly smaller coordinations for the (8,8) CNT and a saturation tendency to the bulk values for the wider pores. However, due to its particular radial positioning (Fig. 2), as compared to I\(^-\), the Cl\(^-\) anion shows lower hydration in the narrow CNTs and higher hydration in the wider CNTs.

The axial electrostatic potential profiles (Fig. 5), determined jointly by the solution components and the external electrostatic field, show the main drop across the channel, reflecting the for-
Fig. 5. Average axial electrostatic potential for the CNTs (8, 8), (10, 10), and (12, 12). Continuous lines correspond to the NaCl solution and dash–dot lines to the polarizable NaI solution.

Fig. 6. Average axial electrostatic potential barriers for the NaCl and NaI solutions as functions of the nanotube radius. Filled symbols and dash–dot lines correspond to polarizable models.

formation of a spatial charge at the membrane walls, which partially neutralizes the applied electric field in the reservoirs. Noteworthy is the significant influence of the nanotube radius and, by contrast, the little dependence on the anion species and on the inclusion of polarizable models. The net potential barrier the charged particles have to overcome to enter the nanotube decreases with increasing pore radius, the nanotube becoming more permissive to the ion passages, as expected. The profiles for the two non-polarizable solutes are practically identical and slightly bent within the pore, while the inclusion of polarizable models appears to straighten them.

The transversely averaged electrostatic potential drop across the channel (Fig. 6), decays almost linearly with the pore radius and is clearly insensitive to the solute type or consideration of polarizable models. While the potential difference between the two nanopore ends caused solely by the applied electric field amounts to 1.2 V, the barriers the ions have to overcome to enter the pore are significantly higher and decrease from about 7 V to about 5 V with increasing pore radius, being a clear consequence of the electrical double layers at the membrane walls.

7. Transport properties

One of the most significant transport features of the present simulations regards the pore radius dependence of the ionic current, the latter being expressed as the net total number of ions transiting the pore per nanosecond, while considering opposite reference directions for anions and cations (Fig. 7). In order to discern the contributions of the different ion species to the total ionic current, the passage rates due to the Na" ions solely have been singled out. In the case of the NaI solution, the profiles corresponding to polarizable models have been depicted, as well.

At first glance, the ion currents show a strong dependence on the pore radius. In particular, the (8, 8) CNT appears to be little permeable to ions, enabling under all conditions low currents of about 0.05 nA. This is in line with the results of Peter and Hummer [6] and Corry [7], evidencing the impermeability for chiralities lower than (7, 7). Qualitatively, the ion current profiles appear to be roughly parabolic and shifted such as to practically vanish for the (8, 8) nanopore.

A manifest though limited selectivity of the CNTs to the anion species can be identified in (Fig. 7), the total currents corresponding to NaI exceeding on average by 30% those for NaCl. This can be corroborated with the fact that the I" ions transit the CNTs preferentially via cylindrical layers of larger average radius than the Cl" ions. However, irrespective of the solute type, the partial Na" ion currents coincide within statistical errors, due to the relative invariability of their spatial profiles under different conditions.

The inclusion of polarizability can be seen to have little impact on the ionic currents, in contrast to the case of the local relative magnitudes of the spatial density profiles.

The ion passage times range, regardless of the ionic species and inclusion of polarizability, between 0.4 and 1.3 ns, showing a gradual decrease with the nanotube radius, as the trajectories become less sinuous. For the (10, 10) CNT, there is a qualitative agreement between the average passage time for Na" (≈ 1 ns) and the value reported by Peter and Hummer [6] (≈ 1.5 ns), which is probably affected by larger fluctuations due to the roughly three times shorter CNT and the more than 30 times shorter data collection time.

The very delicate evaluation of the diffusion coefficients within the pore was accomplished by the Green–Kubo formula, which implies the time integration of the velocity autocorrelation func-
tion [9]. In order to improve the statistics, besides ensemble-averaging, we have also implemented multiple interlaced measurement threads with dynamically allocated velocity sampling intervals, controlled by monitoring the velocity decorrelation for each separate solution component.

The diffusion coefficient for the water molecules and the ions inside the CNT (Table 1) can be seen to increase with the pore radius, but also from Na$^+$ to I$^-$, while the corresponding bulk mobilities are significantly larger ($> 0.4 \text{Å}^2/\text{ps}$). The reduced mobilities inside the pores reflect both the constrained flow along the coaxial layers and the fact that the ions travel partially surrounded by their solvation shells. The latter finding is supported also by the water flux accompanying each exiting ion.

8. Conclusions

A distinct selectivity of the CNTs with respect to the anion species was evidenced, which can be explained by the particular radial structuring of the solution inside the pores, with the more mobile I$^-$ ions transiting the CNTs preferentially via cylindrical layers of larger average radius than the Cl$^-$ ions. Polarizable models for water and ions appear to have little relevance for the ionic currents, despite the enhancement of the spatial structuring of the solution.

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References