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Coarse-grained molecular dynamics simulation of water diffusion in the presence of carbon nanotubes

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ABSTRACT

Computational modeling of the translational diffusion of water molecules in anisotropic environments entails vital relevance to understand correctly the information contained in the magnetic resonance images weighted in diffusion (DWI) and of the diffusion tensor images (DTI). In the present work we investigated the validity, strengths and weaknesses of a coarse-grained (CG) model based on the MARTINI force field to simulate water diffusion in a medium containing carbon nanotubes (CNTs) as models of anisotropic water diffusion behavior. We show that water diffusion outside the nanotubes follows Fickís law, while water diffusion inside the nanotubes is not described by a Fickís behavior. We report on the influence on water diffusion of various parameters such as length and concentration of CNTs, comparing the CG results with those obtained from the more accurate classic force field calculation, like the all-atom approach. Calculated water diffusion coefficients decreased in the presence of nanotubes in a concentration dependent manner. We also observed smaller water diffusion coefficients for longer CNTs. Using the CG methodology we were able to demonstrate anisotropic diffusion of water inside the nanotube scaffold, but we could not prove anisotropy in the surrounding medium, suggesting that grouping several water molecules in a single diffusing unit may affect the diffusional anisotropy calculated. The methodologies investigated in this work represent a first step towards the study of more complex models, including anisotropic cohorts of CNTs or even neuronal axons, with reasonable savings in computation time.

1. Introduction

Computational modeling of the translational diffusion of water molecules in anisotropic environments entails vital relevance to understand correctly the information contained in the magnetic resonance images weighted in diffusion (DWI) and of the diffusion tensor images (DTI). The effectiveness of DTI may be improved by the design of new Contrast Agents increasing the quality, resolution and specificity of the magnetic resonance images We have previously shown that paramagnetic carbon nanotubes (CNTs) are able to perturb the diffusion of surrounding water molecules in an anisotropic manner, with larger effects in the longitudinal than in the transversal directions, constituting at present the first contrast agent for DTI [1]. In the present work we investigated the validity, strengths and weaknesses of a coarse-grained (CG) model based on the MARTINI force field [2,3] to simulate water diffusion in a medium containing CNTs as models of anisotropic water diffusion behavior. The CG approach was chosen as it allows handling time and length scales of systems beyond what is feasible with traditional all-atom models. Thus, we report on the influence on water diffusion of various parameters such as length and concentration of CNTs, comparing the CG results with those obtained from the more accurate classic force field calculation, like the all-atom approach. Although there is a growing number of publications on the use of CG models applied to the study of the interaction between biomolecules and CNTs [4–11], this is the first work, to our knowledge, that treats diffusion of water molecules inside and outside CNTs in a systematic manner using CG molecular dynamics (MD) simulations. The results obtained are compared to the results obtained from classical force field simulations.

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2. Theoretical methods and model systems

The calculations were performed using the Mesocite (CG approach) and Forcite (all-atom approach) modules as implemented in the Materials Studio software [12]. The diffusion behavior of water inside and outside CNTs of different lengths and concentrations was investigated by MD simulations in the NVT ensemble at 310K using a time step of 1 and 20 fs for the all-atom and CG approaches respectively. In both cases, the temperature was regulated using a Nosé–Hoover thermostat [13]. Nevertheless, the use of other thermostats, like the DPD thermostat is also possible [14]. This thermostat may represent an avenue for future improvements. In the CG calculations, the trajectories of the systems were recorded from runs of 30 ns after equilibration periods of 500 ps for all simulations. Due to the long computational times inherent in all-atom calculations, these kinds of simulations were run for only 1 ns. In both types of simulation, the diffusion coefficient of water molecules was derived from the slope of the mean squared displacement (MSD) versus time plots assuming Fickian diffusion (see Eq. (1)) [15,16].

$$\mathrm{MSD} = \sum_{i=1}^{N} < (\mathrm{ri(t)} - \mathrm{ri(0)})^2 >= 6.\mathrm{D.t} \qquad (1)$$

In the CG simulations, the CNT-water interaction was described by the MARTINI force field [2,3] and its extension to CNTs [4]. In the original MARTINI force field, approximately four heavy atoms comprise one particle. Thus, one bead of water represents four water molecules. CNTs were modelled using an approximate 3:1 mapping of the carbon atoms as in reference [4]. It is worth noting that although the variables of the CG system keep their physical meaning, this does not hold for the time scale. Thus, the dynamics in mesoscale simulations is artificially accelerated due to the coarse-graining procedure [17] and to obtain more realistic values of the diffusion coefficient, the time axis should be scaled by a factor of 3–6 [18]. As we are mainly interested in relative values and anisotropic behavior, this scaling factor was not applied to the diffusion coefficients calculated here. In addition, this dynamic acceleration results in a lowering of the freezing temperature. In contrast, in systems containing nucleation sites, confined geometries (CNTs surfaces) and periodic conditions, the opposite holds true also, with freezing temperatures higher than real freezing temperatures. Thus, GC models include two opposite and competing factors affecting freezing temperatures. To overcome the effects of higher freezing temperatures, we used antifreeze particles [18].

The CVFF force field [19] and the flexible SCP force field [20] were used to describe CNT and water respectively in all-atom calculations.

The systems used in the CG calculations consisted of up to four coarse-grained (10, 0) zigzag carbon nanotube (diameter = 15 Å and ranging from 50 to 125 Å in length) inside a periodic cell of varying size (for more details, see Table 1 and Fig. 1) and surrounded by water and 10% AF beads (lower AF percentages led to water immobilization inside CNTs). The distance between CNTs inside the same cell was kept constant at 3.347 Å, the interlayer distance in graphite. The total density of the systems (water+AF particles + CNTs) was fixed at a value of 1 g/cc. In the case of all-atom calculations, a (10, 0) CNT with a length of 50 Å was placed inside a 40 × 40 × 77 Å periodic cell. The distance between CNTs of contiguous cells was kept at 25 Å (see Fig. 1d).

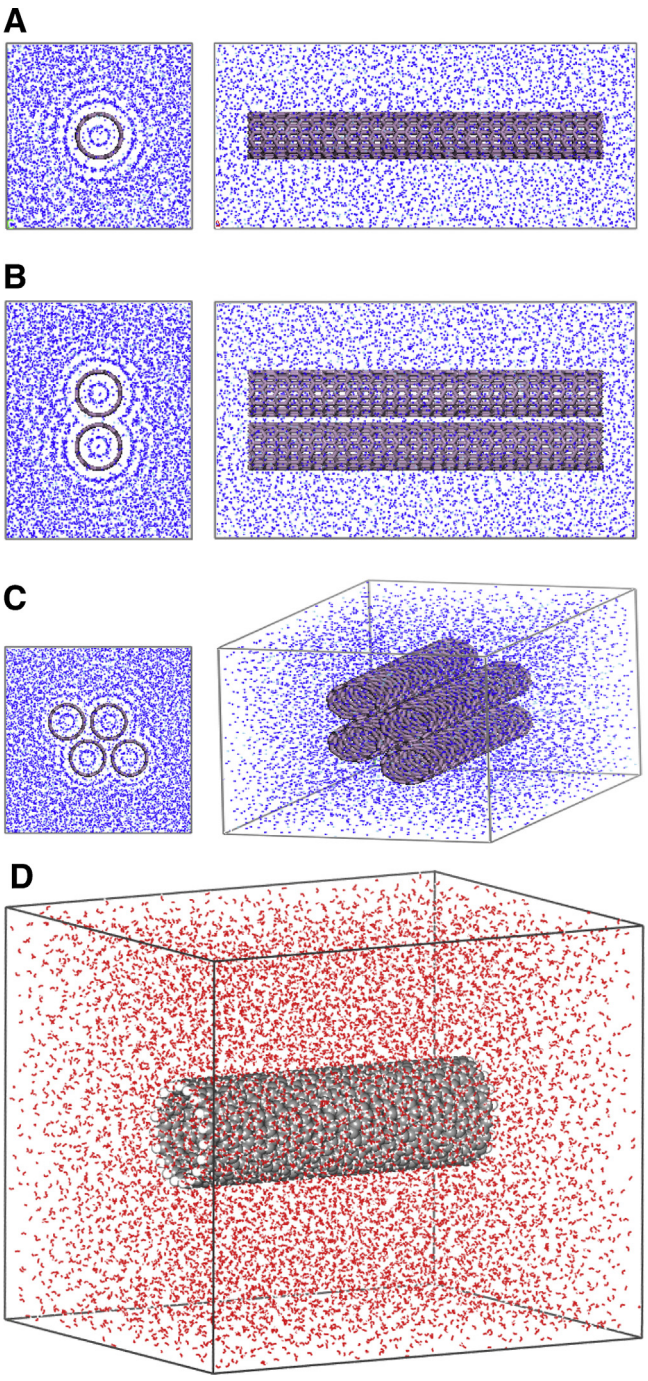

Fig. 1. Models used for CG (A, B, C) and all-atoms simulations (D). In GG models, grey and blue beads represent CNTs and water molecules respectively: A) 1CNT, B) 2CNTs, C) 4CNTs, D) all-atoms model(For interpretation of the reference to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussion

3.1. Translational diffusion of total water (inside and outside CNTs)

Implementing a robust coarse-grained method to simulate anisotropic water diffusion in complex molecular systems, requires its validation, comparing the results obtained from this new methodology with the results of earlier, well proven calculations, like the all-atom calculations.