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Structure and dynamics in methanol and its lithium ion solution confined by carbon nanotubes

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ABSTRACT

Molecular dynamics (MD) simulations have been carried out in the NVT ensemble to explore the particle dynamics and microscopic structure of the liquid methanol (MeOH) and infinitively diluted solution of Li^+ in MeOH confined in carbon nanotubes (CNTs) with diameters of 1.087 nm, 2.035 nm and 2.984 nm. The simulated local order of confined fluid defined in terms of radial distribution function (RDF) and running coordination numbers (r.c.n.) does not differ from bulk. Although the long-range structure defined in terms of cylindrical distribution function and distribution of cosines appears to be helix-like in the parietal area of the CNT. Translational self-diffusion coefficients inside the CNTs are about two times lower than those of bulk and at the same time depend slightly on the CNT diameter. It was clearly observed that diffusion coefficients of MeOH and Li^+ strongly depend on the distance from the CNT inner wall.

1. Introduction

The fuel cells [1–4], which directly transform the chemical reaction energy between hydrogen and oxygen into electric energy, are seen as the energy source of the next-generation. With their environmentally friendly and high efficiency characteristics, the cells are being researched and developed as the future energy for the automobile and as energy generation for the home. The fuel cell has about 10-times the energy capacity compared with a lithium battery, and if used for personal computers, in the future, a continued usage time of several days can be expected.

Carbon nanotubes (CNT) are a completely new carbon system material and are expected become the typical raw material for nanotechnology, applied to such broad fields as hydrogen storage, composite materials and electron devices. Since the CNTs have the possibility of clearly surpassing raw materials used so far, the aspects of applying it to fuel cell electrodes is under consideration.

The most promising fuel cells are based on methanol (MeOH, CH_3OH) which is renewable and easily storable [3]. The adsorption of the fuel (MeOH) on electrode surface is a critical value for this application. The studies of adsorption and decomposition of MeOH [4] have revealed that methanol molecules adsorb on interior sites of the carbon nanotubes and this phenomena has been suggested to be used in a direct liquid fuel cell. As was recently stated [5], transport properties of MeOH are of particular interest for its application.

In view of the present large interest on the methanol behaviour inside nanopores, it will be highly informative to carry out MD simulation on liquid methanol confined by CNTs to elucidate influence of CNT internal diameter on microscopic structure and dynamic (transport) properties of this alcohol.

Further, to some extent bulk methanol is similar (strong H-bonding, close diffusion coefficient values, etc) to its nearest homologue, water. In contrast to MeOH, a number of studies of confined water have already been published [6–10]. Molecular dynamics simulation (MD) is often one of the primmest techniques to investigate confined liquids because of its unique possibilities to feel very fine patterns unavailable for any modern experimental technique. Specifically, it has been shown that in confinements water forms helix structure due to the specific modification of hydrogen network [6]. Transport properties (diffusion, conductivity, shear viscosity) of water inside the CNTs are greatly influenced by CNT diameter and are different in radial and axial directions [7]. Whereas translational self-diffusion coefficients of water decay when CNT diameter decreases, the conductivity and shear viscosity become larger [5]. Inside the CNT, filled with an aqueous moderately concentrated solution of KCl, a very low ion occupancy was observed [5]. The occupancy, however, considerably increases as an external electric field is applied and partial charges on the rim atoms of the CNT are placed. The simulation of water and methanol mixture within CNT [8] has demonstrated that liquid transport is controlled by the pore entrance effect for which hydrogen bonding plays an important role. From the fundamental point of view, it is interesting to explore similarities and differences between methanol and water placed in confinements.

Additional motivation of the present study has been provided by our recent MD simulation of solvation phenomenon in infinitely diluted solution of lithium ion in bulk methanol [11].

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Table 1
Some parameters of the modelled systems and MD simulation details

Designation of the system	System objects (molecules)	Number of MeOH molecules	Number of ions	Internal diameter of CNT, d_{CNT}, (nm)	The side lengths of the boxes, L_{box}, (nm)	Number of carbon atoms in CNT
I	MeOH	324	0	–	–	–
II	MeOH + CNT1[a]	438	0	1.087	2.270	800
III	MeOH + CNT2[a]	890	0	2.035	3.210	1500
IV	MeOH + CNT3[a]	1530	0	2.984	4.151	2200
V	MeOH + Li^+	323	1	–	–	–
VI	MeOH + CNT1 + Li^+	437	1	1.087	2.270	800
VII	MeOH + CNT2 + Li^+	889	1	2.035	3.210	1500
VIII	MeOH + CNT3 + Li^+	1529	1	2.984	4.151	2200

[a] CNT1, CNT2 and CNT3 correspond to armchair (8,8), (15,15) and (22,22) CNTs, respectively.

In this paper, we report the results of our MD simulations on the systems consisted of carbon nanotubes of different diameters immersed in the liquid methanol and infinitively diluted solution of Li^+ in methanol at ambient conditions in the NVT ensemble.

2. MD simulations details

The simulations were performed on the three systems containing armchair CNTs (8,8), (15,15) and (22,22) of different diameters (1.087, 2.035, 2.984 nm) and constant length of 6.026 nm immersed in liquid methanol of bulk density with dielectric constant (786.37 kg/m^3, 32.66, respectively [12]) at 298 K and the three same systems with infinitively diluted solution of Li^+ instead of pure MeOH. For reference, the corresponding properties of bulk solvent and solution were calculated as well. Table 1 summarises the designation, parameters, and some simulation details of the modelled systems.

Open-ended CNTs were located in the parallelepiped cells of the same length of 7.167 nm, so that the symmetry axes and the geometrical centres of both CNTs and model boxes coincided. The volumes of internal and external cavities of the CNTs were 2.183 nm^3 and 9.462 nm^3, 11.992 nm^3 and 25.620 nm^3, 29.710 nm^3 and 49.693 nm^3 for diameters of 1.087 nm, 2.035 nm, 2.984 nm, respectively.

The modelled CNTs were surrounded by a few layers of MeOH molecules (Fig. 1) being free to migrate both inside and outside the CNTs. The simulations were processed using the proprietary software package MDCNT [13] with periodic boundary conditions in all directions.

The site–site interactions between all atom pairs in the system are given by the sum of Lennard–Jones (LJ) 12–6 and Coulomb potentials,

$$U(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{z_i z_j e^2}{4\pi\varepsilon_0 r_{ij}}, \quad (1)$$

where ε_{ij} and σ_{ij} are the LJ parameters between sites i and j of distinct molecules, z_i is the partial charge on site i, and r is the site–site separation. Cross interactions were obtained from Lorentz–Berthelot combining rules, $\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}}$ and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ [14]. Shifted force potential [14] was employed for the LJ part of the potential, whereas the reaction field method [15] was used to calculate the long-range Coulombic part.

The force field model of MeOH parameterised by Haughney et al. [16], denoted as H1, and successfully used in our previous simulations [17] was used in the present MD simulations. Within the H1 model, each methanol molecule was treated as a rigid, non-polarisable object consisting of three sites corresponding to the oxygen (O), the methyl group (Me) treated as a united atom, and the hydrogen of the hydroxyl group (H). Molecular geometry of the methanol molecule was described by two bond lengths, $d_{OH} = 0.9451$ Å and $d_{CO} = 1.4246$ Å, and one angle $\angle COH = 108.53°$.

LJ parameters for Li^+ were restored from van-der-Waals parameters [18] according to the procedure described earlier [19] and already applied in our previous works [11,13,20].

The force field of the CNT was taken to be purely LJ (12, 6) form with potential parameters used earlier for carbon [21]. The geometrical parameters of ideal armchair CNTs were generated by the proprietary algorithm [13] with the length of carbon–carbon bond equal to 0.142 nm. All the potential parameters used in the present MD simulations are listed in Table 2.

The equations of motion were integrated with 1 fs time-step by using an algorithm proposed and developed recently [22]. The MD simulations on all the systems were performed in the NVT ensemble by using Berendsen thermostat [23] with the relaxation time of 0.1 ps during collection runs of the already equilibrated systems. The carbon atoms of the CNTs were held fixed during the MD simulations. Equilibration periods of 200 ps and collection runs of 5 × 500 ps were used.

3. MD simulations results and their discussion

To analyse an ability of CNT to exchange MeOH molecules between internal and external space within the MD simulation cell we have calculated the distribution of a number of molecules inside the CNTs for the systems II–IV during the whole production runs. The corresponding histograms are shown in Fig. 2. As the results of

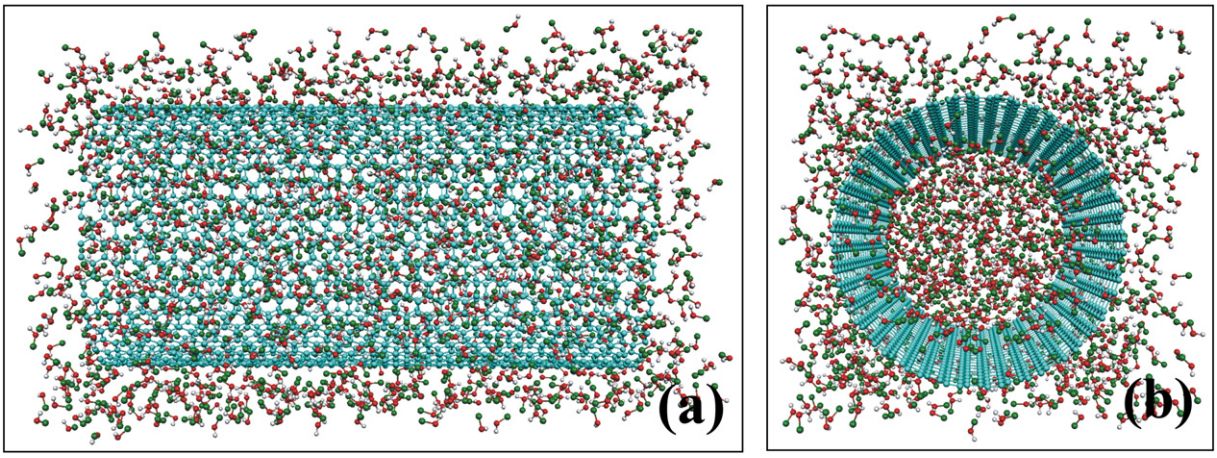

Fig. 1. Sketch of the MD cell (system IV, see Table 1) along with CNT3 (22,22) and MeOH molecules: (a) side view, (b) cross-sectional view.