The Influence of the Rigidity of a Carbon Nanotube on the Structure and Dynamics of Confined Methanol

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In this paper, we compare the behavior of liquid methanol confined by an open-ended single-walled nanotube (SWCNT) under four different simulation conditions by using the molecular dynamics (MD) simulations technique. The first model is a rigid and fixed SWCNT with all its carbon atoms fixed at their initial positions; the second is a flexible and fixed SWCNT with its centre-of-mass fixed at the center of the MD box and with the carbon–carbon bond potential applied; the third is a rigid and floating SWCNT, and the fourth is the most realistic flexible and floating SWCNT model — without fixed atoms and with bond potential. The microscopic structure and transport properties of bulk methanol confined by the four different SWCNTs were analyzed. No changes in the radial distribution functions of the hydrogen bond between MeOH molecules are found, and the self-diffusion constant and microscopic dipole relaxation time are essentially unaffected by the confinements. In spite of the flexible/rigid or fixed/floating (15, 15) SWCNT model used, the structure and transport properties of confined MeOH are found to be very close in all the simulated cases. We conclude that using the approximation of rigid or/and fixed SWCNT does not lead to any systematic errors in properties of the confined liquid. The results show that simulations using rigid carbon nanotubes provide a reliable description of molecular diffusion and other solvent properties in a variety of applications, such as electro-chemical devices, membranes and sensors that rely on these properties.

KEYWORDS: confined fluid, carbon nanotube, molecular dynamics simulation, methanol, intramolecular potentials, diffusion coefficient, hydrogen bond

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1. Introduction

Confined liquids are of exceptional interest because of their unusual properties1,3–5 and high importance for industrial applications.6–11 Molecular dynamics simulations of confined liquids have already become a common practice,1,3,12–14 as their experimental investigation is a difficult problem. Open-ended single-walled carbon nanotubes (SWCNT) with an ideal geometry (zigzag or armchair) provide an excellent model to study the properties of the confined liquids at the microscopic level.

Our present study was inspired by a number of questions arising from earlier reported molecular dynamics (MD) simulations of confined non-aqueous liquids,15–17 These investigations involved SWCNTs with fixed atomic coordinates and caused concern about how rigidity and fixation of the carbon nanotube can influence the properties of the molecules inside the confinements.

The above mentioned problem, namely the effect of rigidity/flexibility was considered in a few recent papers15,16–20 devoted to the MD simulations of gases and water confined by SWCNTs. However, different results were obtained for confined gases and liquids. Chen et al.16 investigated the influence of nanotube flexibility on the transport diffusion of methane (CH4) in (15, 0) and (20, 0) tubes. According to their simulations, the diffusion of CH4 is hugely reduced by SWCNT flexibility at pressure values close to zero but at pressures around 1 bar the corresponding values for rigid and flexible SWCNTs differ on average by less than a factor of two. Jakobtorweihen, et al.12 confirmed the above results also for CH4 at low loadings and showed how the influence of flexible walls can be taken into account by means of a Lowe–Andersen thermostat.13,14

Other authors dealing with transport diffusion of argon19 and with water structure20 found almost no noticeable influence both on molecular structure and transport. Again, neglect of the velocities of the SWCNT sites during MD simulation can be a substantial approximation, possibly distorting dynamical constants of the molecules absorbed inside the SWCNT. We analyze this effect as well.

Hence, in the present paper, we make a comparison among four differing models of the (15,15) SWCNT, representing the most common simplifications applied in practical simulations: rigidity instead of flexibility and centre-of-mass fixation instead of free nanotube motion across the MD cell. Liquid methanol (MeOH) at 298 K was chosen as a test media because of its specific structure in the bulk phase and the novel interest to “SWCNT–MeOH” systems in connection with green chemistry direct methanol fuel cells.21

Below, we compare the structure and transport properties of MeOH confined inside the SWCNT: rigid fixed [the center of (15, 15) SWCNT coincides with a center of the box], fixed flexible, rigid floating (initially placed at the center of the box and then allowed to float as an ordinary particle) and, eventually, flexible floating (the most realistic), denoted as systems I, II, III, and IV, respectively.

2. MD Simulations Details

The four “SWCNT–MeOH” systems (Table I) consisted of the non-capped (15, 15) armchair SWCNT with diameter,
Table I. The potential parameters for the interacting sites of the MeOH and SWCNT.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Site</th>
<th>σ_i (nm)</th>
<th>ε_i (kJ mol(^{-1}))</th>
<th>z_i (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>H</td>
<td>0.0</td>
<td>0.0</td>
<td>+0.431</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>0.3083</td>
<td>0.731169</td>
<td>−0.728</td>
</tr>
<tr>
<td></td>
<td>Me</td>
<td>0.3861</td>
<td>0.757859</td>
<td>+0.297</td>
</tr>
<tr>
<td>SWCNT</td>
<td>C</td>
<td>0.34</td>
<td>0.41</td>
<td>0</td>
</tr>
</tbody>
</table>

### Results and Discussion

The comparison of the fixed and floating versions of the “SWCNT–MeOH” systems (Fig. 1) indicates that the SWCNT can undergo substantial translational and rotational motions on a fairly short time-scale. The left and right panels in Fig. 1 are separated by 2.7 ns. Within this time interval the tube has rotated and moved. The tube mass is 29,520 a.m.u., which is about 923 times larger than the mass of a single methanol molecule. One could expect that such a heavy object would not move much within a nanosecond; however, this is not so. An estimated diffusion coefficient for the SWCNT center of mass is about \(4 \times 10^{-10} \text{ m}^2/\text{s}\), which is only 6 times smaller than that of bulk methanol. A floating CNT tends to orient diagonally in the simulation cell. These results show that a priori one may expect a notable influence of the SWCNT motion on the properties of the confined solvent.

The short-range structure of liquid methanol confined within the different (15,15) SWCNT models has been characterised by a set of radial distribution functions (RDFs), \(g_{\alpha\beta}(r)\), as well as by the running co-ordination numbers (r.c.n.) defined as

\[
    n_{\alpha\beta}(r) = 4\pi \rho_{\beta} \int_{0}^{r} g_{\alpha\beta}(r') r'^2 \, dr',
\]

where \(\rho_{\beta}\) is the number density of species \(\beta\). As an example, the intermolecular O–H RDFs, \(g_{0H}(r)\), and corresponding r.c.n.'s, are displayed in Fig. 2, and the positions/heights of the first maxima and minima in the \(g_{0H}(r)\) are listed in Table II.

The sharp first maximum in the O–H RDF is located at 0.183–185 nm. It is followed by a deep minimum at 0.257–263 nm and a well pronounced plateau in \(n_{0H}(r)\) ≈ 1. The RDF clearly shows formation of two hydrogen bonds by each MeOH molecule in the liquid inside the (15,15) SWCNT as well as in bulk. Table II and Fig. 2 indicate that all five SWCNT models agree with each other. A minor difference in the position and height (Table II) of the RDF maxima for carbons in the flexible SWCNT (systems II and IV) to manage the existing constraints. The interatomic potentials for carbons in the flexible SWCNT (systems II and IV) were taken for sp\(^2\) carbon centres from (25) developed by fitting experimental lattice parameters, elastic constants and phonon frequencies for graphite: Morse bond stretches (\(R_0 = 1.4114\), \(k_0 = 720\), \(D_0 = 133.0\)), cosine angle bends (\(\theta_i = 120\), \(k_\theta = 196.13\), \(k_\sigma = −72.41\), \(k_\tau = 68\)) and a twofold torsion (\(V_\tau = 21.28\)), where all distances are in angstroms, all angles in degrees, all energies in kcal mol\(^{-1}\), and all force constants in kcal mol\(^{-1}\) Å, angstroms and radian units. The density and dielectric constant of MeOH was set equal to the experimental values at 298 K: 786.37 kg/m\(^3\) and 32.66, respectively.

The simulations were performed using the proprietary package MDCNT(27) and GROMACS(28) MD engine. For each system, the equilibration process during 200 ps was followed by the five consecutive collection runs of 500 ps. To eliminate the boundary effect, only the molecules at the current moment located more than 1.0 nm from the SWCNT edge were taken into account when calculating the properties of the MeOH confined inside.

\[d_{\text{SWCNT}} = 2.035 \text{ nm}, \text{ and length, } L_{\text{SWCNT}} = 9.968 \text{ nm}.\]  

The SWCNT was filled with liquid methanol and simulated at 298 K in the NVT ensemble with Berendsen temperature coupling every 0.1 ps and a timestep of 0.001 ps. In each system, the (15,15) SWCNT was placed in a periodic MD cell with box side lengths equal to 4.63791, 4.63791, and 13.75626 nm. The centered SWCNT was additionally surrounded by several layers of MeOH molecules in all directions (Fig. 1) to reproduce a correct interacting potential between MeOH and the (15,15) SWCNT. The intermolecular interactions were represented as a sum of Coulomb and Lennard-Jones (LJ) (12,6) potentials. The techniques of reaction field and shifted force were applied to Coulomb and LJ (12,6) interactions, respectively. The force field of the carbon nanotube was adopted to be purely LJ (12,6) with \(\sigma = 0.34 \text{ nm}\) and \(\varepsilon = 0.41 \text{ kJ/mol}\) parameterized for a graphene sheet. The potential parameters for the interacting sites of the MeOH (force field model H\(^{22}\)) successfully used in our previous simulations(16,23) and carbon atoms of the (15,15) SWCNT\(^{24}\) are listed in Table I. Mixed LJ (12,6) parameters were calculated according to the Lorentz–Berthelot rule. SHAKE algorithm was applied to manage the existing constraints.
This finding is in agreement with the results of Liu et al., who found the same layered distribution inside carbon nanotubes for water by simulating rigid and non-excluded volume effects.

The parts of MeOH molecules that are located near the inner SWCNT wall has no observable impact of the fixation of the SWCNT reinforces solvent–solvent and solvent–tube interaction. This is not observed in our simulations, since the space confinement induced by the SWCNT wall. One may have expected a variation in the solvent constant does not depend on the distance from the SWCNT (system V) methanol molecules from MD simulations.

The dynamics of the MeOH molecules were examined in terms of the normalized velocity autocorrelation functions (VACF) of the translational motion of the MeOH molecules

\[ C_{vv}(t) = \frac{\langle v(0)v(t)\rangle}{\langle v(0)v(0)\rangle}. \]  

The corresponding spectral densities of the hindered translational motion of the MeOH molecules were calculated by the cosine Fourier transformation,

\[ S_{vv}(\omega) = \int_0^\infty C_{vv}(t) \cos(\omega t) \, dt. \]  

The time evolution of \( C_{vv}(t) \) and \( S_{vv}(\omega) \) are shown in Fig. 4. The self-diffusion coefficients of the centre-of-mass of the MeOH molecules were calculated according to the Green-Kubo relation, by integrating the velocity autocorrelation function,

\[ D = \lim_{t \to \infty} \frac{1}{3} \int_0^\infty \langle v(0)v(t)\rangle \, dt. \]  

The resulting \( D_{\text{MeOH}} \) values for all the simulated systems are summarised in Table II. Table III shows that the diffusion constant does not depend on the distance from the SWCNT wall. One may have expected a variation in the solvent mobility near the tube wall due to the difference in the solvent–solvent and solvent–tube interaction. This is not observed in our simulations, since the space confinement induced by the SWCNT reinforces solvent–solvent interactions. A well-defined hydrogen-bonding molecular network, confirmed by the cylindrical distribution function, \( ^{15-17} \) controls the movement of the confined methanol system as a whole.
The $C_{\text{avr}}(t)$ functions of the confined MeOH (Fig. 4) show some changes in comparison with the bulk phase. The minima in the linear VACF for the confined liquid are deeper and more pronounced than for bulk. However, the VACF of the confined liquid depends neither on the (15,15) SWCNT flexibility/rigidity nor on its fixation/flotation. One can also see that in comparison with bulk MeOH, an insignificant blue-shift is observed in $S_{\text{avr}}(\omega)$ upon confinement. The blue-shift indicates the increased dynamical correlation among MeOH molecules for all SWCNT force fields used in the present study. The diffusion coefficients of the confined MeOH molecules are about twice lower compared to bulk,
[16] 1.2–1.3 vs. $2.2 \times 10^{-9}$ m$^2$/s$^{-1}$. The deviations in the diffusion coefficients obtained for the different SWCNT simulation conditions are within the range of the statistical errors (Table II).

To further examine the re-orientational dynamics of the MeOH molecules inside the (15,15) SWCNT, we evaluated the re-orientational ACFs of the unit vector $\mathbf{u}$ along the molecular dipole $\mu$.

\begin{equation}
C_{\mu\mu}(t) = \frac{\langle \mathbf{u}(0) \cdot \mathbf{u}(t) \rangle}{\langle \mathbf{u}(0) \cdot \mathbf{u}(0) \rangle}. \tag{5}
\end{equation}

$C_{\mu\mu}(t)$ as functions of time are displayed in Fig. 5 for the MeOH molecules in the simulated systems. Clearly at the long time, these correlation functions can be reasonably described by exponential decay. The corresponding re-orientational relaxation times of the methanol dipole, $\tau_{\mu}$, calculated from the slopes of $\ln C_{\mu\mu}(t)$ using the least-squares-fit at long times ($4 \leq t \leq 10$ ps) are summarized in Table II. The re-orientational relaxation times are twice larger for methanol inside the (15,15) SWCNT systems than bulk, compare 22–24 ps with 12 ps. The re-orientational relaxation times obtained with the different SWCNT models for the confined solvent agree with each other (Table II).

### 4. Conclusions

The molecular dynamics simulations of liquid methanol confined by differing (15,15) SWCNT models in the NVT ensemble at 298 K were performed in order to determine whether the rigidity and fixation of the SWCNT can affect the properties of the confined fluid. For all systems, neither structural properties nor dynamics of the MeOH were found to differ more than one standard deviation. The diffusion constant of MeOH, $D_{\text{MeOH}}$, inside the (15,15) SWCNT is two times lower than in the bulk and appeared very close in spite of the differences between the (15,15) SWCNT simulation conditions used.

The lack of dependence of the solvent properties on the SWCNT flexibility and mobility can be rationalized by the weak solvent–SWCNT interactions, compared to the solvent–solvent interactions. Liquid methanol forms a strong hydrogen-bonding network both in bulk phase and inside the SWCNT. In the latter case, the network is reinforced and reorganized into helical structures near SWCNT walls due to spatial confinement. The hydrogen bonding network is sufficiently flexible and dynamic in order to respond to small changes in the SWCNT curvature. The low energy acoustic modes, that are active in SWCNTs at room temperature, are characterized by long vibrational periods and small displacement of individual atoms. Methanol molecules are able to respond to these motions of the SWCNT walls quickly and easily. Thus, the diffusion coefficients are not greatly influenced by the motions of the SWCNT at room temperature.
Hence, for ordinary MD studies the aberrations caused by ignoring SWCNT inner degrees of freedom and eliminating its centre-of-mass motion cannot be a source of any systematic errors. The conclusion justifies the numerous reported studies of confined liquids performed using MD simulations in immobile and rigid SWCNTs, and aimed at elucidating liquid properties in such applications as carbon-based membranes, sensors, direct methanol fuel cells, batteries, supercapacitors, etc.6–15,30,31)

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