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Interfacial structure of water/methanol mixture in contact with graphene surface using molecular dynamics simulation

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Abstract. The interaction of an interfacial water/methanol binary mixture with a graphene surface at the atomic scale was investigated by means of molecular dynamics simulation. The contact angle of a pure water droplet and three different concentrations of a water/methanol binary mixture were investigated on the charged and neutral forms of the graphene surface at room temperature. The mass density distribution functions of water, methanol and their binary mixtures were calculated, representing the microscopic structural properties. The novel effects of confinement and charged graphene layers on the interfacial structure of water/methanol system were investigated. The surface tension of mixtures was also calculated and the results were compared to the experimental data.

Keywords: molecular dynamics, wetting, contact angle, graphene, interfacial interaction, water/methanol mixture
1. Introduction

An understanding of the interfacial interactions and structures in liquid-graphene interfaces is essential to their use in electrochemical energy storage systems such as batteries. A unique electronic structure and a high surface area make graphene a good proton exchange membrane for direct methanol fuel cells (DMFCs) and other energy storage systems [1, 2]. It is suggested that a graphene-based membrane (PME) results in higher energy and density outputs [3, 4]. Currently, due to having a large surface to volume ratio, an understanding of the physical behavior of the liquid-membrane interface has important implications in the designing of PMEs in nanostructure devices. To gain more insight into the physical behavior of water/methanol binary mixtures near the graphene surface, we have studied the wetting properties of water/methanol droplets on neutral graphene surfaces as well as in confinement between two oppositely charged graphene surfaces by means of molecular dynamics (MD) simulations. Moreover, the effect of confinement between neutral and charged (positive or negative) graphene surfaces was extended to gain more information at the molecular level. The main innovation of this work stands on the consideration of electrostatic effects on the wetting properties of graphene.

The presence of a liquid droplet on a surface causes a balance between adhesive and cohesive forces, commonly represented in terms of contact angle (CA). The CA is defined by the tangent at the contact line, this being the edge of the interface between the solid and liquid phases. Although the determination of the wetting properties of graphene has been the subject of many research studies in recent years, a quantitative knowledge of its wetting properties was still missing. To address the wetting properties of graphene, one must determine the contact angle of water, methanol and their mixture droplets on a neutral graphene surface and also confined between two sheets with different charges.

The experimental complexity of these measurements is a great challenge, and therefore there is an uncertainty in the reported CA of water on graphene monolayers. Wang et al [5]
showed that the graphene sheet is a hydrophobic smooth material, whereas the graphene oxide sheet is hydrophilic. They found that water has a CA of 127.0° on graphene, 67.4° on graphene oxide and 98.3° on graphite. The wettability of multilayer graphene surfaces by CA measurements has been reported by Ashraf et al [6] and the value of 45 ± 3° for the CA of water on clean multilayer graphene was obtained. These authors carried out MD simulations with the model of Wu and Aluru [7]. Li et al [8] measured the CA of water on clean graphite and obtained the value of 64°, whereas most previous studies reported the CA value of water on graphite in the range of 84–86° [9–12]. They also noted that the samples used in the experimental studies may due to different graphite types. In fact, surface roughness [13], ambient impurities [8] and other factors may affect the CA values. In a classical MD simulation, Taherian et al [14] showed that the value of 127° for the CA of water on a graphene monolayer obtained by Wang et al [5] was not realistic and they predicted the CA of droplets that include 4000 water molecules on a monolayer of graphene to be 100.7 ± 0.3°. The same result was obtained by Shih et al [15] by means of theoretical and MD simulations.

In an experimental work, the CA of water on isolated graphene layers was reported as ∼90° [16], and a quantum molecular dynamics (QMD) simulation study calculated the value of the CA at 87° [17]. In a recent work, Rafiee et al [18] reports that the CA of water on monolayer graphene that was wetting-transparent to copper equals 86.2°, increases very gradually to 88.3° for 2–3 layers, and 90.6° for more than six graphene layers. Very recently, Li et al [19] performed the MD simulations and showed that Stone–Wales and single-vacancy graphene sheets display a higher hydrophobicity of the water droplet than that of a pristine one. They have also shown that Stone–Wales defects cause increasing water-surface tension.

In this work, 6516 water molecules were used on graphene with similar parameters as in Werder et al [20]. The calculated value of 88.3° for SPC (simple point charge) water molecules is closer to the QMD results and the experimental value of the CA of water on graphite. In another QMD simulation we have obtained the value of 93.3° ± 0.2 for the water droplet on a graphene monolayer with an SPC/E (extended simple point charge) water model. Moreover, the CA of three different concentrations of water/methanol droplets on a graphene surface was calculated. Methanol (CH3OH) is the simplest of the alcohols and is the second most abundant organic molecule in the atmosphere next to methane. It is widely used as a solvent and as an alternative fuel. Mixtures of alcohol/water often show quite different properties from their pure components and efforts have been made to study the physical and chemical properties of these solutions [21,22]. In this work, the wetting properties of water, methanol and three different water/methanol droplets near the neutral graphene surface were calculated. Moreover, we should pay our attention not only to the wetting CA on neutral graphene, but also the wetting behavior and interfacial properties of a mixture of alcohol/water confined between two graphene surfaces with different electrostatic charges.

2. Simulation method

MD simulations of the wetting and interfacial properties of water, methanol and water/methanol binary mixtures in contact with neutral graphene monolayer surfaces as
well as in confinement between variously charged graphene surfaces were investigated using the large-scale atomic/molecular massively parallel simulator (LAMMPS) package. Liquid water/methanol and solid graphene calculations were carried out in the constant volume and constant-temperature (NVT) ensemble under periodic boundary conditions. The SPC model of water molecules [23] was used to describe the water–water interactions, while the water–carbon and methanol–carbon interactions were modeled by means of a 12–6 Lennard–Jones (LJ) potential between carbon and oxygen atoms. For the water/methanol wettability of the neutral graphene surface the electrostatic interactions between liquid molecules and carbon atoms were not considered. The CA for a water droplet on an SPC/E on the graphene surface was also calculated. Methanol molecules were considered to be rigid structures with three sites, where O, H and CH$_3$ are set as the interaction sites. The geometrical and LJ energy parameters are taken from [24], and the electrostatic interactions between liquid atoms were taken into account. The LJ and electrostatic interactions between two sites $i$ and $j$ can be given by the following expressions:

\[
U_{\text{LJ}}(r_{ij}) = 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]
\]

(1)

\[
U_{\text{coulomb}}(r_{ij}) = \frac{q_izq_j}{4\pi\varepsilon_0 r_{ij}}
\]

(2)

where $r_{ij}$, $\sigma_{ij}$ and $\varepsilon_{ij}$ are the site–site separation, and the LJ diameter and the LJ well depth for sites $i$ and $j$ and $\varepsilon_0$ is the vacuum permittivity. For unlike atoms, the LJ parameters are determined using a set of combining rules, including the geometric mean for $\varepsilon$ (the Berthelot) and an arithmetic mean for $\sigma$ (the Lorentz rule):

\[
\varepsilon_{ij} = \sqrt{\varepsilon_i\varepsilon_j}
\]

(3)

\[
\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j)
\]

(4)

The carbon atoms of the graphite lattice were fixed at the crystallographic positions with a carbon–carbon distance of 0.142 nm. According to Werder et al [20] the LJ parameters $\varepsilon_i$ and $\sigma_i$ for carbon atoms in graphene are considered to be 0.0564 kcal mol$^{-1}$ and 0.3214 nm respectively, where the global LJ potential cut-off radius is 1 nm. A time step of 2 fs was used and the long-range coulomb interaction was handled using the PPPM technique. The system is equilibrated for 0.5 ns in the ensemble NVT using a Nosé–Hoover thermostat with the temperature maintained at 298 K. In all simulations, we have monitored the $z$-component of the center of mass of the droplet in addition to the temperature and total energy. The computational method for calculating the contact angle is similar to that used in [17].

3. Results and discussion

3.1. Wetting properties and contact angle

Wetting is commonly characterized by the contact angle $\theta$ which is defined as the angle of a macroscopic droplet placed on a flat solid surface, where the interface of liquid or gas may come into contact with the solid surface. To characterize the wetting properties
of graphene, the contact angle of a nanodroplet of water and methanol, as well as three different compositions of water/methanol binary mixtures with 0.123, 0.228 and 0.457 methanol mole fractions on a $15.01 \times 14.96 \text{nm}^2$ graphene sheet were calculated.

Lundgren et al [25] calculated the contact angle of water, ethanol and their mixtures on graphite surfaces using atomistic simulations. They reported that water has a wetting CA of $83^\circ$, which is close to the experimental macroscopic value; whereas upon the addition of ethanol, the contact angle decreases to $30^\circ$ and complete wetting occurs. Moreover, Surblys et al [26] reported the contact angle of water/methanol mixtures with a methanol mole fraction ranging from 0.047 to 0.23 on a three-layer fcc non-polar surface by MD simulations and obtained the value of $90^\circ$ for the CA. This leads one to expect that the calculated CA in this study for a water/methanol mixture on graphene is similar to those obtained by Surblys. In both results, an increase in alcohol mole fraction leads to an increase in the CA continuously and monotonically. They obtained CA values of $65.8^\circ$ and $58.66^\circ$ for mixtures with 0.13 and 0.2 mole fractions respectively, while this study shows CA values of $75.8^\circ$ and $58.8^\circ$ for mixtures with 0.123 and 0.228 methanol mole fractions. The difference in CA values may be due to the effect of graphene versus graphite surfaces.

The density of liquid mixtures was taken from [27,28]. Snapshots of water/methanol binary mixtures with a 0.228 methanol mole fraction during the spreading are shown in figure 1. Upon relaxing a nanodroplet-graphene surface system in 0.5 ns, the CA was calculated by using an MD trajectory of 1 ns. MD trajectories exhibit partial wetting for pure water and three different mole fractions of water/methanol binary mixtures. The complete wetting for pure methanol is shown in figure 2. To compute the CA, a $z$-axis through the center of mass of the droplet normal to the surface was defined. The system was divided into cubic meshes and the average density of the liquid in each mesh was calculated. Meshes with a mass density greater than $0.3 \text{kg m}^{-3}$ were recorded. A circle in parallel direction to the surface is fitted for a selected layer of meshes with nearly equal density. The first water mass density profile peak was set as zero height ($z = 0$). The calculated CA was $87.48^\circ \pm 0.3$ for a pure SPC/E water droplet on the graphene surface. The nearest peak in the mass density distribution function of water droplets close to the graphene surface was at $0.31 \text{nm}$. In cases where the mass density of liquids was not zero, the value of $88.3^\circ \pm 0.4$ was obtained ($z$ was set to zero at $0.25 \text{nm}$ above the surface, the
Interfacial structure of water/methanol mixture in contact with graphene surface

Figure 2. Methanol nanodroplet on graphene after 0.25 ns.

Table 1. The contact angle of pure water and water/methanol nanodroplets on a graphene surface in 298.15 K.

<table>
<thead>
<tr>
<th>Pure water</th>
<th>Pure water</th>
<th>Methanol mole fraction of water/methanol mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPC model</td>
<td>SPC/E model</td>
<td>0.123</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.228</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.457</td>
</tr>
<tr>
<td>88.3° ± 0.4</td>
<td>93.3° ± 0.2</td>
<td>75.8° ± 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>58.8° ± 0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>32.7° ± 0.4</td>
</tr>
</tbody>
</table>

nearest point of the droplet to the surface where the mass density of liquid is not zero). The value of $z$ was set to zero for three other mixtures at 0.25 nm above the graphene surface and the calculated CA is shown in table 1. For an SPC/E water droplet on the graphene layer with the same water-surface interaction parameters, a CA of 93.3 ± 0.2 was obtained. The results indicate that an increase in methanol concentration decreases the CA. For SPC water droplets the calculated CA is at 88.3° ± 0.4. It is close to the calculated value of 87° from the QMD simulation [9] and the macroscopic experimental value of 86° for graphite. The value of 93.3 ± 0.2 is obtained for the same droplet with SPC/E water molecules. The simulation procedure for calculating the wetting CA on graphene surfaces is similar to that used in [17]. Our calculation of CA values is different from the value of 100.7° ± 0.4 for 4000 SPC/E water molecules [14]. A reduced CA in our simulation work may be due to a value of parameters which is different from Taherian’s work [17] in addition to the greater number of water molecules (6516 SPC/E water molecules) performed in this work, which decreases line tension.

To analyze the structure of nanodroplets and interactions along a liquid–solid interfacial, the mass density distribution of pure water and methanol/water in z-direction normal to the substrate was calculated and shown in figure 3. The water/methanol droplets have three relatively intense maxima on their mass density distribution plots due to the water/methanol mixture forming three layers on the graphene surface. There is a two-layer structure for pure water near the graphene surface as previously presented [14,17]. Moreover, in all water/methanol systems, water peaks are slightly closer to the surface. In all the mixtures, the first peak height of methanol is higher than water.
Methanol tends to concentrate in an air–liquid interfacial more than water molecules. Likewise, methanol is intensely concentrated in the solid–liquid interface. For pure water droplets the first peak is located at 0.31 nm near to the surface, while for water/methanol binary mixtures the first maxima is located at 0.33 nm for 0.123 and 0.228 methanol mole fractions and at 0.35 nm for 0.457 methanol mole fractions. The first peak of a water molecule is located at 0.31 nm for 0.123 and at 0.33 nm for 0.228 and 0.457 methanol mole fractions. The first layer of methanol in droplets from the surface is located at 0.35 nm near to the graphene surface. Figure 4 shows the mass density distribution of liquid molecules in a layer between $z = 0.188–0.49$ nm and between $z = 0.49–0.88$ nm near to the graphene surface for 0.228 methanol mole fractions. It shows that by increasing the distance from the center of a droplet in parallel to the surface, the density of liquid decreases, but in a normal direction, the next layer has a higher mass density. In the center of the first layer, the mass density is higher than the density of the bulk mixture, and in the outer layers, the density is nearly half of the bulk mixture. The mass density between the internal density and the outer layers is close to the bulk mixture.

### 3.2. Surface tension

In an independent simulation, the surface tension of pure water, pure methanol and water/methanol mixtures at room temperature was calculated. In this part of the
Figure 4. The mass densities of the first two layers of a water/methanol mixture with a 0.228 methanol mole fraction close to the graphene surface.

Figure 5. The box of simulation of water/methanol mixtures to calculate surface tension.

Simulation a slab of liquid placed between two empty regions was used. The simulations were performed for pure water with 4270 molecules, pure methanol with 1885 molecules and three different compositions of water/methanol binary mixtures of 0.123, 0.228 and 0.457 methanol mole fractions with 2803, 3423 and 3765 molecules at constant temperature and volume in an orthorhombic simulation cell of dimensions of $L_x = L_y = 4 \text{ nm}$ and $L_z = 80 \text{ nm}$. This setup is expected to stabilize two planar vapor–liquid interfaces perpendicular to the $z$-axis of the simulation cell. For the calculation of the surface tension, the potential model of water was considered as SPC/E, which has previously shown that the SPC/E, TIP4P/Ew and TIP4P/2005 models provide better agreement with experiments [29].

Figure 5 shows the simulation box. The surface tension of the planar interface perpendicular to the $z$-axis is given by [30]

$$\gamma_v = \int_{-\infty}^{\infty} (P_N - P_T)dz$$

where $P_N$ are $P_T$ are the normal and tangential components of the pressure tensor at position $z$ respectively. The $\gamma$ from a 2 ns trajectory was calculated. Table 2 lists the

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Table 2. The calculated and experimental surface tensions (mN m\(^{-1}\)) of pure water, pure methanol and water/methanol mixtures at 298.15 K.

<table>
<thead>
<tr>
<th></th>
<th>pure water (SPC/E)</th>
<th>Pure methanol</th>
<th>methanol mole fraction of water/methanol mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>53.35 ± 1.3</td>
<td>18.72 ± 1.1</td>
<td>0.123 0.228 0.457</td>
</tr>
<tr>
<td>Experimental</td>
<td>72.01</td>
<td>22.51</td>
<td>40.75 ± 1.2 31.94 ± 1.3 25.89 ± 1.3</td>
</tr>
</tbody>
</table>

Figure 6. The calculated and experimental interfacial tensions of the water/methanol liquid–vapor interface at various methanol mole fractions.

calculated and experimental surface tensions, where the experimental values are from [31]. There is a better agreement with experimental data for water/methanol mixtures and pure methanol in contrast to pure water. Figure 6 shows the calculated and experimental interfacial tensions of the water/methanol liquid–vapor interface versus the methanol mole fraction \((x_{\text{meth}})\) at 298 K. The change in interfacial tension is greater at low methanol concentrations, i.e. at a methanol mole fraction of 0.4 the surface tension of water is reduced to about half.

Furthermore, Surblys et al [26] obtained the vapor–liquid interfacial tensions for water–methanol mixtures with 0.052 to 0.25 methanol mole fractions. According to their results, an increase in methanol molecules decreases vapor–liquid interfacial tensions which is consistent with the results of this study. However, there is a better agreement with experimental data between our calculated vapor–liquid interfacial tensions.

Figure 7 represents the mass density distribution for pure water, pure methanol and water/methanol binary mixtures. In a longer simulation a symmetric mass density profile is obtained. The mixture density profiles are quite smooth and no long-range structures are expected near the interface. However, the individual mass densities for methanol and water are less uniform across the surface in normal directions. Figure 7
Figure 7. Mass density distributions along the simulation box for water (a), methanol (b) and water/methanol mixtures (c)–(e). Red curve for methanol contribution, blue curve for water contribution and black curve for mixture. The methanol mole fraction is selected as 0.123 (c), 0.228 (d) and 0.457 (e).

shows that as water density increases, the methanol density is reduced and vice versa. This finding suggests that there may be a local structure and clustering of water and methanol consistent with prior MD simulation [32] and experimental results [33, 34]. Methanol tends to concentrate on the surface for $x_{\text{meth}} < 0.4$ in agreement with existing density profiles for water/methanol droplets. At this concentration, a significant decrease in the water/methanol surface tension is observed. For $x_{\text{meth}} = 0.457$, the distribution of methanol molecules is more homogeneously at the molecular level in bulk water/methanol mixtures. At low concentrations, methanol prefers to adsorb at the interface to favor hydrophobic interactions with the vapor, whereas at high concentrations it prefers the formation of clusters consistent with [35].

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The CA of a macroscopic liquid droplet with spherical symmetry on the ideal solid surface is well described by the Young equation [36]:

$$\cos \theta = \left( \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \right)$$

where \(\gamma_{lv}\), \(\gamma_{sv}\) and \(\gamma_{sl}\) represent the liquid–vapor, solid–vapor and solid–liquid interfacial tensions respectively. From the calculated CA and surface tension, and by means of the Young equation, we have calculated the difference between the interfacial tension of vapor-surfaces and liquid-graphene interfaces to be \(\nabla \gamma = \gamma_{sv} - \gamma_{sl}\) (table 3) for graphene in contact with pure water and water/methanol binary mixtures.

### 3.3. Water/methanol confined between two graphene sheets

The effect of charging of the solid–liquid interface has been investigated by a number of experimental and theoretical works [38–40]. It has been shown that the charging of the solid–liquid interface causes many changes in the physical behavior of liquid near a solid such as the lubrication and charge transfer enhancing performance of interfaces in batteries and other applications. The interfacial behavior of water/methanol binary mixtures in contact with neutral graphene monolayer surfaces, as well as in confinement between variously charged graphene surfaces were studied. The simulation box, which is represented in figure 8, consisted of 947 water and 797 methanol molecules enclosed between two graphene sheets. Separation of the two sheets was set at 3.2 nm. Periodic boundary conditions were applied in three directions while the first and second graphene layers were located at \(z = 0\) and \(3.2\) nm respectively in a box with \(L_z = L_x = 4.15\) and \(L_y = 6.25\).

Figure 9 represents the initial configuration of the mass density distribution of a water/methanol mixture confined between two graphene sheets. The water and methanol densities oscillate when confined between two graphene layers, indicating the occurrence of layering of water and methanol. Moreover, in order to find out how the charges affect wetting properties, the effect of confinement between neutral-charged (positive or negative) and charged–charged graphene surfaces was studied. Mass density profile averaging over 3 ns is shown in figure 10. The effect of charge on the interfacial structure of water/methanol was simulated using a confined mixture between two graphene sheets, which carried as (i) both surfaces are neutral; (ii) \(\pm 10 \mu C cm^{-2}\), in which all carbon atoms carry a \(\mp 1.547 \times 10^{-2}\) multiple of electron charge; (iii) \(\pm 20 \mu C cm^{-2}\), in which all carbon atoms carry a \(\mp 3.094 \times 10^{-2}\) multiple of electron charge; (iv) one surface is neutral and the other surface is \(\mp 20 \mu C cm^{-2}\); (v) one surface is neutral and the other surface is \(+20 \mu C cm^{-2}\).
Figure 8. Simulation box of a water/methanol mixture confined between two graphene surfaces.

Figure 9. The initial configuration of the mass density distribution of a water/methanol mixture confined between two graphene sheets. Red curve for methanol contribution, blue curve for water contribution and black curve for mixture.

According to figure 10(a), a water/methanol binary mixture confined between two neutral graphene layers has higher peaks than a droplet-surface system. There is a fourth carbon layer structure of water/methanol mixture near each neutral graphene surface with an equal first peak position for water, methanol and their binary mixture at 0.33 nm to the graphene surface. The second and third peaks for the water layer are slightly closer to the surface in contrast to the methanol peaks at positions of 0.65 and 0.70 nm of the surface. In figures 10(b) and (c), it is shown that there is a fourth and fifth carbon layer structure of liquid near the positive and negative charged graphene surface respectively. There are two highest peaks of methanol near the $-10$ (or $-20$) $\mu$C cm$^{-2}$, at 0.33 and 0.45 nm. As shown in figures 10(b)–(e), increasing the graphene charge increases the height of the first peak. The second peak is absent in the mass density profiles of both a positively charged surface and droplet/surface system. For positively and negatively charged surfaces, the
first peak of water molecules is located at 0.31 nm to the surface. Water molecules tend to concentrate near the positively charged graphene layer. For mixtures near the negatively charged surface, there is a small maxima before the first peak of mass density distribution for positive graphene surfaces.

An obvious increase in the mass density of water molecules near positively charged surfaces is observed with increasing charge density of the graphene surface from 0 to +20, in contrast with the negatively charged layer. The tendency of methanol molecules to diffuse near the positively charged surface decreases as the charge of the graphene sheet increases. Methanol molecules make a two-layer structure very close to each other near the $-10$ charged surface. By increasing the charge density on the negative layer from $-10$ to $-20$ the mass density of the second layer decreases where the mass density of water molecules increases.

Figure 10. The mass density distribution of a water/methanol mixture between two graphene surfaces: (a) neutral surfaces; (b) $\pm 10 \ \mu C \ cm^{-2}$ charged surfaces; (c) $\pm 20 \ \mu C \ cm^{-2}$ charged surfaces; (d) one surface is neutral and the other surface is $-20 \ \mu C \ cm^{-2}$; (e) one surface is neutral and the other surface is $+20 \ \mu C \ cm^{-2}$.
4. Conclusion

The wetting CA of water and three binary mixtures of water/methanol droplets on a graphene surface was calculated and compared with the experimental data. The CA of $88.3^\circ \pm 0.4$ and $93.3^\circ \pm 0.2$ for SPC and SPC/E water droplets on the graphene surface was calculated. An increase in methanol concentration tends to decrease the CA of water/methanol droplets on a graphene surface. A complete wetting for pure methanol on the graphene surface was observed.

Furthermore, the neutral graphene surface, as well as in confinement between two oppositely charged graphene surfaces and electrostatic effects on wetting properties of graphene by means of molecular dynamics (MD) simulations. For this purpose the mass density distribution of a confined mixture between variously charged graphene layers including $\pm 10 \mu C \text{ cm}^{-2}$, $\pm 20 \mu C \text{ cm}^{-2}$, neutral- $+20 \mu C \text{ cm}^{-2}$ and neutral- $-20 \mu C \text{ cm}^{-2}$ was investigated and a five-layer structure near the charged surface was observed. In both neutral and charged surfaces, methanol diffused closer to the graphene surface than water molecules. Water molecules diffused more closely to the positively charged surfaces. Methanol diffused near the negative surface more than the neutrally and positively charged surfaces. In all water/methanol droplet and bulk systems in contact with the graphene layer, the first molecules near the surface are water.

The surface tension of water/methanol under different concentrations is obtained and compared with the experimental data. The simulation values are smaller than the experimental values and there is a better agreement between calculated and experimental data for pure methanol and water/methanol mixtures than pure water. The difference in interfacial tension between vapor–liquid surfaces and liquid–solid interfaces is obtained for a water/methanol mixture in contact with a graphene surface.

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