Wetting and Hydrophobicity of Nanoscale Systems with Impurities

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ABSTRACT

Molecular dynamics simulations are performed to study the influence of surface and fluid impurities on water-carbon interfaces. In order to quantify these interactions we consider both the canonical problem of wetting of a doped flat graphitic surface by a water droplet with impurities and the influence of static dipole moments perpendicular to the wall of a carbon nanotube on its wetting behavior. As model fluid impurities we consider aqueous solutions of KCl with molar concentrations up to 1.8 M. The contact angle is found to decrease weakly with increasing ionic concentration, from 90° at 0 M to 81° at 1.8 M concentration, and with increasing dipole moments across the nanotube wall from 109° to 93°. The influence of solid impurities, modeled by H and OH groups, is found to be more significant, yet it is dependent on the partial charge distribution on the carbons near the doping site.

1 INTRODUCTION

Carbon nanotubes are envisioned as key components for the development of nanoscale devices, such as sensors and actuators. The method of choice to investigate their behavior and the interaction with their environment are molecular dynamics (MD) simulations. Since many of the applications of carbon nanotubes are targeting biological systems, aqueous environments are of highest interest.

MD simulations depend crucially on the underlying interaction potentials and so the calibration of these potentials is essential for obtaining quantitative results in agreement with experiments. In [1], Gogotsi et al. proposed, based on electron microscopy studies, that the interior of a multi-walled carbon nanotube (MWCNT) was hydrophilic. Our own studies, however, based on fitting carbon-water potentials to experimental observations of nano-droplets on a graphite surface [2] and ab initio and DFT calculations [3], showed that graphite surfaces — and therefore also the interior of a MWCNT — were, in fact, hydrophobic. A later study by Gogotsi et al. [4] attributed the observed hydrophilic behavior to impurities on the MWCNT interior.

Given the importance of impurities in real-world carbon graphite interactions, we wish to establish a model for which these can be effectively simulated using molecular dynamics. This model comprises three types of improvements:

In recent density functional theory (DFT) studies it was found that carbon nanotubes exhibit significant dipole moments across their surface due to their curvature [5]. We validate these results and investigate their influence on the water carbon nanotube interaction by performing MD simulations of water droplets in carbon nanotubes. Improvements to current molecular dynamics potentials for the water-carbon nanotube interaction are discussed.

Next, we consider the effect of surface impurities — H and OH groups — on the wetting behavior of water on a graphite surface. We show that the effect of adding partial charges to a graphite surface greatly depends on how the partial charges are distributed on the carbon atoms.

Finally, we consider the influence of fluid impurities on the contact angle. As model fluid impurities we consider aqueous solutions of KCl with molar concentrations up to 1.8 M. Quantum chemistry calculation are performed to derive pair potentials for the ion-graphite interactions.

2 METHODS

All simulations were performed using the parallel molecular dynamics code fasttube [2; 6; 7]. All simulations are carried out with an integration time step of 2 fs and a cutoff distance of 1.0 nm for the Lennard-Jones potentials. The water model used in this study is the rigid extended Simple Point Charge potential SPC/E [8].

The graphite surface was modeled as two staggered, rigid hexagonal carbon sheets with an inter-layer spacing of 3.4 Å. The carbon nanotube in the dipole simulations was modeled either as described in Walther et al. [6], using a Morse potential for the bonds, a harmonic angle potential and a twofold torsion potential or it was modeled rigidly.

Given a particular water model, the wetting properties of the fluid-solid interface are determined solely by the water-carbon interaction potentials as demonstrated in [7]. The present study employs the potential model of [7], which involves a 12-6 Lennard-Jones potential.
acting between the carbon and oxygen atoms of the water. The parameters of the potential are \( \sigma_{CO} = 3.19 \text{ Å} \) and \( \varepsilon_{CO} = 0.392 \text{ kJ} \text{ mol}^{-1} \).

The potassium-water interactions used in the fluid impurity simulations are described by a 12-6 Lennard-Jones interaction between the potassium and the oxygen atom of the water and by a Coulomb potential between all charges. The ionic charges for potassium and chloride are \( q_K = +1e \) and \( q_{Cl} = -1e \), respectively. The Lennard-Jones parameters are \( \sigma_{KK} = 3.26026 \text{ Å} \) and \( \varepsilon_{KK} = 0.482331 \text{ kJ mol}^{-1} \), cf. Borodin et al. [9]. The potentials governing the chloride-water interaction are taken from Smith et al. [10] with a 12-6 Lennard-Jones potential and a Coulomb interaction. The parameters for these potentials are \( \sigma_{ClO} = 3.550 \text{ Å} \), \( \varepsilon_{ClO} = 0.406415 \text{ kJ mol}^{-1} \).

The potassium-potassium interaction is described by a 12-6 Lennard-Jones and a Coulomb interaction. The parameters for the Lennard-Jones potential are obtained by inverting the Lorentz-Berthelot mixing rules with the values for \( \sigma_{KO} \) and \( \varepsilon_{KO} \) from Borodin et al. [9], and with the SPC/E oxygen-oxygen values. This results in \( \sigma_{KK} = 3.3545 \text{ Å} \) and \( \varepsilon_{KK} = 0.5782 \text{ kJ} \text{ mol}^{-1} \). The chloride-chloride interactions are obtained from Ref. [10] and consist of a 12-6 Lennard Jones interaction with \( \sigma_{ClCl} = 0.49623 \text{ Å} \) and \( \varepsilon_{ClCl} = 0.19384 \text{ kJ mol}^{-1} \), a Coulomb interaction, and a polarization term to model the dipole interaction with \( D_{ClCl} = -0.61036 \text{ kJ} \text{ mol}^{-1} \text{ Å}^4 \).

Finally, the KCl interactions were estimated by Smith et al. [10], and consist of a 12-6 Lennard-Jones potential with \( \varepsilon_{KCl} = 0.26336 \text{ kJ} \text{ mol}^{-1} \) and \( \sigma_{KCl} = 0.43663 \text{ Å} \) [10], a polarization term with \( D_{KCl} = -0.34041 \text{ kJ} \text{ mol}^{-1} \text{ Å}^4 \), and Coulomb interactions. In the fluid impurities simulations we included a quadrupole term between the ions and the carbon atoms, as described in [11].

The partial charges of the chemisorbed hydrogen and hydroxyl groups are estimated from \textit{ab initio} MP2 calculations of isobutane \( (\text{CH}_3)_2\text{CH} \) and tert-butanol using the Gaussian98 package with the 6-311G(d,p) basis set. The partial (Mulliken) charge for the chemisorbed hydrogen atom is \( +0.10 \text{e} \) and that of the oxygen and hydrogen of the OH groups are \( -0.3836 \text{e} \) and \( +0.2240 \text{e} \) respectively. Besides this Coulombic interaction, the chemisorbed hydrogens interact through a 12-6 Lennard-Jones potential with the oxygen atoms of the water molecules. The corresponding parameters of \( \varepsilon_{OH} = 0.051908 \text{ kJ} \text{ mol}^{-1} \) and \( \sigma_{OH} = 2.633 \text{ Å} \) are taken from the AMBER96 [12] force field.

From the MD simulation trajectories, the location of the equimolar dividing water surface is determined within every single horizontal layer of the binned drop.

<table>
<thead>
<tr>
<th>( \mu_C ) [Debye]</th>
<th>tube model</th>
<th>( \varepsilon_{CO} ) [kJ mol(^{-1})]</th>
<th>contact angle</th>
</tr>
</thead>
<tbody>
<tr>
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<td>flex.</td>
<td>0.3135</td>
<td>111.0(^\circ)</td>
</tr>
<tr>
<td>0.0</td>
<td>rigid</td>
<td>0.3135</td>
<td>109.0(^\circ)</td>
</tr>
<tr>
<td>0.0</td>
<td>rigid</td>
<td>0.3920</td>
<td>98.4(^\circ)</td>
</tr>
<tr>
<td>0.03273</td>
<td>rigid</td>
<td>0.3920</td>
<td>95.4(^\circ)</td>
</tr>
<tr>
<td>0.06546</td>
<td>rigid</td>
<td>0.3920</td>
<td>92.9(^\circ)</td>
</tr>
<tr>
<td>0.32732</td>
<td>rigid</td>
<td>0.3920</td>
<td>62.7(^\circ)</td>
</tr>
</tbody>
</table>

Table 1: Influence of the dipole moment per carbon atom \( \mu_C \) across the nanotube shell on the contact angle of a water droplet inside a carbon nano tube.

Second, a circular best fit through these points is extrapolated to the graphite surface where the contact angle \( \theta \) is measured.

### 3 CARBON NANOTUBE DIPOLE

The simulation setup chosen to investigate the dipole effect on the water carbon nanotube interaction is similar to the one presented by Werder et al. [2]. A (64,0) single wall carbon nanotube with a diameter of 5 nm, is used and filled with a droplet of 2112 water molecules. The system is equilibrated and the contact angle of the water droplet within the carbon nanotube is assessed in order to investigate the water carbon nanotube interaction. The initial setup was an initially flat 2.37 nm thick drop, which corresponds to 12 layers of randomly orientated water molecules. The system is equilibrated for 200 ps with a Berendsen thermostat at a temperature of 300 K. Statistics are then collected during 200 ps with samples taken every 0.04 ps.

For the carbon water interaction, two different Lennard-Jones type potentials between the carbon and the oxygen atoms are used. To ensure consistency with the simulations presented in [2], validation runs are performed with the interaction potential presented by Bojan and Steele [13], with \( \varepsilon_{CO} = 0.3135 \) and \( \sigma_{CO} = 0.319 \). Production runs are performed with the interaction potential suggested by Werder et al. [7].

The dipole arising due to the curvature of the nanotube is modeled using two charges of \( \pm 0.5 \text{e} \) each. The charges are placed in radial direction inside and outside the carbon nanotube around each carbon atom in order to reproduce the desired dipole moment, as predicted by Dumitrića et al. In order to estimate the maximal effect of the dipole in multi-walled carbon nanotubes twofold and tenfold dipole moments of the predicted ones are considered. In these cases, the charges are taken to be 1 and 5.0e respectively.

From these simulations (Table 1) we can conclude that although the dipole effect is small, it still changes the carbon nanotube interaction with its environment, causing a change in contact angle of at least 3\(^\circ\).
placed in a regular cubic lattice (20 tributary charge model, the doped carbon atom (C) are distributed in the graphite plane. In the first, disordered charge model causes significantly smaller contact an-
distribution between the carbon atoms, where the sim-
ulations (Table 2) demonstrate that the wetting behavior

droplet. The impurities studied were H and OH groups

face impurities on the contact angle of a water nano-
droplet in vacuum to study the effect of the graphite
surface (Figure 1).

The simulations consist of 2000 SPC/E water molecules
placed in a regular cubic lattice (20 × 20 × 5 molecules)
above a graphite bilayer with a separation of 3.4 Å. The
doping sites are chosen randomly such that no two
are separated by less than three bonds in the graphite
surface. In the first half of the 200 ps equilibration time,
the water is coupled to a Berendsen thermostat at a
temperature of 300 K, whereas in the second half of the
equilibration and for the sampling a constant energy
simulation is performed.

Two sets of simulations were run with eight cases of
H and OH doping each with 5%, 10%, 15% and 18%
of the surface carbons doped with two different charge
models each, resulting in 16 simulations. A control case
without doping was also run to evaluate the contact an-
gle on a pristine graphite surface.

The two charged models differ in the way charges
are distributed in the graphite plane. In the first, dis-
tributed charge model, the doped carbon atom (C_d)
has a charge of −0.2270 e and the neighboring carbons (C_n)
of 0.0395 e when doped with hydrogen and of −0.0345 e
and 0.0647 e respectively when doped with OH. In the
second, simple charge model, the C_n are charge neutral
whereas the doped carbon has a charge of −0.1084 e
when doped with hydrogen and −0.1596 e when doped
with OH.

The contact angles resulting from the different simu-
lations (Table 2) demonstrate that the wetting behavior
of a graphite surface depends principally on the charge
distribution between the carbon atoms, where the sim-
ple charge model causes significantly smaller contact an-
gles.

4 SURFACE IMPURITIES

Based on our work in [7], we study the effect of surface
impurities on the contact angle of a water nanodroplet. The impurities studied were H and OH groups
[14] bound to single carbon atoms on the graphite sur-
face (Figure 1).

The simulations consist of 2000 SPC/E water molecules
placed in a regular cubic lattice (20 × 20 × 5 molecules)
3 Å above a graphite bilayer with a separation of 3.4 Å.

The doping sites are chosen randomly such that no two
are separated by less than three bonds in the graphite
surface. In the first half of the 200 ps equilibration time,
the water is coupled to a Berendsen thermostat at a
temperature of 300 K, whereas in the second half of the
equilibration and for the sampling a constant energy
simulation is performed.

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lations (Table 2) demonstrate that the wetting behavior
of a graphite surface depends principally on the charge
distribution between the carbon atoms, where the sim-
ple charge model causes significantly smaller contact an-
gles.

5 FLUID IMPURITIES

The water molecules are initially placed on a regu-
lar lattice. For the KCl simulations two different initial
configurations for the water are considered: a 4.2 × 4.2 ×
3.0 nm ("cubic") layout and a 5.2 × 5.2 × 2.0 nm ("flat")
configuration. The ions are placed within the water lat-
tice, replacing the water molecule at that location. For
each case, the number of molecules in the water lattice
is adjusted to 2000 water molecules. The ionic concen-
tration ranges from 0.0 (reference) to 1.8 M, the latter
corresponding to 64 ions pairs, with intermediate concen-
trations represented by 4, 8, 16, 32, and 48 pairs,
respectively. One simulation was also performed with a
droplet in vacuum to study the effect of the graphite
surface (case 16).

Two validation studies were performed on the pris-
tine system (zero ionic concentration) to assess the in-
fluence on the contact angle of the initial conditions
(cases 1 and 2), and on the numerical treatment of the
Coulomb interaction (cases 1 and 3). As demonstrated
in Table 3, starting from a cubic or flat configuration
of the water has little effect on the equilibrated con-
tact angle, with a deviation less than 0.3 %. Clearly,
for pristine systems with an atomistically smooth sur-
face the advancing and receding contact angle are equal.

The effect of using the Smooth Particle Mesh Ewald
(SPME) method versus a smooth truncation (STC) is
also small with deviations less than 1.4 %, cf. Table 3,
and confirms the result obtained in [7], that the con-
tact angles from simulations using a truncation of the
Coulomb interaction at 1.0 nm are independent of the
cutoff. The total potential energy of the three system is
−44.61, −44.66, and −43.09 kJ mol⁻¹ (cases 1–3) reflect-
ing the convergence of the simulations. The 3 % lower cohe-
sive energy obtained from the simulation using trunca-
tion is consistent with the observed (1.4 %) lower contact
angle as compared with the SPME simulations.

Snapshots from these simulations (cases 4 and 15),
cf. Figure 2, confirm that the potassium ions have moved
to the graphite surface, leaving the chloride solvated in
the vicinity of the liquid-vapor interface.

The complete precipitation of potassium ions onto
the graphite surface (Figure 2b) persists at higher con-
centrations until the surface saturates. For the particu-

Table 2: Contact angles for the 16 different surface im-
purities simulations and the control simulation. The
missing contact angle for the simple charges and OH-
doping mean that the graphite surface was wet com-
pletely (no drop discernible).

<table>
<thead>
<tr>
<th>Coverage</th>
<th>Distributed</th>
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<tr>
<td>5%</td>
<td>97.09°</td>
<td>88.27°</td>
</tr>
<tr>
<td>10%</td>
<td>98.84°</td>
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</tr>
<tr>
<td>15%</td>
<td>100.96°</td>
<td>77.91°</td>
</tr>
<tr>
<td>18%</td>
<td>100.97°</td>
<td>75.15°</td>
</tr>
<tr>
<td>H</td>
<td></td>
<td></td>
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<tr>
<td>5%</td>
<td>107.20°</td>
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</tr>
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<td>10%</td>
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<tr>
<td>15%</td>
<td>99.34°</td>
<td>–</td>
</tr>
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<td>18%</td>
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<td>–</td>
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<tr>
<td>OH</td>
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</tr>
<tr>
<td>5%</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>10%</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>15%</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>18%</td>
<td></td>
<td>–</td>
</tr>
<tr>
<td>none</td>
<td>0%</td>
<td>95.14°</td>
</tr>
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</table>
Table 3: Overview of the MD simulations of droplets of aqueous solutions of KCl on graphite. $N_C$ is the number of carbon atoms, $N_{\text{KCl}}$ the number of ion pairs, and $\theta$ the contact angle. The method refers to the numerical treatment of the Coulomb interaction: Smooth Particle Mesh Ewald (SPME) or Smooth Truncation (STC).

<table>
<thead>
<tr>
<th>case</th>
<th>$N_C$</th>
<th>$N_{\text{KCl}}$</th>
<th>$\theta$(deg)</th>
<th>IC</th>
<th>method</th>
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<tr>
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</tr>
<tr>
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<td>flat</td>
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<td>85.42</td>
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<td>SPME</td>
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<td>cubic</td>
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<tr>
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<td>0</td>
<td>4</td>
<td>-</td>
<td>cubic</td>
<td>SPME</td>
</tr>
</tbody>
</table>

lar droplet size considered this appears to be at concentrations exceeding approximately 1 M. At higher concentrations, K-Cl clusters form at the liquid-vapor interface as shown in Figure 2d. The precipitated potassium attracts the chloride towards the graphite surface, and the simulations indicate that K-Cl surface crystals form at concentrations exceeding $\approx 0.5$ M. As the chloride binds to the potassium at the surface, the electrostatic attraction is reduced, leaving the remaining chloride at the liquid-vapor interface to form nano-crystals at higher concentrations.

The change in contact angle with the increasing ionic concentration is small. Moreover, at this droplet size, the accuracy of the simulations does not allow us to measure the expected initial increase in surface tension which would lead to an increase in the contact angle. However, as the ions precipitate onto the surface, the contact angle is reduced from an initial $90^\circ$ to $82^\circ$ at a concentration of 1.8 M.

6 CONCLUSIONS

The impurities and system properties studied in this work all have non-negligible qualitative effects on the wetting behaviour of carbon surfaces and should therefore be taken into account when realistic models are to be established. The quantitative effects, however, are strongly dependent on details of the model and its parametrisation. These details are the subject of ongoing research.

REFERENCES