

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 1.8M. The contact angle is found to decrease weakly with increasing ionic concentration, from 90° at 0M to 81° at 1.8M 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 1.8M. 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

$$U_{12-6}(r_{ij}) = 4\epsilon_{CO} \left[\left(\frac{\sigma_{CO}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{CO}}{r_{ij}} \right)^6 \right],$$

acting between the carbon and oxygen atoms of the water. The parameters of the potential are $\sigma_{CO} = 3.19 \text{ \AA}$ and $\epsilon_{CO} = 0.392 \text{ kJ mol}^{-1}$.

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 $\sigma_{KO} = 3.26026 \text{ \AA}$ and $\epsilon_{KO} = 0.482331 \text{ kJ mol}^{-1}$, 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 $\sigma_{ClO} = 3.550 \text{ \AA}$, $\epsilon_{ClO} = 0.406415 \text{ kJ mol}^{-1}$.

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 σ_{KO} and ϵ_{KO} from Borodin *et al.* [9], and with the SPC/E oxygen-oxygen values. This results in $\sigma_{KK} = 3.3545 \text{ \AA}$ and $\epsilon_{KK} = 0.35782 \text{ kJ mol}^{-1}$. The chloride-chloride interactions are obtained from Ref. [10] and consist of a 12-6 Lennard Jones interaction with $\sigma_{ClCl} = 0.49623 \text{ \AA}$ and $\epsilon_{ClCl} = 0.19384 \text{ kJ mol}^{-1}$, a Coulomb interaction, and a polarization term to model the dipole interaction with $D_{ClCl} = -0.61036 \text{ kJ mol}^{-1} \text{ nm}^4$. Finally, the KCl interactions were estimated by Smith *et al.* [10], and consist of a 12-6 Lennard-Jones potential with $\epsilon_{KCl} = 0.26336 \text{ kJ mol}^{-1}$ and $\sigma_{KCl} = 0.43663 \text{ \AA}$ [10], a polarization term with $D_{KCl} = -0.3404 \text{ kJ mol}^{-1} \text{ nm}^4$, 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 *ab initio* MP2 calculations of iso-butane ($(\text{CH}_3)_3\text{CH}$) 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 $0.108e$ and that of the oxygen and hydrogen of the OH groups are $-0.3836e$ and $0.2240e$ 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 $\epsilon_{OH} = 0.051098 \text{ kJ mol}^{-1}$ and $\sigma_{OH} = 2.633 \text{ \AA}$ 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.

μ_C [Debye]	tube model	ϵ_{CO} kJ mol ⁻¹	contact angle
0.0	flex.	0.3135	111.0°
0.0	rigid	0.3135	109.0°
0.0	rigid	0.3920	98.4°
0.03273	rigid	0.3920	95.4°
0.06546	rigid	0.3920	92.9°
0.32732	rigid	0.3920	62.7°

Table 1: Influence of the dipole moment per carbon atom μ_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 θ 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 $\epsilon_{CO} = 0.3135$ 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 $\pm 0.5e$ 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 e 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°.

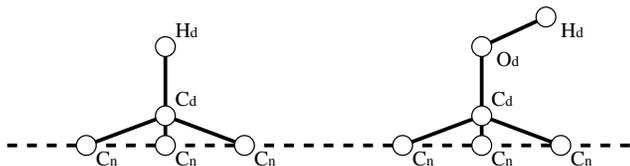


Figure 1: H and OH doping of carbon atoms. C_d is the doped carbon atom and the C_n are the three neighboring carbons.

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 surface (Figure 1).

The simulations consist of 2000 SPC/E water molecules placed in a regular cubic lattice ($20 \times 20 \times 5$ molecules) 3 \AA above a graphite bilayer with a separation of 3.4 \AA . 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 angle on a pristine graphite surface.

The two charged models differ in the way charges are distributed in the graphite plane. In the first, distributed 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 simulations (Table 2) demonstrate that the wetting behavior of a graphite surface depends principally on the charge distribution between the carbon atoms, where the simple charge model causes significantly smaller contact angles.

5 FLUID IMPURITIES

The water molecules are initially placed on a regular lattice. For the KCl simulations two different initial configurations for the water are considered: a $4.2 \times 4.2 \times 3.0 \text{ nm}$ (“cubic”) layout and a $5.2 \times 5.2 \times 2.0 \text{ nm}$ (“flat”)

	Coverage	Distributed	Simple
H	5%	97.09°	88.27°
	10%	98.84°	82.95°
	15%	100.96°	77.91°
	18%	100.97°	75.15°
OH	5%	107.20°	–
	10%	110.56°	–
	15%	99.34°	–
	18%	90.84°	–
none	0%	95.14°	–

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

configuration. The ions are placed within the water lattice, 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 concentration ranges from 0.0 (reference) to 1.8 M, the latter corresponding to 64 ions pairs, with intermediate concentrations 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 pristine system (zero ionic concentration) to assess the influence 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 contact angle, with a deviation less than 0.3%. Clearly, for pristine systems with an atomistically smooth surface 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 contact 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 $-43.09 \text{ kJ mol}^{-1}$ (cases 1–3) reflecting the convergence of the simulations. The 3% lower cohesive energy obtained from the simulation using truncation 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 concentrations until the surface saturates. For the particu-

case	N_C	N_{KCl}	θ (deg)	IC	method
1	15048	0	90.99	cubic	SPME
2	15048	0	91.20	flat	SPME
3	15048	0	89.73	cubic	STC
4	15048	4	91.83	cubic	SPME
5	15048	4	88.99	flat	SPME
6	15048	4	88.99	flat	STC
7	15048	8	90.77	cubic	SPME
8	15048	8	89.23	flat	SPME
9	15048	16	90.12	cubic	SPME
10	15048	16	92.92	flat	SPME
11	15048	32	88.99	cubic	SPME
12	15048	32	87.46	flat	SPME
13	15048	48	85.22	cubic	SPME
14	15048	48	85.42	flat	SPME
15	15048	64	81.41	cubic	SPME
16	0	4	-	cubic	SPME

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_{KCl} the number of ion pairs, and θ the contact angle. The method refers to the numerical treatment of the Coulomb interaction: Smooth Particle Mesh Ewald (SPME) or Smooth Truncation (STC).

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 ≈ 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° to 82° 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.

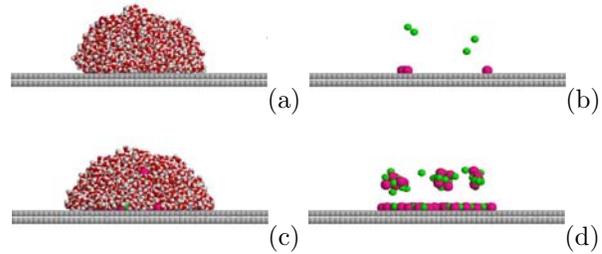


Figure 2: The equilibrated structure of the dilute (0.11 M) and concentrated (1.8 M) droplets of KCl on a graphite surface. The dilute droplet (a) reveals a contact angle of $\approx 90^\circ$, and a precipitation of the potassium ions onto the surface (b, same as a but without water molecules). In the concentrated drop, the ions precipitate onto the graphite surface and some forms crystals at the liquid-vapor interface (d).

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