Water-Carbon Interactions: Potential Energy Calibration Using Experimental Data

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ABSTRACT

The water-graphite interaction is characterized by molecular dynamics simulations of water droplets on a graphite surface. The binding energy of a single water molecule on graphite is found to be directly proportional to the well depth (ε_{CO}) in the Lennard Jones potential for the pairwise carbon-oxygen interaction and inversely proportional to the droplet contact angle. ε_{CO} is adjusted to enable the simulation results to match the literature value for the contact angle at 300 K (86°). This results in a binding energy of -7.3 kJ/mol for a single water molecule on graphite and a value of 0.4389 kJ/mol for ε_{CO}.

Keywords: carbon nanotubes, water, molecular dynamics, contact angle, potential energy.

1 INTRODUCTION

Functionalized carbon nanotubes (CNT) are being studied for use as nanoscale biosensors (Nguyen 2002) and water or proton channels (Hummer 2001, Werder 2001, Noon 2002). Several molecular dynamics (MD) studies of water in carbon nanotubes have recently been performed to gain further insight into the latter, but in these MD studies a wide range of intermolecular potentials for water and water-carbon interactions was employed (see Werder 2002 for details). In general, experimental data are not available for calibrating the strength of the water-carbon interaction, so it is difficult to assess the accuracy of these potentials. In the present study, we use MD simulations to compute the static contact angle for nanometer-size water droplets on graphite and compare the results with available experimental data (Fowkes 1938 as cited in Adamson and Gast 1997). This leads to a new approach for determination of the interaction potential parameters.

2 RESULTS AND DISCUSSION

We use the SPC/E water model (Berendsen 1987) and compare different strength water-carbon interactions for the case of a 2000-molecule water droplet on a graphite surface (a typical case is shown in Figure 1). The graphite is modeled by two 119x118 Å graphene sheets fixed in a staggered configuration 3.4 Å apart. The water-carbon interaction is modeled by a pairwise Lennard-Jones potential, $E_{CO} = \sum 4\varepsilon_{CO}[(\sigma_{CO}/R_i)^{12} - (\sigma_{CO}/R_i)^6]$, where the index i runs over all pairs of C and O atoms and R_i is the distance between atoms in the *ith* pair. The well depth and position of the minimum in the potential are given by ε_{CO} and $(2^{1/6})\sigma_{CO}$, respectively.
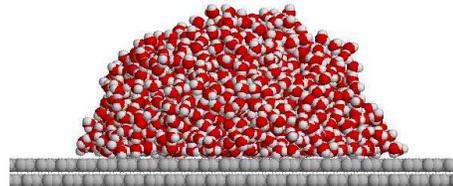

Figure 1: Snapshot of water droplet on graphite from MD simulation at 300 K using the SPC/E water model, and a carbon-oxygen Lennard-Jones potential with parameters $\varepsilon = 0.4389$kJ/mol and $\sigma = 3.19$ Å..

For each set of water-carbon parameters, we calculate the static contact angle (θ) of the droplet (see Figure 2) and the binding energy (ΔE) of a single water molecule on the graphite surface. In so doing, we demonstrate that the contact angle, which is commonly used to characterize the wettability of a substrate, is sensitive to changes in the carbon-water interaction strength. We also demonstrate that our small-droplet results can be extrapolated to macroscopic droplets, which allows us to use the experimental value for the contact angle of water on
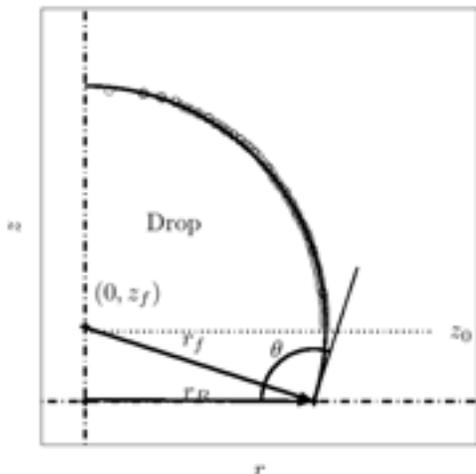
Figure 2: Schematic for calculating the contact angle of a water droplet on graphite from MD simulations. The contact angle is measured by fitting a circle with center $(0, z_f)$ and radius r_f to the points of the equimolar dividing plane (circles) with $z > z_0 = 8$ Å to exclude the near wall region. The droplet has a base radius r_B.

graphite (86°) to calibrate the water-carbon potential. Using a series of water-carbon potentials that range from hydrophobic ($\theta > 90°$) to complete wetting ($\theta = 0°$) behavior in our MD simulations, we determine the relationship between the binding energy of a single water molecule on graphite and θ for the droplet (Figure 3) and between ΔE and the value of ε_{CO} in the water-carbon potential (Figure 4). The data show complete wetting for $\Delta E < -13.1$ kJ/mol and linear relationships between ΔE and θ for other values and between ΔE and ε_{CO}. Thus, we can
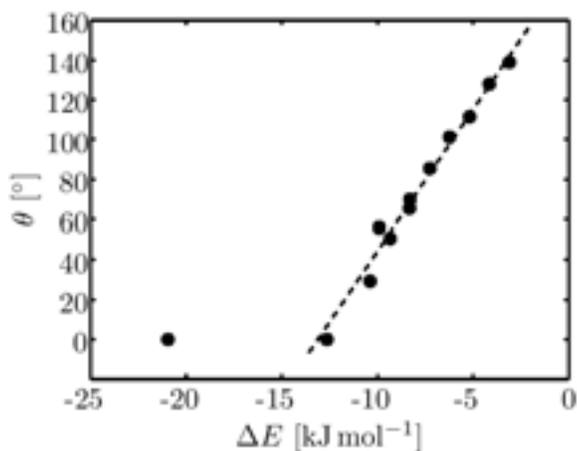

Figure 3: Static contact angle θ of water droplets on graphite as a function of ΔE, the binding energy of a single water molecule on graphite.
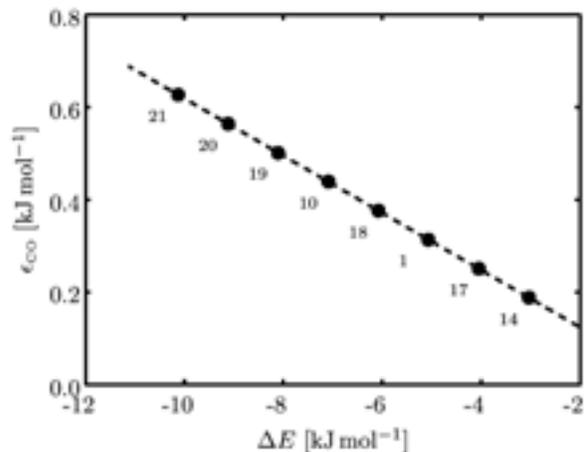

Figure 4:Lennard-Jones well depth parameter ε_{CO} for the water-graphite interaction as a function of ΔE, the water molecule binding energy on graphite.

accurately predict the binding energy for a water molecule on graphite to yield a specific θ and use that ΔE value to determine the optimal value for ε_{CO}. This represents a new method for calibrating molecular dynamics interaction potentials. Our procedure leads to the recommendation of new water-carbon Lennard-Jones parameters $\varepsilon_{CO} = 0.4389$ kJ/mol and $\sigma_{CO} = 3.19$ Å (Werder 2002). These results are summarized in Table 1.
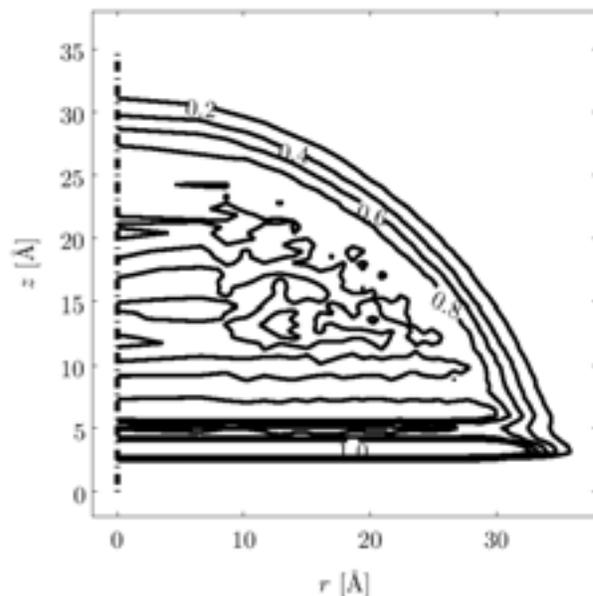

Figure 4:Isochore profile for a water droplet on graphite. The density values for the isochores are 0.2, 0.4, 0.6, 0.8 and 1.0 g/cm^3.

We have used this new potential to compute the binding energy of a single water molecule on graphite (ΔE = -7.3 kJ/mol) and the contact angle for a water droplet (θ = 85.5°). We have also characterized the water-graphite/carbon nanotube interface. Figure 5 shows the time-averaged isochore profile for a 2000-water molecule droplet using the new water-carbon parameters. That profile shows layering of the water at the graphite surface with a thin layer of high density ($\rho > 2\rho_{bulk}$) centered 3.2 Å above the surface and second layer ($\rho = 1.5\rho_{bulk}$) centered at a height of 5.5 Å. The droplet assumes bulk water density approximately 10 Å above the surface. The liquid-vapor surface of the droplet where the density drops from the bulk value of 1.0 g/cm3 to nearly zero is about 5 Å thick.

Based on our analysis of the water-carbon interaction strength, we can comment on the results of various studies of graphite or carbon nanotube interactions with water. In particular, the carbon-oxygen potentials employed by Markovic (1999) and Noon (2002) are too strongly attractive. This leads to enhanced hydrophilic behavior and wetting. On the other hand, the potential used by Walther (2001) results in insufficient attraction between the water and the carbon surfaces leading to enhanced hydrophobic behavior. We are currently repeating some of these simulations using the new water-carbon interaction potential.

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Table 1. Summary of Water-Carbon Interaction Models Considered in the Present Study[a]

Study	Water Model	σ_{CO} (Å)	ε_{CO} (kJ/mol)	ΔE (kJ/mol)	θ (°)
Markovic 1999	SPC	3.190	.3910	-12.64	0.0
Gordillo and Marti 2000	SPC-FLX[b]	3.280	.3890	-9.91	55.9
Walther 2001	SPC-FLX	3.190	.3135	-5.19	111.3
Hummer 2001	TIP4P	3.275	.4785	-8.33	48.0
Koga 2001	TIP4P	3.262	.3876	-6.70	
Noon 2002	TIP3P	3.296	.5781	-16.72	0.0
Present Study	SPC/E	3.190	.4389	-7.26	85.5

a. The Markovic, Gordillo and Noon models also included pairwise Lennard-Jones potential terms between carbon atoms and the water hydrogen atoms.
b. SPC-FLX is a flexible water model that allows OH stretch and HOH bending motions.