

Simulation and Modeling of Wetting and Adsorption Phenomena Associated with Nanomaterials

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Abstract: Atomic Force Microscopy of hydrophobic material surfaces in water shows the presence of closely spaced soft domains. The radii of curvature of these features are of the order of 100 nm and their heights above the substrate are in the range 20-30 nm. The consensus interpretation of these features is that they are nanosized gas bubbles formed on the substrate following immersion. A recent study on interfacial wetting at epitaxial graphene, with its combined use of experimental and computational approaches, showed that the macroscopic contact angle of water on epitaxial graphene layers is correlated with the number of layers. Based on these results, the small amount of the epitaxial buffer layer of bi-layer graphene that makes direct contact with water helps explain its macroscopic contact angle being close to the value for bulk graphite, that is $\sim 93^\circ \pm 3^\circ$. This contact angle value for bulk graphite, independent of the number of graphene layers, n , was also obtained after it was found that the water-exposure coverage of G_n (n -layer graphene) was close to unity. These results agree with ours reported previously, specifically the room temperature contact angle value of water on graphite. On another front, we note that recent studies involving permeation of water through single wall nanotubes via Molecular Dynamics (MD) simulations is an alternate means of showing phase transitions not manifested on the macroscopic scale because of confinement effects of matter at the nanometer scale of gases. We illustrate this effect with several MD simulations.

1 Introduction

For the past several years there have been several relevant studies relating to computer simulation of random sphere packing [Li, Zhao and Liu (2008)], computational nanomechanics [Shen, Atluri (2004)], computational studies on mechanical and thermal properties of carbon nanostructures [Chakrabarty and Cagin (2008)], and

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multiscale nonlinear constitutive modeling of carbon nanostructures based on interatomic potentials [Ghanbari and Naghdabadi (2009)]. These studies have provided insight into the understanding of interactions at the interface of water and solid surfaces and aided modeling of substrates formed by layers of materials. The experimental and Molecular Dynamics study of wetting on epitaxial graphene by Zhou et. al. [Zhou, et. al. (2012)] is of particular interest as it expands on the results of our previous study [Elnaiem, Casimir, Misra and Gatica (2009)].

2 Nanobubbles

In recent years, there has been an accumulation of evidence for the existence of nanobubbles at the interface of water and hydrophobic solid surfaces [Parker, Claesson and Attard (1994); Zhang, Li, Maeda and Hu (2006); Zhang, Kahn and Ducker (2007)]. In our study [Elnaiem, Casimir, Misra and Gatica (2009)], we calculated the contact angle of nanobubbles at a water-solid interface. The model of the atom-solid potential that has been used extensively to study adsorption or wetting properties is the “3-9 potential” given by the expression

$$V(z) = \frac{4C^3}{27D^2z^9} - \frac{C}{z^3} \quad (1)$$

where $V(z)$ is the adsorption potential that is taken to be a function of just the surface-normal distance, z . It is shown in Fig. 1 that as the temperature increases, the shape of the bubble changes continuously from a spherical cap with low curvature to a complete sphere.

With the ability to account for individual graphene layers, in contrast to our study which assumes a bulk macroscopically thick and smooth substrate, the authors of [Zhou, et. al. (2012)] uncovered a surprising correlation between macroscopic contact angle and the number of layers. The epitaxial buffer layer of a single graphene layer on a substrate of SiC was found to be more of a hydrophilic system compared to n -layer graphene. Perturbation effects of the underlying SiC substrate, functional groups, and surface defects were all shown to be responsible for the behavior mentioned above. From the vertical density profiles obtained from their classical molecular dynamics simulations for multiple water models and graphite configurations, which agreed with experimentally determined values of two distinct layers peaked at 3.2 and 6.1 angstroms, Zhou et al. [Zhou, et. al. (2012)] were able to confirm the van der Waals nature of the interaction of water with bulk graphite. This also supports the functional form and parameters of the interaction potential used in our study [Elnaiem, Casimir, Misra and Gatica (2009)], which was mainly geared towards reproducing the van der Waals interaction between the adsorbate and surface.

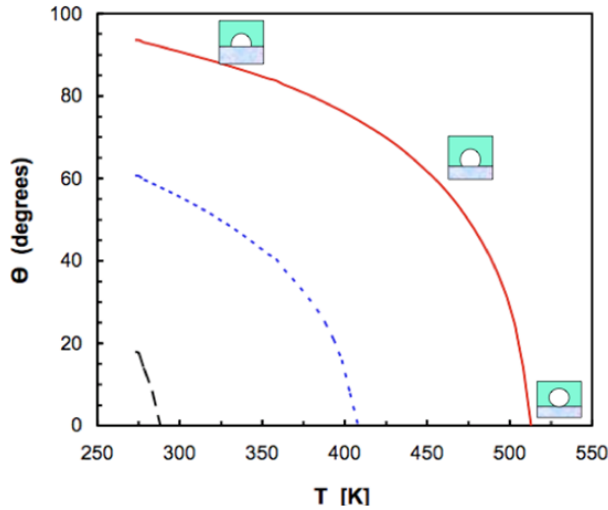


Figure 1: Contact angle for water on various surfaces with parameters $C=1074 \text{ meV \AA}^3$ and $D=100 \text{ meV}$ (red solid line), $D=200 \text{ meV}$ (blue dashed line) and $D=300 \text{ meV}$ (black short-dashed line). The insets represent schematic diagrams showing how the shape of the bubble changes.

3 Simulation of Physical Adsorption in Carbon Nanotubes

Physical adsorption (physisorption) of molecules in carbon nanotubes has been extensively studied via Grand Canonical Monte Carlo simulations. When a substrate is exposed to a vapor, physisorption occurs at a vapor pressure higher than the pressure of uptake, P_u , and below saturated vapor pressure (SVP). The value of P_u depends on the strength of the force of the substrate and the temperature of the system. If after having adsorbed molecules from the vapor, the temperature is increased, the molecules are “desorbed”.

The accuracy of the computer simulations depends on the model of the potential interaction used. In most cases, carbon nanotubes are typically modeled as smooth cylinders made of carbon with the same areal density of graphene. This so-called “continuous approximation” provides an accurate description of the adsorption process; however, it fails in describing commensurate phases of the adsorbates. The continuous approximation is usually adopted to save computing time and may be justified by the lack of information about the chirality of the nanotubes forming a bundle. In the case where an atomistic model is desired, for example if details of the structure of the adsorbed layers are relevant, the nanotube- adsorbate interaction is modeled as a pair wise sum of carbon-adsorbate interactions, V_{c-a} . The potential

V_{c-a} is usually approximated by a Lennard-Jones type potential.

Another interesting effect worth mentioning here is that of the compression or expansion of the substrate produced by the force of the adsorbate. Although this effect has been observed experimentally and investigated computationally, an overwhelming majority of the theoretical studies have assumed that the environment provides a fixed static potential in which the adsorbate moves; the relaxation of the substrate is not limited to affecting the capacity of the uptake, but has dramatic consequences on the physical properties of the adsorbates, such as phase transitions and energetics in low dimensions. For example, ^3He in a rigid 1D pore is a gas, whereas in a non-rigid carbon nanotube it is a liquid.

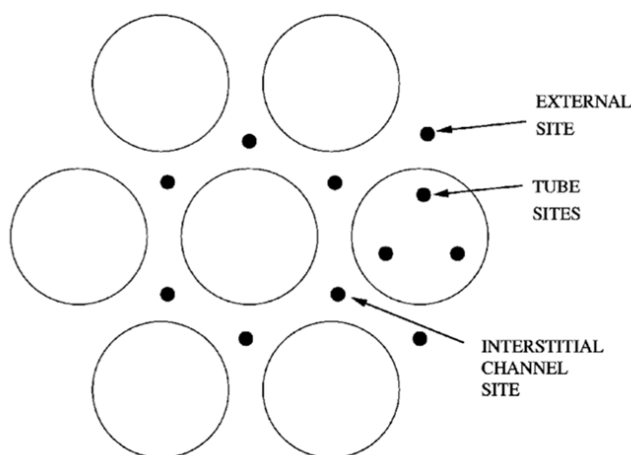


Figure 2: Schematic picture of the adsorption sites in a bundle of carbon nanotubes.

Figure 2 shows the various adsorption sites accessible, in principle, to an adsorbate in a bundle of carbon nanotubes [Casimir, Gatica and Misra (2011); Stan, Bojan, S.Curtarolo, Gatica and Cole (2000)]. The external surface region includes the so-called groove between pairs of nanotubes, an energetically favorable site because of the high coordination number of C atoms. Interestingly, between a triad of nanotubes within the bundle lie “interstitial channels” (ICs). If not blocked at the end, the ICs may be accessible to small atoms or molecules. Finally, there exists the “endohedral” region inside the individual tubes; access to this region usually requires chemical treatment to open the tube.

We summarize below the main aspects of endohedral and exohedral adsorption. Endohedral adsorption of a molecule strongly depends on the radius (R) of the nanotube and the “size” of the molecule. As a result of the analysis of the potential

interaction between the adsorbate and the nanotube, it can be seen that adsorption is possible for values of R higher than 0.9σ (where σ is the LJ parameter of the adsorbate). For $0.9\sigma < R < 1.212\sigma$, adsorption is restricted to the axis of the nanotube, and for $R > 1.212\sigma$, the adsorbate forms a cylindrical shell. For wider tubes, an axial line appears surrounded by a cylindrical shell, mimicking the formation of layers on a flat surface. These predictions have been confirmed by computer simulations. Typical values of σ are, for example, 0.256 nm, 0.305 nm, 0.34 nm, 0.345 nm for He, H₂, Ar and CH₄, respectively. Exohedral adsorption, as opposed to endohedral, is possible for all adsorbates regardless of size. The binding energy in the grooves is typically a factor 1.7 times as large as that on graphite. Adsorption starts in the grooves at the uptake pressure. If the pressure of the vapor is increased, keeping the temperature constant, the adsorbate will form a monolayer that includes the atoms in the groove, and eventually a second layer or multilayers before SVP sets in.

4 Flow of Water in Carbon Nanotubes

The permeation of water through a single wall nanotube studied through Molecular Dynamics (MD) is an alternate way of showing phase transitions not manifested on the macroscopic scale due to confinement effects of matter at the nanometer scale [Cohen, Zhu, Tajkhorshid and Huang; Humphrey, Dalke and Schulten (1996); Hummer, Rasaiah and Noworyta (2008)]. MD simulations done on side by side carbon nanotubes in between two layers of water are illustrated in Figs. 3 and 4 and show water in ordered one dimensional lines spontaneously and continuously filling the non-polar carbon nanotubes. Because hydrogen bonding is applicable when the adsorbate is water, this can cause the liquid to separate from non-polar solids, creating a separate vapor layer between the surface and bulk fluid phase. The fluctuations in density in the bulk water outside of the nanotubes, and strong hydrogen-bonded chain of water molecules along the nanotubes' radii results in the fast and concerted directional motion of the molecules in the nanotube. The shielding of the hydrogen bonds in the nanotube from external fluctuations results in a negligible percentage of non-bonded water pairs in contrast to the external water bath.

The highly oriented nature and longer lifetime of the hydrogen bonds inside the nanotube compared to that outside is also attributable to shielding from the single wall nanotube (swnt). For example, in the simulations inside the nanotube, less than 15% of the hydrogen bond angles were greater than 30° , while 37% of the angles of the same bonds in the external water exceeded this angular value. The respective lifetimes of the hydrogen bonds for water molecules inside and outside the nanotube were also found to be 5.6 ps and 1.0 ps, respectively [Hummer, Ra-

saiah and Noworyta (2008)]. In MD simulations of this system, water molecules not only enter into the nanotube opening, but also travel through the entire length of the nanotube, entering through one end and exiting through the other.

The simulation done by [Hummer, Rasaiah and Noworyta (2008)] recorded an average of 17 of these permeation events per nano-second, while in the simulations that produced Figs. [3, 4] in our study, there were 20 such permeation events in both directions along all of the nanotubes over the last 2.5 ns of the 3 ns simulation.

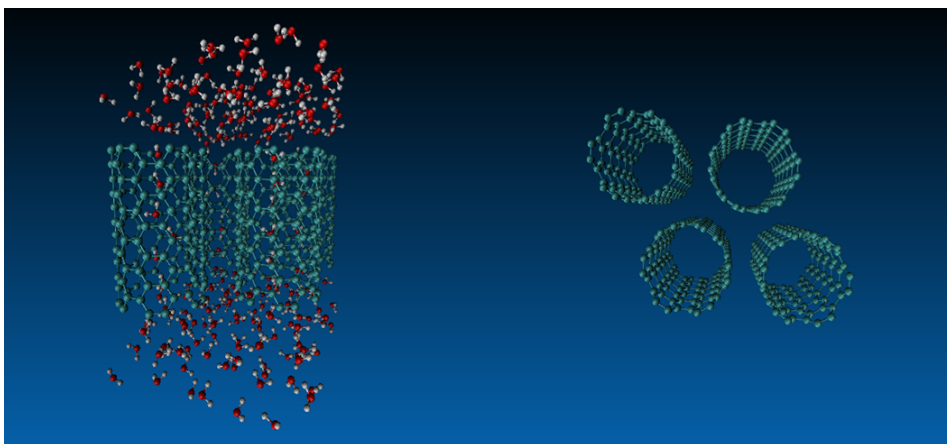


Figure 3: Configuration of equilibrium simulation of single wall nanotubes immersed in water (left) and single wall nanotube arrangement in equilibrium simulation of water permeation (right) .(duration 3.0 ns, 248 water molecules).

5 Conclusions

To summarize, much progress has been made in understanding the interactions of liquid at carbonaceous surfaces. We have shown that for bulk graphite expressed in the limit of an infinite atomically smooth substrate, this interaction, expressible largely by the contact angle, can be controlled through variations of the interaction potential of the surface. In a short amount of time, the control of macroscopic wettability through variations of hydrophobicity of intrinsic graphene and defective patches of the epitaxial buffer layer on the micron-scale has been elucidated. It appears that the hybridization character of graphene and similar nanomaterials - the relative amounts of sp^2 vs sp^3 carbon responsible for many of its exceptional properties - seems to influence its wettability, in addition to quantum confinement effects.

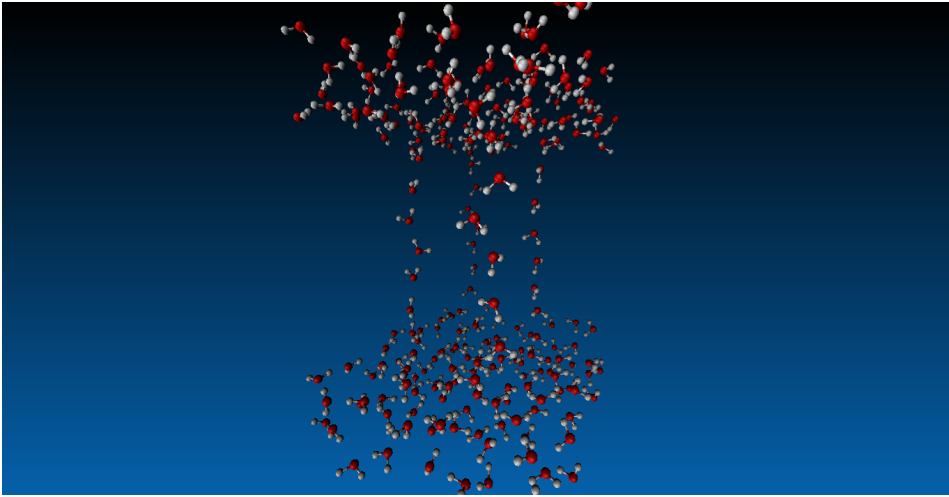


Figure 4: Equilibrium simulation configuration - with nanotubes removed - showing the directionality of the hydrogen bonds inside the carbon nanotubes.

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