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Adhesion of single functional groups to individual carbon nanotubes: Electronic effects probed by *ab initio* calculations

Giancarlo Cicero,[1,2] Jeffrey C. Grossmann,[3] and Giulia Galli[1,4,*]

[1]*Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550, USA*

[2]*Department of Physics, Politecnico of Torino, Torino, Italy*

[3]*Center of Integrated Nanomechanical Systems, University of California, Berkeley, California 94720-1740, USA*

[4]*Department of Chemistry, University of California, Davis, California 95616, USA*

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We investigated the interfacial interaction of simple functional groups ($-NH_2$, $-CN$, $-CH_3$, $-CHOCH_2$) with single wall carbon nanotubes, using *ab initio* calculations. We computed binding energies and attachment forces using the density functional theory (DFT) in the local density approximation, and we employed Quantum Monte Carlo calculations to test DFT accuracy in describing weak interactions for the controversial case of an oxygen molecule. We find that computed energies and forces are very sensitive to small variations of the electronic charge on the nanotube. In particular, the presence of a solvent (polar or nonpolar), and thus of a small charge transfer from or to the tube, may alter the relative strength of adhesion forces for different functional groups, as compared to the vacuum.

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I. INTRODUCTION

Carbon nanotubes[1] (CNTs) display a unique combination of geometrical flexibility, material strength, and electronic properties, which may enable a variety of applications ranging from nanoelectronic circuits[2,3] and biosensors,[4] to field emitters,[5] membrane filters,[6] and reinforcing fibers for composite materials.[7–9] The majority of these applications pair nanotubes with other materials through noncovalent interactions,[10] whose understanding and control is thus of critical importance for an efficient design of functional composites. Yet, direct experimental measurements of interaction energies and forces are extremely difficult, due to the very small size of CNT interfaces, and calculations of adhesion forces from first principles face numerous computational and theoretical challenges.

A reliable and promising technique employed to analyze weak interactions is chemical force microscopy,[11] which uses atomic force microscopy (AFM) tips functionalized with specific groups. By performing pull-off experiments of the functionalized AFM tip bound in an adhesion complex to a substrate, e.g., a tube, one may obtain details on the adhesion strength of the specific functional group. However to date only forces between bundles of tubes or so-called nanotube paper have been measured,[12] and experimental data on the strength of single molecule interactions with single wall carbon nanotubes (SWCNT) are not yet available.

From a theoretical standpoint, pull-off experiments involving single CNTs have not been modeled or simulated directly; only very recently an *ab initio* simulation of noncontact AFM experiments involving a semiconductor surface[13] [InAs(110)], and a silicon tip represented by a SiH_3 radical, has appeared in the literature. However, binding energies between SWCNT and several simple molecules have been computed,[14] using different levels of theory, in particular, density functional theory (DFT) in the local density approximation (LDA) and gradient corrected Perdew-Burke-Ernzerhof (PBE) and Becke-Lee-Yang-Parr (BLYP) approximations.[14–16] Some of these results are rather controversial, notably the case of the O_2 binding[15–17] and highlight the need for a more thorough understanding of weak interactions between simple molecules and NTs.

In this paper, we report on *ab initio* simulations modeling AFM pull-off experiments. In particular, using DFT, we computed adhesion forces of four chemically different groups ($-NH_2$, $-CN$, $-CH_3$, and epoxy [$-CHOCH_2$]), which are noncovalently bonded to a SWCNT. By choosing functional groups used in recent experiments,[12] we investigated the dependence of adhesion forces on the chemical identity of the terminal group of functionalized AFM tips. In addition, with the goal of understanding the influence of the tube surrounding environment (e.g., the presence of a solvent) on adhesion forces, we studied how interfacial interactions are modified upon small changes of the charge on the SWCNT.

The rest of the paper is organized as follows: in Sec. II the calculation method is briefly presented, in Sec. III the results are presented and discussed, and finally, conclusions are outlined in Sec. IV.

II. COMPUTATIONAL APPROACH

In our simulations, we considered a (14×0) SWCNT, which has a diameter of about 11 Å and is semiconducting, as the majority (70–80 %) of the CNTs produced in standard synthesis procedures.[3] The NT structure was generated using the experimental C–C distance of graphite (1.42 Å) and simulated by a supercell periodically repeated along (x,y,z). The supercell contained two periodic replica of the NT irreducible part, and enough vacuum to accommodate the various attached molecules (four periodic replica systems were also used to test the accuracy of our results).

All pull-off computational experiments were carried out using DFT; these were performed using a plane wave formulation of *ab initio* molecular dynamics (MD),[18] as implemented in the GP and Qbox codes.[19] Electron/ion interactions were treated with nonconserving pseudopotentials of the Hamam type,[20] and Kohn-Sham orbitals were expanded in plane waves up to an energy cutoff of 60 Ry (80 Ry cutoff was applied to oxygen containing systems). The integration over the Brillouin zone was performed using only the Γ point. In order to test the accuracy of LDA (Ref. 21) and the generalized gradient approximation (GGA) (Ref. 22) to describe noncovalent interactions of nanotubes with simple molecules, we carried out diffusion Quantum Monte Carlo (QMC) calculations to compute the binding energy of O_2 to a SWCNT, which despite numerous experimental and theoretical studies remains an open question. We note that the QMC approach, which typically recovers 90–95 % of the many-body correlation energy, has been shown to provide near chemical accuracy for a wide range of systems.[23]

The weakly bonded O_2 molecule is known to abundantly surround CNTs, even long after the synthesis process, and under numerous experimental conditions. Therefore, a number of experimental and theoretical investigations have attempted to ascertain the attachment affinity of oxygen molecules to CNT side walls. Because of the weak nature of the interaction, reliable predictions require a very high level of accuracy, and large discrepancies between different theoretical approaches have yet to be resolved.[15–17] Using QMC, we find that the oxygen molecule is bound by 0.06(2) eV, compared with 0.10 eV in LDA, and zero or negative binding in GGA, depending on the functional employed. Thus, while there is a quantitative difference between LDA and QMC, LDA at least correctly finds a positive binding energy[24] and gives an interaction energy close to the one obtained by Ricca and Drocco at the Møller-Plesset level.[17] Furthermore, when a smaller (7×0) CNT is used, both the LDA and QMC binding energies remain roughly the same as for the (14×0) case [i.e., 0.11 eV for LDA and 0.06(2) eV for QMC], indicating that binding energy trends as a function of CNT size may also be suitably described within LDA. Based on our QMC calculations for the O_2 binding and on the comparison of PBE and LDA results reported in the literature on weak binding,[25] we have chosen to carry out all simulations of pull-off experiments using LDA. We note that it has been previously reported that LDA may indeed be more suitable than GGA for the study of weak interactions; for example, Okamoto and Miyamoto[26] found that the LDA interaction energy curve of molecular hydrogen with planar graphitic cluster is in very good agreement with that obtained by second order Møller-Plesset (MP2) calculations; and Tournus and Charlier[14] reported that the graphite interlayer distance calculated within the LDA agrees very well with the experimental value (3.33 Å) whereas GGA overestimates it by ~30%.

In our simulations, AFM tips were modeled by SiH_3CH_2-X molecules, where X represents the chemical functional groups ($-CN$, $-CH_3$, $-NH_2$, $-CHOCH_2$), the Si atom represents the edge of the tip, and the $-CH_2-$ represents the short alkyl chain connecting the functional group ($-X$) to the tip, respectively. We were able to accurately simulate the pullout forces, by slowly increasing the NT-tip distance,[27] while simultaneously optimizing the tube and tip structure. The structural simplicity of these small molecules connected to the tube allowed us to fully explore orientations and tip/NT alignment in our calculations. The functional groups—some of which were used in recent experiments[12]—were chosen to present different kinds of interactions with the NT. The $-CN$ group interacts with the NT wall through the lone pair (LP) localized on the N atom, while the $-CH_3$ group interacts through the $-H$ atoms. Finally the amino ($-NH_2$) and epoxy ($-CH_2OCH_2$) group may present both types of interactions depending on the group orientation.

TABLE I. Interaction energies (ΔE) and equilibrium distances (d_{eq}) for the AFM tips interacting with neutral (left), positively (center), and negatively (right) charged SWCNT. For the $-NH_2$ and $-CH_2OCH_2$ functionalized tip the interaction through their lone pair (LP) is explicitly indicated.

	Neutral SWNT		Positively charged SWNT		Negatively charged SWNT	
Functional group	ΔE (eV)	d_{eq} (Å)	ΔE (eV)	d_{eq} (Å)	ΔE (eV)	d_{eq} (Å)
$-CN$	−0.15	2.9	−0.21	2.9	−0.06	2.9
$-CH_3$	−0.09	2.5	−0.06	2.5	−0.09	2.4
$-NH_2$	−0.15	2.1	−0.09	2.1	−0.21	2.1
$-NH_2$ (LP)	−0.19	2.8	−0.25	2.8	−0.11	2.8
$-CH_2OCH_2$	−0.14	2.3	−0.10	2.2	−0.16	2.2
$-CH_2OCH_2$ (LP)	−0.13	2.8	−0.22	2.7	−0.01	2.7

III. RESULTS AND DISCUSSION

The simulations of pull-off experiments are summarized in Tables I and II. In particular, in the first columns, we report the calculated binding energies and maximum pull-off

TABLE II. Maximum pull-off force (F) calculated at the inflexion point (d_{infl}) of the potential energy of the AFM tips interacting with neutral (left) and negatively (right) charged SWCNT. For the $-NH_2$ and $-CH_2OCH_2$ functionalized tip that may interact either through their lone pair (LP) or a $-H$ atom, only the lowest energy interaction configuration was considered in our pull-off calculations (dashes indicate systems that would give lower force values).

	Neutral SWNT		Negatively charged SWNT	
	F (pN)	d_{infl} (Å)	F (pN)	d_{infl} (Å)
$-CN$	150	3.30	86	3.30
$-CH_3$	110	2.84	135	2.78
$-NH_2$			258	2.42
$-NH_2$ (LP)	220	3.06		
$-CH_2OCH_2$	150	2.61	188	2.81
$-CH_2OCH_2$ (LP)				

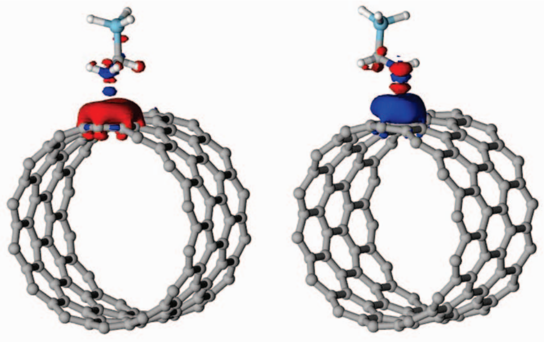

FIG. 1. (Color) Ball and stick model of the equilibrium structure for the $-NH_2$ functionalized tip interacting through the lone-pair (left panel) and a H atom (right panel). Gray spheres represent C atoms, dark blue (light blue) represent nitrogen (silicon) atoms, and white sphere hydrogen atoms. The isosurfaces represent the electron density difference between the interacting and noninteracting tip/NT system: blue (red) surfaces correspond to a charge density increase (decrease), respectively.

forces for four chemical groups interacting with a neutral SWCNT. The computed energy curves present very shallow minima, thus we have chosen to provide equilibrium distances with a precision of tenths of Å. We note that the magnitude of the computed forces (varying from 110 to 220 pN) is consistent with those measured very recently by dynamic force microscopy[28] using Si tips on SWCNT; the measured forces (for tubes with a diameter of 13.8 Å) varied from 200 and 212 pN, depending on the position of the tips with respect to the carbon rings. Consistent with the experiment we also found that computed interaction energies varied very little (few percent) when the tip approached the tube on the center of the ring or in correspondence of C–C bonds. On the other end, as expected the forces computed here differ by an order of magnitude from those measured for a nanotube paper,[12] where measurements of single molecule interactions are not achieved. Nevertheless, the relative strength of $-NH_2$ and $-CH_3$ functionalized tips found in our calculations is in agreement with experimental findings;[12] in addition the relative strength and magnitude of forces agree with experimental data normalized to tip radius, in order to describe single group interactions. In particular, we find that the $-NH_2$ tip has the largest force (2.2×10^2 pN), followed by the $-CN$ (1.5×10^2 pN), and the $-CH_3$ group (1.1×10^2 pN). The interaction energies follow the same trend as the maximum force, with $-NH_2/-CH_3$ the most (0.19 eV/cell)/least (0.09 eV/cell) bound group; furthermore, in the case of neutral CNTs the energy difference between LP or $-H$ interaction ($-NH_2$ and $-CHOCH_2$ tip) is rather small. We note that the interaction energy obtained for the $-NH_2$ group interacting with the tube through its lone pair compares well with the value of 0.18 eV reported by Chang *et al.*[14] for the adsorption of ammonia on a (10×0) NT.

To understand the mechanism behind the NT/tip adhesion in the case of LP and $-H$ interactions, we analyzed the electronic structure of the interacting molecule/NT complex. In Fig. 1, we report the electron density difference between the interacting and isolated tip/NT systems for the case of $-NH_2$, for two different orientations of the amino group. The red and blue iso-surfaces represent, respectively, charge depletion and accumulation when the tip is in "contact" with the nanotube. In both cases the interaction has an electrostatic contribution, although the charge polarization depends on the $-NH_2$ orientation. In particular, when a species with a lone pair approaches the tube, a positive polarization charge appears on the tube: the interaction through the lone pair induces a depletion of charge in the underlying carbon ring which leads to an attractive force with the negatively charged lone pair (right panel of Fig. 1). The opposite situation occurs when the tip interacts through the hydrogen atom (left panel of Fig. 1), which is partially positively charged. Long range electrostatic contributions to tip-tube interactions have been found also in the case of silicon tips, where they may amount to about one half of the interaction strength.[28]

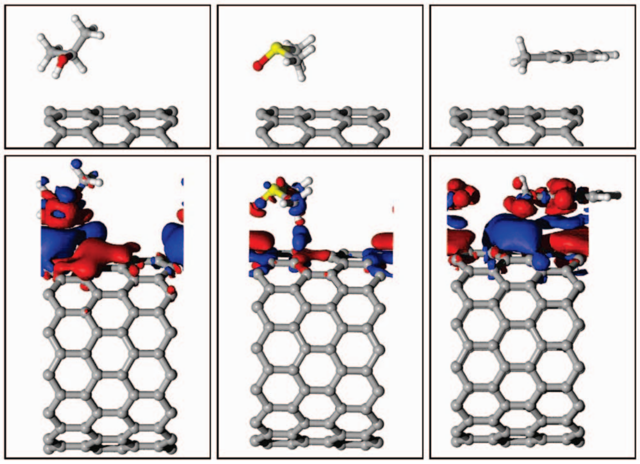

FIG. 2. (Color) Ball and stick model of the equilibrium structure for the isopropanole (left), DMSO (center), and toluene (right) molecules. Gray spheres represent C atoms, yellow spheres sulphur, red spheres oxygen, and white spheres hydrogen atoms. The isosurfaces represent the electron density difference between the interacting and noninteracting tip/NT system: blue (red) surfaces correspond to a charge density increase (decrease), respectively.

This analysis suggests that charge transfer to the tube from the surrounding media may play a key role in determining adhesion energy and forces. Indeed, if the number of electrons per NT increases, the localization of a positive polarization charge at the NT wall by contact with LP containing groups ($-CN$, $-NH_2$, and $-CH_2OCH_2$) would be more difficult and a weaker interaction is expected. The effect would be the opposite for the interaction through H atoms ($-CH_3$, $-NH_2$, and $-CH_2OCH_2$).

In order to test this hypothesis, we computed interaction energies of the tips with systems representing positively charged (possibly *p*-doped) and negatively charged (possibly *n*-doped) NTs. These were obtained by removing or adding one electron per unit cell (e.g., 0.009 el. per C atom), respectively. For the case of negatively charged tubes, we carried out the same pull-out simulations as in the neutral case. Our results are reported in Tables I and II. As expected, simulations of negatively charged NTs showed a decrease in the interaction energy through the lone pair for all the functional groups, while the interaction through the $-H$ atom slightly increased. In the case of a positively charged NT, the opposite trend is observed. In general, the computed forces show different adhesion trends, depending on the charge of the tube. For the case of a −CN functionalized tip, we computed the maximum pull-off force for both charged states and we found a value of 2.9×10^2 and 0.9×10^2 pN respectively, showing a variation of about 200 pN depending on the NT charge state. These results present a compelling case in favor of charge transfer to or from the tube (possibly *n*- or *p*-doping character) by the surrounding media being a key factor in determining noncovalent molecular binding.

Frequently AFM measurements are carried out in solution and thus one may expect electronic doping of the CNT to arise from the charge transfer from or to the surrounding solvent. Although the doping character of carbon NTs is currently under debate, and most experiments assume that carbon NTs are *p* doped,[3] some recent investigations do not rule out possible *n* doping, particularly in the case of NTs immersed in a polar solvent, e.g., water or alcohols,[29] and polymers containing amine groups.[30]

To study the effect of the solvent on the nanotube charge state and whether it may be responsible for the charging of the tube, we have analyzed the interaction of several representative single solvent molecules of different polarity with nanotube walls; we used the same *ab initio* scheme as the one described above. In particular, we considered isopropanole, dimethyl solfoxide (DMSO), and toluene, which are among the solvents employed most often in AFM experiments (see, e.g., Refs. 29–31). These three molecules stick at the NT surface and their interaction energy changes slightly by changing their orientation. For the lowest energy configuration we found a binding energy of 0.23, 0.22, and 0.34 eV for isopropanole, DMSO, and toluene, respectively. In each case the interaction has a polar contribution. In the case of toluene, the molecule resides flat at the NT wall; indeed, in this configuration, a $\pi-\pi$ interaction between the delocalized π orbital on the nanotubes and benzene ring takes place, that stabilizes the complex. An analysis of the electronic structure shows that a small hybridization between the highest occupied molecular states of the nanotube and the toluene occurs (no hybridization was found when the molecule was at a noninteracting distance of about 6 Å from the NT wall).

For the three solvent molecules studied here, we report in Fig. 2 the electron density difference between the interacting and noninteracting complexes. The NT charge is affected by the presence of the solvent and polarization charges appear at the NT wall. Nevertheless a definite conclusion on the final charge state of the NT induced by the solvent is hard to draw: the charge difference depends on the molecule orientation, which may continuously evolve and change in a liquid environment. In addition, ordering effects[32] and liquid density increase observed at a semiconductor surface,[33] could also play a role. The global effect of a solvent may be captured with a long MD simulation, which currently goes beyond the scope of our work.

Charge transfer effects are subtle, but, as previously shown, even a small charge transfer from the solvent to the nanotube changes the interaction strength between the molecule and the nanotube wall and needs to be taken into account when measuring weak interactions.

IV. CONCLUSIONS

In conclusion, we have proposed an interaction mechanism between simple molecules used to functionalize AFM tips and SWCNTs which may have wide-ranging implications for the design of carbon nanotube composites and functional materials. In particular, we have computed the adhesion forces of a set of noncovalently bonded molecules to a SWCNT side wall. Our results are consistent with existing experiments in discriminating $-NH_2$ and $-CH_3$ functionalized tips and predict strength of interactions for additional groups, which may be compared with future AFM data. In addition, our results show that the electronic charge of the CNT plays a fundamental role in noncovalent binding. Therefore the environment surrounding the tube can be a key factor in determining adhesion properties, as a result of subtle, electronic effects of charge transfer from the solvent to the nanotube. These effects could be probed experimentally by measuring single group adhesion forces in different solvents.

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*Author to whom correspondence should be addressed.

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