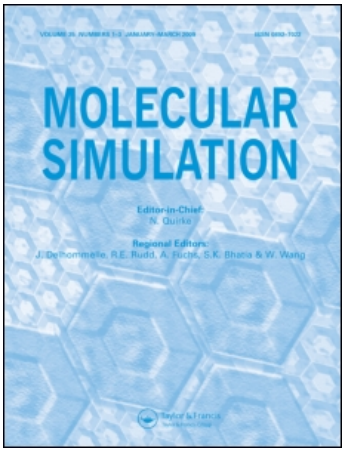

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Modelling and simulations of adhesion between carbon nanotubes and surfaces

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Modelling and simulations of adhesion between carbon nanotubes and surfaces

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Recent experiments showed that there are very strong adhesion forces between nanotubes and surfaces. These forces are much stronger than the adhesion forces of gecko's foot hairs on substrates. Thus, nanotubes become candidates to be used in dry adhesives. Here, we present theoretical investigations on the adhesion between nanotubes and graphite surfaces. Molecular dynamics simulations and energy minimisation calculations were performed. Layer-by-layer deformations of the nanotube tips were observed. Parallel and perpendicular components of the forces were calculated for different contact angles of nanotubes. Adhesion forces are found to be maximised at 15° impact angles of nanotubes with respect to surface normal.

Keywords: nanotubes; adhesion; gecko's foot; molecular dynamics

1. Introduction

Carbon nanotubes (CNTs) have attracted great interest in the field of nanotechnology because of their remarkable mechanical, electrical and transport properties [1–5]. The mechanical properties of nanotubes are very important as many potential applications depend on these properties. Over the past couple of years, there have been many studies on mechanical properties and deformation on CNTs such as bending, buckling, twisting and curvature effects using molecular dynamics (MD) simulations [4]. With the development of new experimental techniques, the buckling behaviour of the CNTs has been observed under large deformation [6].

Recent experiments showed that there are very strong adhesion forces between nanotubes and surfaces. Yurdumakan et al. [7] measured the adhesion force on multiwalled CNTs (MWNTs). In the experiment, MWNT brushes on polymethyl methacrylate polymer surfaces were prepared. Then, scanning probe microscopy (SPM) was used to measure the strong adhesion forces of the MWNT brushes. They found that the forces were 200 times higher than that of gecko's foot hairs [8]. Thus, nanotubes are good candidates to be used in dry adhesives.

In this research study, we perform theoretical investigations of CNTs interacting with surfaces. To study the deformation behaviour and adhesion of CNTs, atomistic simulations of capped armchair (10, 10) nanotubes with two different lengths are performed on rigid and relaxed graphite surfaces. There have been many theoretical studies of CNT tips interacting with surfaces [9–13]. These studies were mainly focused on employing CNTs as SPM tips. We started with a similar system; however, besides studying the deformation of CNTs, we have focused on parallel and perpendicular components of the forces for different contact angles to investigate the adhesive behaviour of nanotubes.

2. Model

Atomic models of (10, 10) armchair single-wall nanotubes were created and combined with atomic models of graphite surfaces that are multilayer periodic graphite lattice structures. Two capped nanotubes of different lengths were selected such that the shorter tube had 790 atoms and the longer tube had 1990 atoms. The lengths between two extreme ends of the tubes were 46.5 and 122 Å, respectively. Then these tubes were combined with the graphite surfaces consisting 10 layers. In the longer tube case, the lattice constants of the overall structure were $a = 49.2$ Å, $b = 49.2$ Å and $c = 163$ Å, and for the shorter tube case $a = 36.9$ Å, $b = 36.9$ Å and $c = 86$ Å were chosen. The number of atoms of the nanotube, from the uncapped end, which were chosen to be fixed, was 120. The nanotubes were initially positioned at 6 Å above the top layer of the graphite surface. The simulations were performed by using Cerius^2 with the universal force field [10].

During the simulations, the fixed nanotube atoms were moved towards the surface in increments of 0.1 Å for energy minimisation calculations and 0.2 Å for the MD simulations. In MD simulations, the entire system was allowed to equilibrate for 5000 steps and then moved

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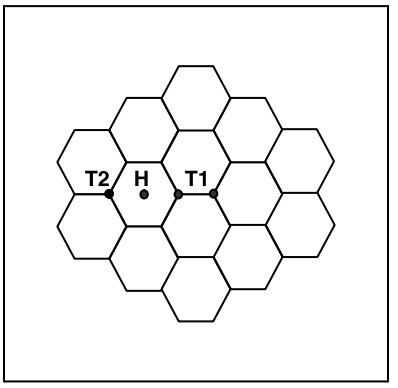

Figure 1. The hollow (H), top1 (T1) and top2 (T2) sites on the top-most layer of the graphite surface.

towards the surface. There were 500 MD steps in between each increment of the displacement of the tip. All MD simulations were performed at constant NVT. The temperature was selected as 10 K and the time step was 0.001 ps.

3. Deformation of the nanotubes and adhesion forces

The first series of simulations were energy minimisation calculations and nanotubes were facing hollow, top1 and top2 atomic sites of the graphite surface. These atomic sites are shown in Figure 1. Energy minimisation calculations were performed for both short and long nanotubes on rigid and relaxed surfaces. The total potential energy (E) was calculated during the simulations and the variation of E as a function of z displacement for a short nanotube on three different atomic sites is presented in Figure 2. In the figure, the first major peak represents the critical position of the tip in which repulsive interaction between the graphite surface and tip reaches a maximum. When the tip was moved closer to the surface, a layer of carbon atoms from the tip moved into the tube, which resulted in the first deformation of the tip and caused the energy to drop. Snapshots of the tip deformation for the hollow atomic site case are shown in Figure 3.

When the tip is moved towards the graphite surface, the nearest atoms of the capped end are first attracted by the graphite layers up to a critical position. Then the repulsive forces push them back along the tube axis. When the tip is moved further, the repulsive forces are increased and they cause layer by layer the compression of the cap into the interior of the nanotube. The sharp end of the cap changes gradually from an original concave shape to a convex shape, which also was observed in previous simulations [11]. The symmetrical deformation of the inversed cap of the tip was observed for the hollow site but not necessarily for the top1 and the top2 sites. Two results from these calculations appeared to be interesting at this point. One result is the layer-by-layer compression of the tip surface that is related with the discrete atomic nature of the tip structure. Another result is the atomic surface site dependence of the energy variation and deformation. It appeared that local atomic structure is important for the energy variation and deformation of the nanotube cap.

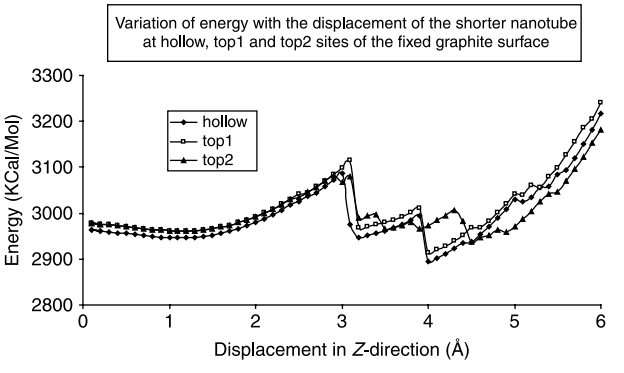

Figure 2. Variation of the total potential energy as a function of tip displacement for the shorter nanotube on a fixed graphite surface. The nanotube tip was initially 6 Å above the surface. Positive z-direction is towards the surface.

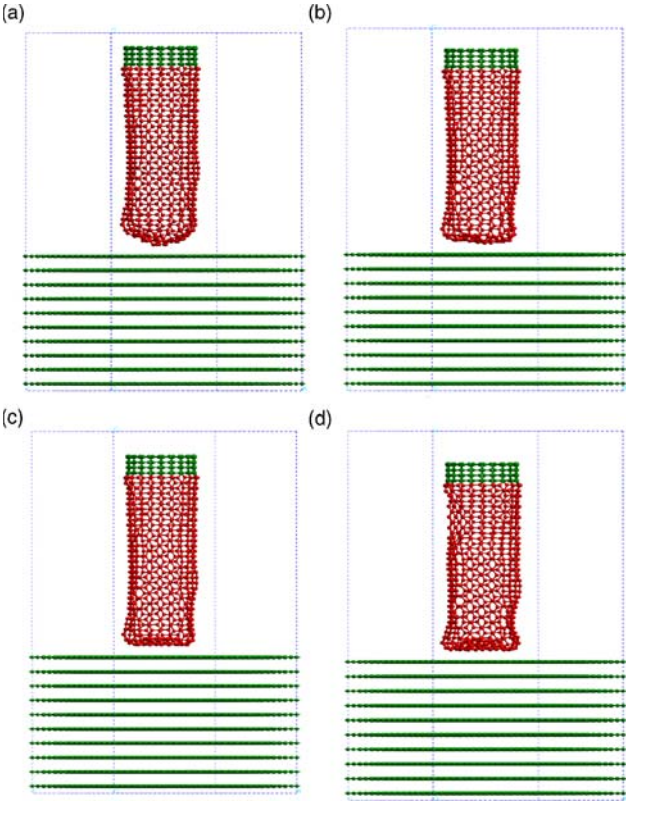

Figure 3. Snapshots from the energy minimisation of the interaction of a capped [10, 10] nanotube with fixed graphite layers at hollow position for (a) $\Delta Z = 2$ Å (b) $\Delta Z = 3.5$ Å (c) $\Delta Z = 4.3$ Å and (d) $\Delta Z = 6$ Å.

After further compression, the structural deformation of the side wall increases gradually and then changes into buckling of the nanotube. The large deformation of the longer nanotube with buckling, bending and slipping from MD simulations is presented in Figure 4. As it can be seen in the figure, the front part of the nanotube after the onset of buckling makes an angle with the graphite surface. After buckling and bending, the slipping of the tip on the graphite surface was observed.

Another series of simulations were performed for different contact angles of nanotubes on graphite surfaces. The contact angle (or impact angle) here is the angle between the nanotube axis and the normal of the graphite surface as shown in Figure 5.

Simulations were performed for seven impact angles in intervals of 5° from 0 to 30°. The nanotubes were initially positioned 6 Å above the graphite surface and moved along the axes of the nanotubes (the direction of the motion is shown by an arrow in Figure 5) up to 20 Å axial displacement. One important quantity for the adhesion is

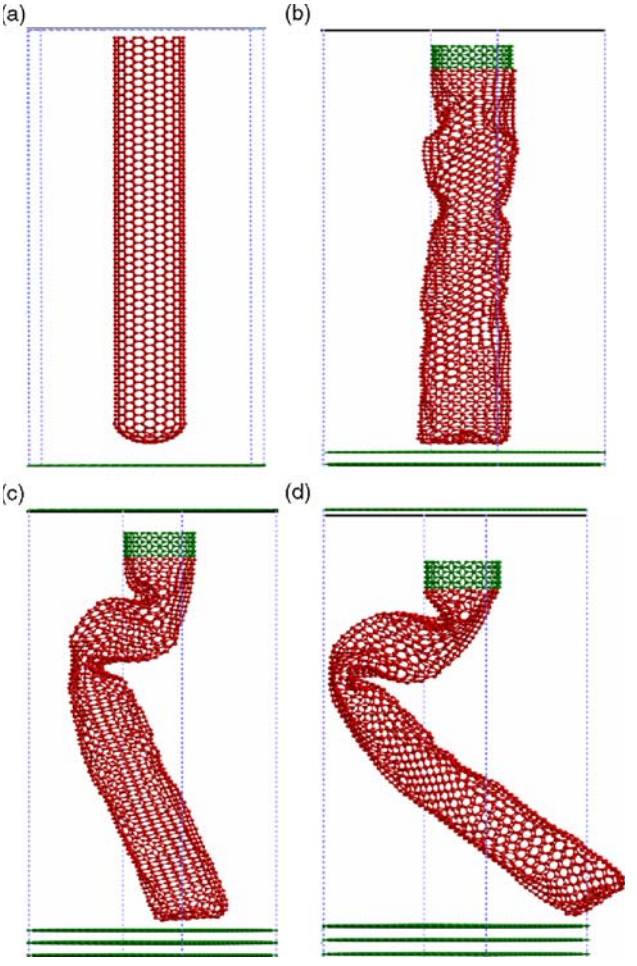

Figure 4. Snapshots from the MD simulations of a long capped (10, 10) nanotube on a fixed graphite surface at hollow position for (a) $\Delta Z = 0$ Å (b) $\Delta Z = 10$ Å (c) $\Delta Z = 20$ Å and (d) $\Delta Z = 40$ Å.

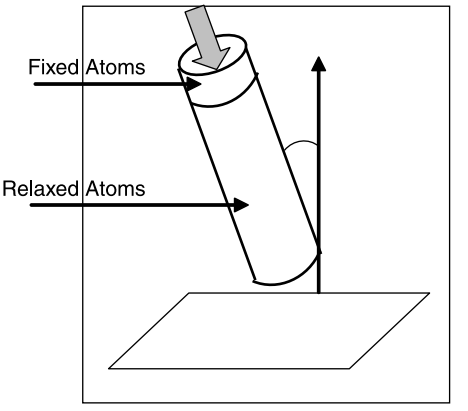

Figure 5. Schematic of the tilted nanotube. The contact or impact angle Θ is defined with respect to the surface normal.

the length of the front part of the nanotube after buckling (i.e. buckling length). The front part would become parallel to the surface after further compression and the main contribution to the adhesion force would be coming from this part. Although van der Waals interaction between the nanotube and the surface is long range, it significantly increases in the 3–4 Å range. When the front portion of the buckled nanotube becomes parallel to the surface, the effective contact area increases which is within the 3–4 Å range. This contact area increase results with stronger interaction between the nanotube and the surface. The buckling length of a buckled nanotube is from the point of buckling to the capped end of the nanotube. The buckling length as a function of impact angles is presented in Figure 6.

In the figure, we can see the variation of buckling length of the shorter tube, which increases slowly at first with the impact angle, and then increases rapidly between 15 and 20° and finally becomes nearly constant after 25°. Beyond 30°, slipping occurs quickly so that buckling of the nanotube could be observed rarely beyond this point. It can

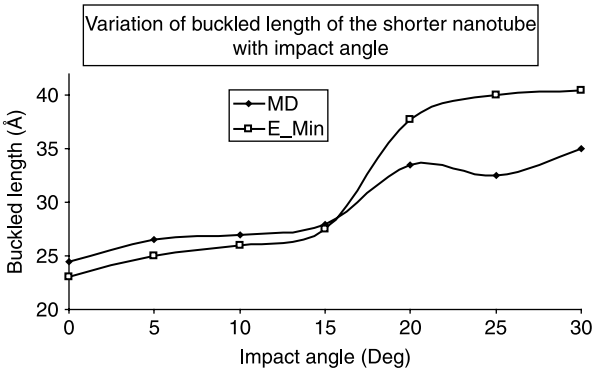

Figure 6. Impact angle dependence of the buckling length of the shorter tube determined from MD simulations and energy minimisation calculations.

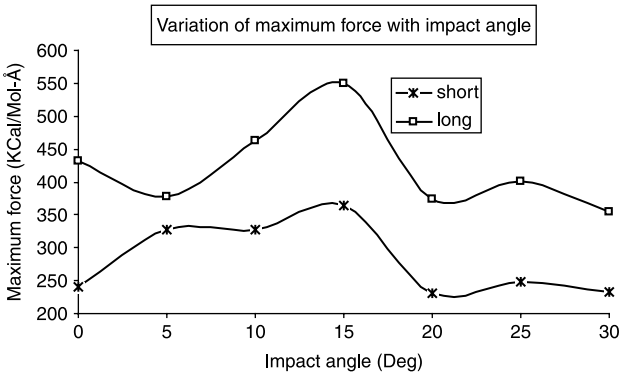

Figure 7. Impact angle dependence of the maximum force experienced by the atoms of tip surface.

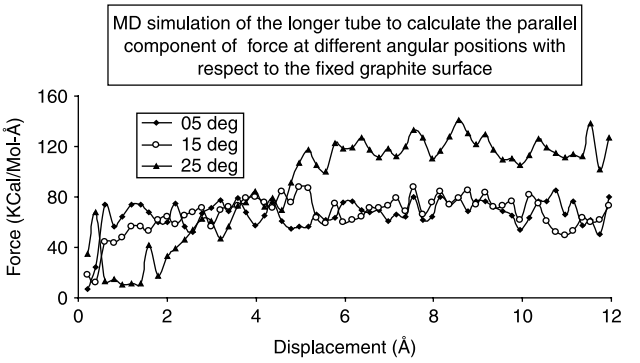

Figure 9. Variation of the parallel component of the total force on the longer nanotube for different impact angles.

be seen clearly in the figure that the buckling length change appears to be significantly larger in the energy minimisation case. This is due to the temperature dependent relaxation of the atoms in the MD simulations. Similar results were also obtained for the longer nanotube.

By performing MD simulations, maximum force values on the nanotubes for different impact angles were determined. These force values are presented in Figure 7. There are two ways to calculate the total force on the nanotube tip. In the first way, the total force is taken as the minus derivative of total potential energy with respect to tip displacement. In the second way, the total force is the vector sum of the forces acting on the individual atoms. Here, for the MD simulations, the second way is used and the maximum force is the magnitude of the maximum calculated force on the nanotube tip during the simulation. The results presented in Figure 7 show that the maximum force depends on the impact angle and has a maximum force at 15°. This angle coincides with the angles, where sudden change in the buckling length was occurred.

The components of the adhesion forces were also investigated. In Figures 8 and 9, we present perpendicular and parallel components of the total force on the nanotube as a function of nanotube displacement along the z-direction for different impact angles. The parallel component of the force was much weaker than the perpendicular component. At zero impact angles, initially the total force is completely from the perpendicular component, however, deformation of the nanotube tip results with buckled nanotube, which makes an angle as it can be seen in Figure 4. This creates a parallel component of the force. For non-zero impact angles, naturally, part of the load is in parallel direction. The perpendicular component of the force first decreases and then increases with the impact angle. We believe this behaviour is due to local atomic structure and local deformation of the nanotube tip. On the other hand, for tilted orientations of the nanotubes, the parallel component increases with the increase of the impact angle as more load is applied in the parallel direction.

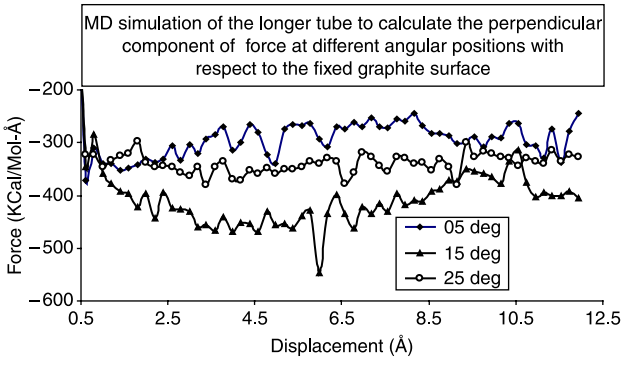

Figure 8. Variation of the perpendicular component of the total force on the longer nanotube as a function of displacement in the z-direction for different impact angles.

The force/area value due to an array of nanotube bundles can be estimated from our MD simulation results. We assume SWNTs form a bundle of radius 25 nm and 0.5 μm is taken as the bundle–bundle separation. If we consider average 31.3 nN force from each nanotube, and assume all of the nanotubes are touching the surface, the estimated force/area value would be 1.02×10^{-1} nN/nm^2. This value is significantly higher than the estimated value 1.6×10^{-2} nN/nm^2 in the experiment. However, when the bundles are in contact with a surface, only smaller number of nanotubes in a bundle would be contributing to the adhesion.

4. Conclusions

Theoretical investigations on the adhesion between nanotubes and graphite surfaces were performed. Atomistic simulations of capped armchair (10, 10) nanotubes with two different lengths on rigid and relaxed graphite surfaces were carried out. Layer-by-layer compression of the tip surface was observed, which is related to the discrete atomic nature of the tip structure. The total potential

energy and deformation of the nanotube cap were dependent on the local atomic surface sites. The buckling length increased slowly at first with the impact angle, and then increased rapidly between 15 and 20°. The maximum force on the nanotube depends on the impact angle and has a maximum at 15°.

Acknowledgements

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