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Interfacial shear strengths between carbon nanotubes

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Abstract
Interfacial shear strengths or static frictions between carbon nanotubes (CNT) in contact at different cross angles are studied by using atomic mechanics. It is shown that the axial interfacial shear strengths between parallel CNTs in commensurate are two orders of magnitude greater than those in incommensurate. This strong chiral dependence is not surprising and is similar to that of the friction between two graphite basal planes. In contrast, we find that the interfacial shear strengths of crossly contacted CNT pairs are much less dependent upon chirality. The estimated values of interfacial shear strengths, ranging from 0.05 to 0.35 GPa, agree very well with experimentally measured results available in the literature. These results may thus be used as a basis for explaining the observed tension strengths of CNT bundles and films that are mainly bonded by van der Waals interactions and the mechanical behaviors of composite materials with highly concentrated CNTs.

1. Introduction
Carbon nanotubes (CNTs) often exist in bundles and/or films, where they are bonded by the van der Waals interaction. The measured tensile strengths of CNT bundles or films have diverse values [1–5], and a quantitative explanation of this diversity is still lacking. In addition, carbon nanotube networks are often observed in highly concentrated CNT composites [6, 7] with the mechanical properties of these composites being remarkably enhanced [6–12]. To understand these phenomena, one can first study the looseness mechanisms of two contacting CNTs. Separation is one of the main looseness modes, and another is relative slide. Since CNTs usually have very large aspect ratios and consequently are flexible against bending, sliding should be a more dominant looseness mechanism. However, unlike the results extensively reported so far about adhering and separating behaviors [13–20], very few have been reported about interfacial shear strengths—the strengths or maximum static frictions per unit contacting area against sliding between two contacting CNTs. Liu et al [18] studied the shear moduli against axial sliding for single-walled CNT bundles. Bhushan [21–23] measured the static and kinetic frictions between two perpendicular CNTs. To the best of our knowledge, this is the sole experimental investigation available in the literature to date on static and kinetic frictions between two CNTs, and neither a theoretical nor molecular dynamics study on this important behavior has been seen. On the contrary, there have been quite a number of studies on frictions between CNTs and graphite, graphite and graphite, and the inner and outer tubes of multiwalled CNTs [24–30]. Here we will show, through atomic mechanics simulations, that the sliding behaviors and interfacial shear strengths between two crossly contacting CNTs are quite different from those of all the above-mentioned three cases.

2. Computational model
The simulation model consists of two single-walled CNTs in contact at different cross angles, bonded by the van der Waals interaction. We adopt the adaptive intermolecular reactive
empirical bond order (AIREBO) potential [31] to model the intratube atom interactions, and the standard 12-6 Lennard-Jones potential [32] \( \phi(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^6] \) with \( \varepsilon = 2.84 \times 10^{-3} \) eV, \( \sigma = 0.34 \) nm [31], and a cutoff length of 2.0 nm to characterize the intertube van der Waals interaction. The AIREBO potential proposed in 2000 [31]:

\[
E = \frac{1}{2} \sum_{i,j \neq i} \left[ E_{ij}^{\text{REBO}} + E_{ij}^{\text{LJ}} + \sum_{l \neq i,j} \sum_{m \neq i,j,k} E_{ijkl}^{\text{tors}} \right]
\]

is a development of the REBO potential \( E_{ij}^{\text{REBO}} \) [33], which characterizes the covalent bonding interactions, through adding the Lennard-Jones interactions \( (E_{ij}^{\text{LJ}}) \) among intratube carbon atoms and torsion interactions \( (E_{ijkl}^{\text{tors}}) \). Since its proposal AIREBO has become a widely used potential for more accurate simulations of systems of carbon and/or hydrogen atoms [34, 35]. In our study we use exactly the same parameters as chosen and justified in [31].

The length of each CNT is taken as 19.3 nm, that is about ten times of the largest CNT’s diameter we simulated. One tube is constrained by setting zero axial displacements for all its end atoms and forcing the mass center of atoms at each end to be immobile. These boundary conditions do not restrict the radial deformation and axial rotation of the tube at all. Another CNT is modeled quasi-statically sliding along its axial direction. It is first put in contact with the constrained CNT at a given cross angle. We determine the configuration at minimized energy of the two tubes. The constraints on the sliding tube are null transverse displacements in the cross plane of all atoms at both ends and null axial displacements of all atoms at one end. These constraints will fix both the cross angle and axial position of the sliding tube, but not its deformation or axial rotation. Then, after having shifted the sliding tube from its initial energy-minimized configuration along its axial direction by a distance of 0.01 nm, we perform a similar procedure to obtain the new energy-minimized configuration and the total free energy. Such a 0.01 nm shift and energy minimization procedure is repeated again and again for modeling the quasi-static sliding motion at a given cross angle. The axial drag force \( F_d \), the force applied by the constrained CNT to the sliding one, is calculated as the gradient \( dU/ds \) of total free energy \( U \) with respect to axial displacement \( s \) by using the difference method. As the drag force \( F_d \) is positive, it prevents the sliding motion; and a negative \( F_d \) accelerates the motion. The positive drag force gives the atomistic origin of static friction [36], or the interfacial shear strength. The latter is defined as the maximum value of \( F_d \) per unit contact area. In the special case where the two studied CNTs are parallel to each other, we adopt a periodic boundary condition with the super-cell length of 19.3 nm. In kinetic friction motion, however, a positive or negative \( F_d \) results in a sticking or slipping phenomenon, respectively, and the well-known stick-slip motion [37, 38]. The damping during this motion is the atomistic origin of kinetic friction [36, 39]. In this paper, we limit ourselves to investigating the interfacial shear strengths.

3. Results and discussions

3.1. Quasi-static sliding behaviors of two parallel CNTs

The simulated drag forces between two parallel CNTs versus axial relative quasi-static sliding distances are plotted in figure 1(a). The pairs of CNTs we modeled are two armchair (5, 5) tubes (A–A tubes), two zigzag (9, 0) tubes (Z–Z tubes), and one (5, 5) plus one (9, 0) tubes (A–Z tubes). The diameters of the armchair and zigzag tubes are both approximately equal to 0.67 nm. The results shown in figure 1(a) reveal that the maximum drag forces per unit axial length for the A–A and Z–Z CNTs are almost the same 43.2 pN nm\(^{-1}\). In comparison, the maximum drag force per unit length of the A–Z tubes is just 0.08 pN nm\(^{-1}\), only 1/540 of those of A–A or Z–Z tubes. Such a conclusion, that an incommensurate A–Z CNTs pair in contact has a much smaller interfacial shear strength than that of a commensurate A–A or Z–Z CNTs pair, is consistent with previous results for relatively sliding inner and outer tubes of multiwalled CNTs [40] and sliding small graphite flakes on graphite basal planes [41].

We also calculated the drag forces for some larger CNTs. The obtained maximum drag forces per unit length and the interfacial shear strengths versus CNT diameters are depicted in figures 1(b) and (c). For estimating the strengths, the contact areas are calculated as the total occupied regions of all atoms on the sliding tube that are distant from the constraint tube by less than 0.34 nm. These results lead to following conclusions. Firstly, the interfacial shear strengths of Z–Z tubes are approximately five times of those of A–A tubes. They tend to constant values of \( \sim 0.25 \) and \( \sim 0.05 \) GPa, respectively, for Z–Z and A–A tubes when the diameters become larger than 1 nm, and for smaller tubes both of them have remarkably higher strengths. Secondly, although the interfacial shear strengths of A–Z tubes increase with the enlarged diameters, their values (0.5–1.0 MPa) are in general 2–3 orders in magnitude lower than those of the commensurate tubes (A–A and Z–Z tubes). Thirdly, for engineering applications, it is useful to define the nominal strength as the maximum drag force per unit length divided by the tube diameter. From figure 1(d) we noticed a dependence of the nominal strengths to diameters similar to those of the usual strengths (figure 1(c)).

To understand why the interfacial shear strength increases as the CNT diameter reduces in the diameter region \(< 1 \) nm, we made cartoons of the sliding motions based on the simulated energy minimization configurations for a series of ‘time’—sliding distance. Figures 2(a) and (b) show the frame series versus sliding distance selected from two typical cartoons (supplementary information, available at stacks.iop.org/Nano/21/115704/mmedia) for the tube pairs (10, 10)@10, 10) and (5, 5)@(5, 5). We find that the sliding motion of the former accompanies a significantly larger swing than that of the latter, allowing the former to move along the lowest energy groove (blue solid line in figure 2(c)) from an AB stacking contact to another AB stacking contact. This property is common for all the simulated larger tubes, and thus leads to diameter-independent interfacial shear strengths. The sliding trajectory of the pair (5, 5)@(5, 5) is however not along an AB stacking sequence (purple dashed line in figure 2(d)).
Figure 1. The drag forces versus axial sliding distances and interfacial shear strengths of two parallel CNTs. (a) The red line with triangle symbols and blue line with square symbols are for two (5, 5) and (9, 0) tubes, and the black line in the insert is for the (5, 5)@(9, 0) tube pair. (b)–(d) The maximum drag forces, interfacial shear strengths, and nominal interfacial shear strengths versus tube diameters, the red line with circle symbols and blue line with square symbols are for Z–Z and A–A tubes and the black line with triangle symbols in the inserts is for A–Z tubes.  

It experiences a more furious fluctuation and consequently a greater sliding resistance.

3.2. Interfacial shear strengths between cross contacting CNTs

Figure 3 shows the plots of simulated interfacial shear strengths of three 0.67 nm- and three 2.0 nm diameter tube pairs with different chiral combinations. From these plots we have three conclusions as follows. First, the strengths of all tube pairs are weakly dependent upon cross angles, except for a sharp peak (double the average values that are about 0.2 GPa for the three small tube pairs or 0.18 GPa for the three large pairs) at 30° cross angle for the A–Z tubes, or at 60° cross angle for the A–A and Z–Z tubes. It is noticed that in either sharp peak cross angle, the tube pair reaches its commensurate contact. This is not surprising because the energy barrier of sliding in commensurate contact is much larger than that in the incommensurate case. Thus, the interfacial shear strength will reach a peak at those angles. Second, the strengths of the three smaller tube pairs with diameters about 0.67 nm are double those of the three larger pairs with diameters about 2.0 nm correspondingly. This property is consistent with what we have observed for parallel tube pairs (figure 1) and can therefore be explained in a similar way. Third, it is somewhat surprising that the interfacial shear strengths of cross contacting tube pairs are almost independent of their chiral combinations. In particular, the interfacial shear strengths of the A–Z tube pairs are almost the same as those of the A–A and Z–Z tube pairs with similar diameters. All the above results could be explained by the following understanding. For sliding an incommensurate contact area, the van der Waals interaction energy fluctuations of individual atoms will be canceled by each other if the contact area is large enough. This is just the case for axial sliding between two parallel incommensurate tubes, when the interfacial shear strength becomes very small. In contrast, although the contacts at most cross angles for A–A or Z–Z tubes except 60° are incommensurate, their interfacial shear strengths remain on the same levels as those for commensurate
Figure 2. (a), (b) Frame series versus sliding distance, and (c), (d) equipotential surfaces as a function of the relative position of two CNTs for tube pairs (10, 10) and (5, 5), respectively. The original of coordinates denotes the initial energy-minimized structure (i.e. AB stacking position). The red regions in (c) and (d) corresponds to the highest potential and dark blue regions the lowest potential. The blue solid line and purple dashed line indicate the sliding trajectories of (10, 10)@(10, 10) and (5, 5)@(5, 5) CNT pairs, respectively.

Figure 3. Interfacial shear strengths of different chiral CNTs with different diameters as a function of cross angles.

contacts because of the small contact areas in the cross sliding mode. This understanding has an additional implication that the interfacial shear strengths with incommensurate cross contacts will decrease as the tube diameters increase.

3.3. Comparison with experiments

Recently, Bhushan et al [22] measured the static frictions between a single-walled CNT of 1.43 nm diameter and a multiwalled CNT of 70 nm diameter at 90° cross contact. They found that the friction force is about 1.3 nN. Using the Hertzian contact relation for two isotropic and homogeneous cylinders with the assumption of Young’s modulus being equal to the CNT axial modulus, about 1060 GPa, they estimated that the static friction or interfacial shear strength is 1.4 GPa, one order of magnitude greater than our simulation results (0.05–0.25 GPa, see figure 3). However, it is known that multiwalled CNTs are highly anisotropic, with much a lower radial modulus (about 30 GPa [42]) than the axial one. Due to the compression nature, the Hertzian contact area, which is inversely proportional to \( E^{2/3} \), is dominated by the radial rather than the axial modulus. The interfacial shear strength, which is inversely proportional to contact area, will be proportional to \( E^{2/3} \). We thus conclude that the interfacial shear strength 1.4 GPa claimed by Bhushan et al [22] must have been overestimated by \( (1060/30)^{2/3} \approx 10.7 \) times. The above analysis leads to a revised experimental value, which may give an excellent approval of our atomic simulation predictions of interfacial shear strengths between two CNTs.

4. Conclusions

In the present work, the interfacial shear strength between two CNTs at different cross angles is investigated with atomic simulations. The interfacial shear strength is considered as caused by van der Waals interaction. For two parallel SWCNTs, it is shown that the axial interfacial shear strengths...
of CNTs having the same chiralities (e.g. Z–Z and A–A pairs, commensurate contact) are about two orders of magnitude larger than those of CNTs having different chiralities (e.g. A–Z pairs, incommensurate contact). The interfacial shear strength of a Z–Z CNT pair is about 5 times larger than that of an A–A CNT pair and about 500 times larger than that of an A–Z CNT pair. In addition, CNTs with diameters larger than 1.0 nm will slide relatively from an AB stacking position to the next nearest AB stacking position while smaller ones do not slide through AB stacking positions. The former needs to overcome a lower van der Waals energy barrier and has a lower interfacial shear strength. For two cross contacting CNTs, the magnitude of interfacial shear strengths of different CNT pairs (e.g. Z–Z, A–A, A–Z pairs) are on the same level, much less dependent upon chirality, because the van der Waals interaction energy fluctuations of individual atoms can not be effectively canceled by each other in the small contact areas. The estimated interfacial shear strengths between two CNTs agree reasonably with existing experimentally measured results. The present results are expected to be helpful in understanding the enhancement mechanism of CNT networks in our future work.

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