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Gearlike rolling motion mediated by commensurate contact: Carbon nanotubes on HOPG

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We report on experiments in which multiwall carbon nanotubes (CNT's) are manipulated with atomic force microscopy (AFM) on a graphite highly oriented pyrolytic graphite (HOPG) substrate. We find certain discrete orientations in which the lateral force of manipulation dramatically increases as we rotate the CNT in the plane of the HOPG surface with the AFM tip. The threefold symmetry of these discrete orientations indicates commensurate contact of the hexagonal graphene surfaces of the HOPG and CNT. As the CNT moves into commensurate contact, we observe the motion change from sliding/rotating in-plane to stick-roll motion.

The interaction between two bodies in contact is ultimately determined by the interaction between atoms. The arrangement of the atoms in two interacting surfaces has been shown to play a critical role in the energy loss that occurs when one body slides over a second both in experiment,[1,2] and simulation.[3–5] In particular, in the case of two contacting solid crystalline surfaces, the degree of commensurability has been shown to have a clear effect on friction.[6–8] Understanding the effect of these atomic interactions on energy loss[9–12] and object motion is important for designing lubrication strategies and self-assembly processes, and will determine the forms of atomic-scale actuating devices.[13] Current microelectromechanical (MEMS) devices have features typically in the size scale of ten microns, and gears have been fabricated with teeth measured in the same size range. It is of great interest to understand the ultimate scale of actuating devices, and in what manner atomic interactions will play a determining role.[14] Atomic force microscopy (AFM) manipulation studies provide unique opportunities to probe the mechanical behavior between objects in that more motional degrees of freedom can be accessed (sliding, rolling, rotating in-plane) than in tip-on-substrate friction studies. Whether in the context of nanometer scale mechanical devices, biological systems, or the basic understanding of energy loss mechanisms in frictional processes, it is of interest to study both sliding and rolling contacts and why a system prefers one mode of motion over the other.

In the present work, we describe experiments in which we are able to controllably tune the commensurability between the two contacting atomically smooth crystalline surfaces. As a model system for such studies, CNT's and highly oriented pyrolytic graphite (HOPG) offer a well defined geometry with atomically smooth surfaces that can remain relatively clean in ambient laboratory conditions. We show that the interlocking of the atomic lattices in the contact region of two bodies increases the force required to move the CNT, and can determine whether the CNT slides or rolls. In essence, the atomic lattice can act like a gear mechanism.

Our evidence for rolling motion has been published previously.[15] Briefly, this evidence consists of topographical changes consistent with rolling, translation without in-plane rotation, and lateral force traces during rolling showing periodicity equal to the nanotube circumference. The periodic lateral force traces indicate rolling without slipping motion. This along with the evidence for commensurate contact that we are presenting here, imply that the nanotube remains in commensurate contact through the entire rolling period. The atoms of the tube and substrate are meshing as in a rack-and-pinion gear mechanism. We have manipulated CNT on mica, MoS_2, SiO_2, Si_3N_4 and observed no example of commensurate contact or rolling. In all of our observations, commensurate contact is a necessary condition for rolling.

The CNT's were prepared by the arc-discharge method.[16] A suspension was prepared by sonicating the CNT material in ethanol and then drip dispersing and evaporating onto HOPG. AFM (Ref. 17) manipulations, performed in ambient conditions, employ an advanced operator interface called the nanomanipulator (nM).[18–20] This system provides ability to perform complex manipulations, as well as transparent switching between low force noncontact AFM for imaging and contact AFM for manipulation. During each manipulation, the calibrated lateral force[21,22] is monitored as a measure of the CNT substrate friction. As the AFM tip is pushed into contact with the CNT in a trajectory perpendicular to its axis, the CNT undergoes either a sliding in-plane rotation motion, or rolling with a constant in-plane rotational orientation[15] (Fig. 1, lower inset). The CNT's move as rigid bodies, which is expected for CNT's of this size (10–50 nm diameter, 500–2000 nm length) considering their high stiffness and the low friction of the graphite substrate.[23]

When a CNT lying in an incommensurate state is manipulated, it slides smoothly and rotates in-plane.[15] However, this motion is interrupted at discrete in-plane orientations in which the CNT ''locks'' into a low-energy state,[24,25] indicated by an increase in the force required to move the CNT. Figure 1 shows a lateral force trace illustrating the pronounced change in the force in going from the commensurate to incommensurate state and visa versa. The change in lateral force is roughly an order of magnitude, which is typical of our measurements we have made on other CNT's. We resolve no gradual change in lateral force between the two states. The change of force as a function of in-plane rotation angle is discontinuous within our ability to measure it $(+/-1$ degree).

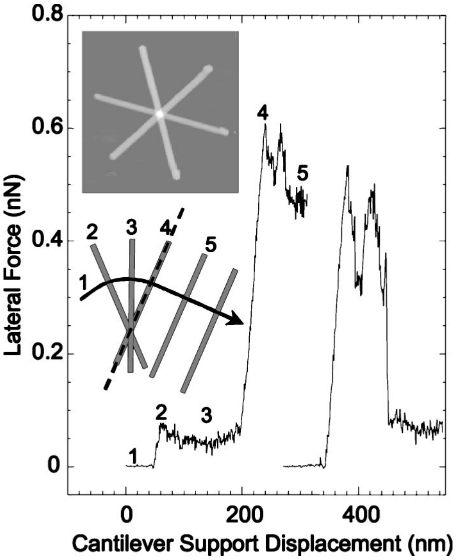

FIG. 1. Lateral force trace as a CNT is rotated into (left trace) and out of (right trace) commensurate contact. The lower inset shows a top-view schematic, the process for the left trace. The AFM tip is moving along in contact with the graphite substrate (1), the CNT is contacted (2) and begins rotating in-plane (3), the commensurate state is reached (indicated by the dashed line) and the lateral force rises dramatically (4) before rolling motion begins (5). The right trace begins with the tip on the substrate, the tip then contacts the CNT in the commensurate state, begins rolling and then pops out of commensurate contact and begins rotating in plane with a corresponding drop in lateral force. The upper inset is a composite of three AFM images of a CNT in its three commensurate orientations. Note that the nanotube was not rotated about its center as the composite implies. The images were translated in order to emphasize the 60 degree intervals.

As the nanotube is rotated in-plane, several of these discrete commensurate orientations are observed, each separated by 60+/−1 degrees (Fig. 1, upper inset). These orientations and the associated increase in lateral force are reproducible for a given tube. We believe this registered state corresponds to graphitic ABA stacking. Our hypothesis is supported by molecular statics calculations[26] of CNT on HOPG. These calculations show pronounced energy minima separated by 60 degree intervals as the CNT is rotated in-plane, that correspond to ABA stacking.

The sequence in Fig. 2 shows two CNT's lying on the same immediate area of the graphite substrate. While each CNT shows the complete set of commensurate locking behaviors described above, the two CNT's have lock-in orientations that differ by 11 degrees. The sequence depicts a series of manipulations in which the tubes are rolled individually across the same region in order to verify that the difference in their orientations is not due to an inhomogeneity in the graphite substrate. If lock-in orientations are due to commensurate registry, the particular set of commensurate orientations is determined by the CNT chirality (the wrapping orientation of the outer graphene sheet of the CNT). Large multiwall CNT's of different diameters are expected to have different chiralities[27] and should show different commensurate orientations.[26]

Another manipulation emphasizes the robust gearlike motion of CNT's in the atomically registered state. We have manipulated two CNT's into a collision to observe the subsequent motion [Fig. 2(c)]. The lateral force trace [Fig. 2(d)] shows characteristic periodicity for the first tube before the collision, then an increase in the lateral force after the collision. Both CNT remain in their commensurate orientations after the collision.

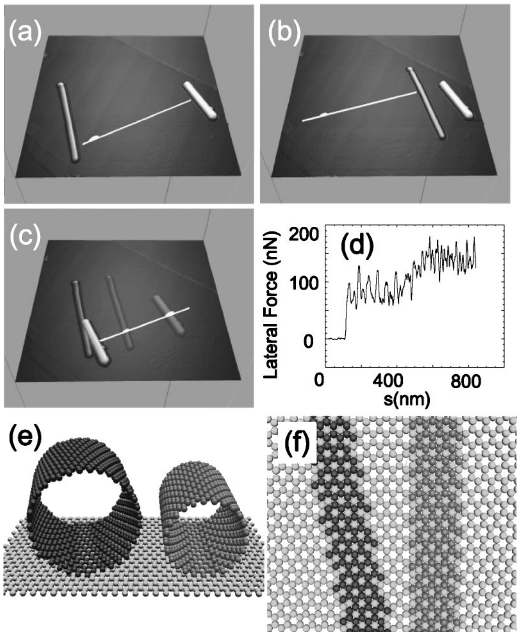

FIG. 2. Manipulation of CNT on HOPG. The threefold locking axes for the tubes are off by 11 degrees relative to each other. (a) The white streak indicates the trajectory of the AFM tip during the manipulation, from lower left toward upper right. Both CNT are pushed from lower left to upper right (a)–(b). After (b), both CNT's are individually pushed back across the same area and as (c) indicates, the shorter CNT has been pushed into contact with the longer CNT such that both tubes translate further (the fainter CNT's show the original position and the bold CNT's show the final position). Figure (d) shows the lateral force during this manipulation. (e) Model of two nanotubes resting in commensurate contact on a HOPG surface. Lying on the left is a (25, 5) CNT and on the right, a (25, 0) CNT. (f) Shows the contact zone of the commensurate lattices. The tube axes of the two CNT's are 11 degrees relative to each other when in commensurate contact. This model of the two tubes is shown to stress the point that tubes of differing chiralities will have differing orientations of the tube axis when in commensurate contact.

The fact that these commensurability effects are robust in ambient conditions suggests that despite environmental contamination and capillary condensation of water, the contact zone remains relatively clean and dry. It is possible that the commensurate effects occur with intervening contamination layer, but we find this possibility unlikely. Any contamination and water are most likely simply being excluded from the contact zone. Graphite is hydrophobic and should have no appreciable water layer at the relative humidity in which we performed the experiment (2–20% R.H.). We observe no humidity dependence of the phenomena within this range. In order to address organic contamination from the air, we cleaned the sample before all experiments using ultraviolet radiation.

We have presented results on what we believe to be the first demonstration of tunable commensurability in a nanometer scale contact. The contrast of the friction in the commensurate and incommensurate states is dramatic (order of magnitude) and abrupt (a discrete change within our uncertainty). We find that for this system, the transition from the incommensurate to commensurate state is accompanied by a transition from sliding motion in which the CNT rotates in-plane, to gearlike rolling motion. Our present experimental plans are to gain further insight into commensurate state through electrical transport measurements across the CNT/HOPG interface, and measurements focusing on atomic scale features in the lateral force.

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