Nanotechnology **8** (1997) 95–102. Printed in the UK PII: S0957-4484(97)80523-5

Molecular dynamics simulations of carbon nanotube-based gears

Jie Han†, Al Globus, Richard Jaffe and Glenn Deardorff

NASA Ames Research Center, Moffett Field, CA 94035, USA

Received 30 December 1996, in final form 17 March 1997

Abstract. We use a molecular dynamics simulation to investigate the properties and design space of molecular gears fashioned from carbon nanotubes with teeth added via a benzyne reaction known to occur with C_{60}. Brenner's reactive hydrocarbon potential is used to model interatomic forces within each molecular gear. A Lennard–Jones 6–12 potential or the Buckingham (exp +6) potential plus electrostatic interaction terms are used for intermolecular interactions between gears. A number of gear and gear/shaft configurations are simulated on parallel computers. One gear is powered by forcing the atoms near the end of the nanotube to rotate, and a second gear is allowed to rotate by keeping the atoms near the end of its nanotube constrained to a cylinder. The meshing aromatic gear teeth transfer angular momentum from the powered gear to the driven gear. Results suggest that these gears can operate at up to 50–100 GHz in a vacuum at room temperature. The failure mode involves tooth slip, not bond breaking, so failed gears can be returned to operation by lowering the temperature and/or rotation rate.

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1. Introduction

The unique properties of fullerenes in dimension and topology allows one to design various nanodevices and molecular machinery parts. Figure 1 illustrates a carbon nanotube-based gear approximately two nanometers across. Shafts are single-walled carbon nanotubes and gear teeth are benzyne molecules bonded onto the nanotube. Compared with the diamonoid molecular planetary gear designed by Drexler [1], and Robertson *et al*'s fullerene based nanogear [2], the nanotube-based gears shown in figure 1 are much simpler in structure and may be synthetically accessible.

The idea of carbon nanotube-based gears comes from recent progress in fullerene science and technology. Multiwalled and single-walled nanotubes have been successfully prepared and rapid advances have been made in controlling tube diameter, length, chirality and the number of concentric shells [3]. Carbon nanotubes have many attractive material properties. For example, experiment and theory have demonstrated that nanotubes have exceptionally high Young's modulus and nanotube electronic properties vary as a function of diameter and chirality [4]. These properties have opened doors to electronic, optical, magnetic and mechanical applications. It has been shown that nanotubes can be used as atomic-scale field emitters [5], electronic switches [6], and pinning materials in high-T_c superconductors [4]. In addition, the functionality of fullerene materials provides opportunities to fabricate novel nanodevices. Filled nanotubes leading to improved catalysts and biosensors are being developed [7] and monoadducts and multiple adducts on C_{60} are finding applications [8]. Therefore, it may be possible to make gears by bonding rigid molecules (gear teeth) onto nanotubes. It may be practical to position molecular teeth in atomically precise positions required for gear design by, say, scanning tunneling microscopy (STM) techniques. Recently, IBM scientists [9] have succeeded in positioning individual molecules at room temperature by purely mechanical means. They used the extremely fine tip of an STM to position organic molecules having a total of 173 atoms and a diameter of 1.5 nm.

Our extensive quantum chemical calculations and molecular simulations support the chemical feasibility of nanotube-based gears [10]. A simple approach is to bond rigid planar benzyne molecules onto a nanotube. The calculations are in agreement with experiment for napthylene and buckyballs (C_{60}) while experimental verification using nanotubes has not been reported. This paper evaluates the nanotube-based gears via molecular dynamics simulation. By studying the rotational dynamics of gears under various conditions, we determine favorable gear working conditions and characterize gear performance.

2. Simulation details

We have chosen Brenner's potential to describe bonded interactions [11]. This potential realistically describes

† To whom correspondence should be addressed. E-mail address: han@nas.nasa.gov

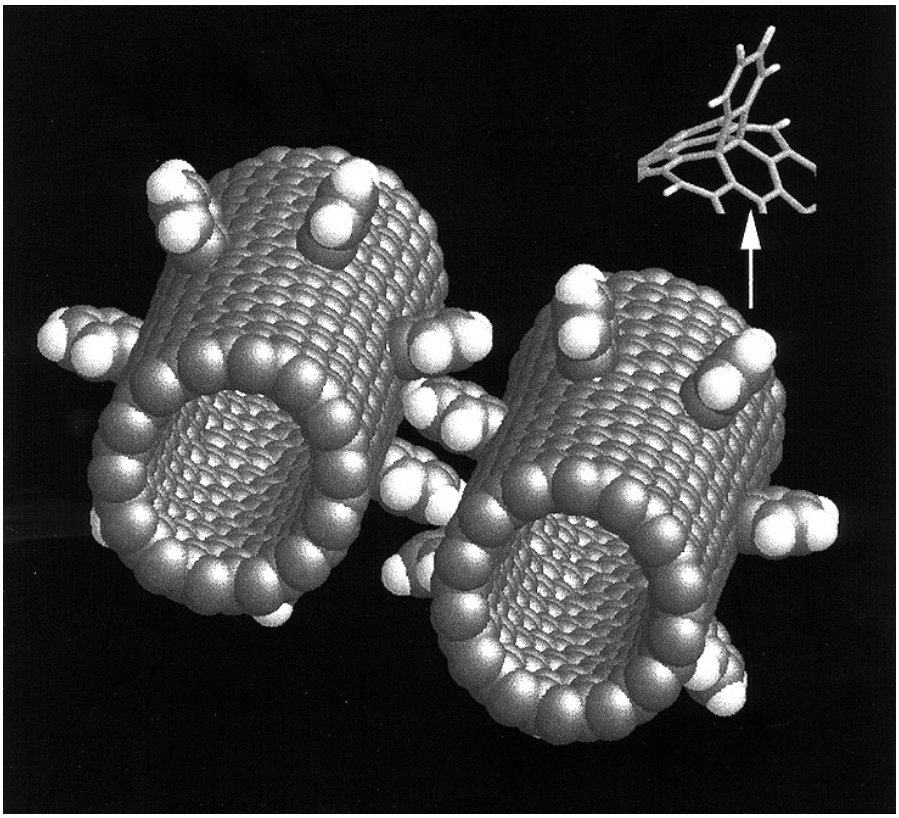

Figure 1. Carbon nanotube-based gears with benzyne teeth.

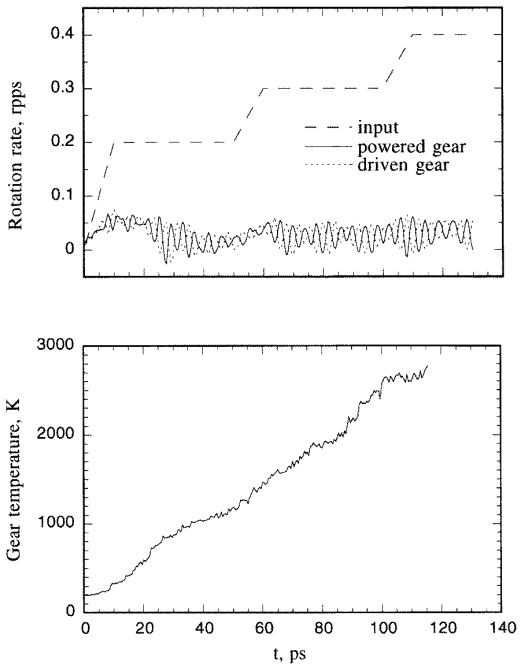

Figure 2. Rotation rate and gear temperature for gear simulation without temperature control.

bonding structure and properties in graphite, diamond materials and small hydrocarbon molecules. In addition, its proper description of bond forming and breaking can be used to observe possible reactive molecular gear failure modes. For intermolecular interactions between different gear atoms, we used and tested several force field potentials: Lennard–Jones (6–12) with parameters derived from fitting graphite and C_{60} experimental data [12] and the Buckingham (exp +6) plus electrostatic interaction terms derived from benzene dimer energy and structure [13]. We carried out molecular mechanics calculations of C_{60}, nanotubes and molecular gears to test these force fields. Minimized energy and C–C bond length are the same as reported values for C_{60} and nanotubes [14]. Energy minimization shows that the nanotube-based gears are stress-relaxed structures, with a slight higher energy than nanotubes ($< 5\%$, depending on length). A detailed comparison with quantum chemistry results is given separately [10]. It shows that Brenner's potential is in good agreement with most of our quantum chemistry results.

Molecular dynamics (MD) simulations were performed on the energy optimized structures. The equations of motion were integrated using a fourth-order predictor-corrector algorithm with a time step of 0.5 fs. The Brendersen's thermostat [15] was used to control the gear's temperature with a time constant of 0.4 ps. This constant was chosen to give a reasonable fluctuation of $\sim$10 K around the assigned temperature. The average temperature had a variation of $\sim$2 K for all the constant temperature simulations. The rotational velocity components in the total atomic velocity were subtracted for evaluation of the thermodynamic temperature. Angular velocity was

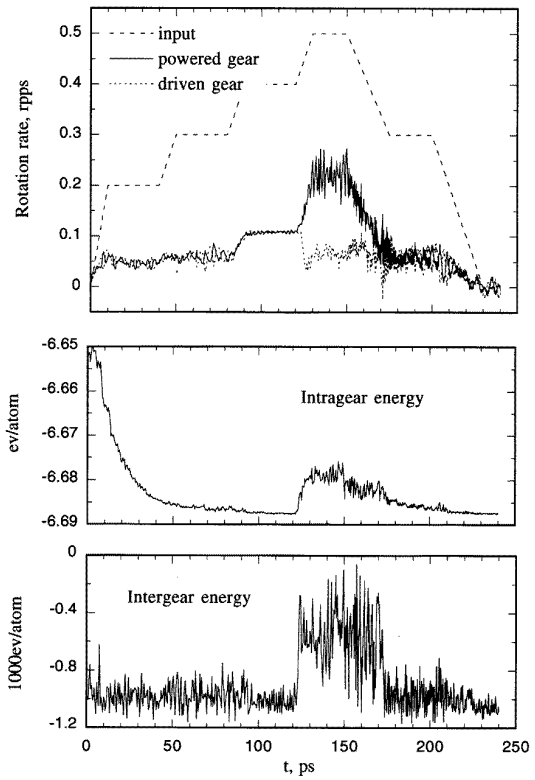

Figure 3. Rotation rate and energy for gear simulation with temperature control.

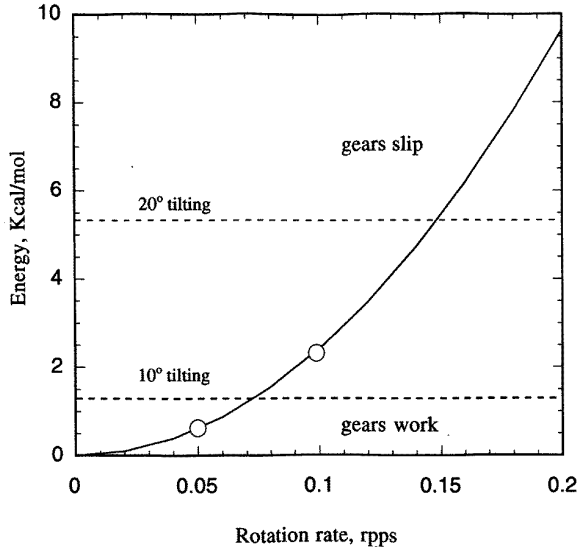

Figure 4. Predicting gear operations as a function of rotation rate and tooth tilting energy.

measured for each atom and averaged for each gear for each input angular velocity. Most MD runs were done on the NAS (NASA's numerical aerospace simulation facility) SP2 by a parallel MD algorithm using replicated data.

In simulations of gear rotation, the gears must be kept correctly positioned relative to each other. This is accomplished by constraining the atoms near the end of each tube (usually two rows of rings at each end). In our simulations, a spring model was used to connect the end atoms to a massless mount and model the interaction between them and massless mount atoms. The interaction potential was simply represented by a harmonic function similar to a bond stretching potential with a force constant of 19.0 eV. This value was found to be appropriate for limiting translation of nanotubes within a range of $\sim$2 Å. No buckling was observed. We call this method the 'hot end model'. In contrast, if the end atoms are only allowed to rotate, with no thermal motion, we call this the 'cold end model'. The cold end model was used by Robertson *et al* [2]. These two models can constrain tube end atoms to stay on a cylinder and therefore maintain the relative position of two gears near a constant value. However, the hot end model is more realistic for temperature effects since it includes the thermal contribution of the end atoms on gear performance. In this paper, we only used the hot end model.

One gear must be powered to rotate. A MD simulation study showed that nanotubes could be rotated by adding charges to the tube and applying one or two oscillating laser fields [16]. We model the powered gear by giving its tube end atoms an angular velocity every time step. Once the end atoms are driven to rotate, strain between them and neighboring atoms is induced. In order to release strain, neighboring atoms must rotate with the end atoms. Thus, rotational momentum is transferred to all other atoms and the gear rotates due to interatomic interactions. Since such interaction use strong bonded forces, one can expect a very effective momentum transfer and a very high rotation rate.

When the powered gear turns, the flat face of each aromatic tooth pushes against the face of the corresponding aromatic tooth on the driven gear. Van der Waals repulsion forces the driven gear teeth out of the way and the induced strain with the driven tube causes the entire driven gear to turn at a rate approximately that of the powered gear.

3. Results

3.1. Adiabatic rotation dynamics of gears

The system of interest is shown in figure 1. The two gears were made of [14, 0] nanotubes with a diameter of 11.0 Å. Each nanotube has seven benzyne teeth where each benzyne is bonded onto the bond between six-membered rings (2 + 2 adduct in organic chemistry [10]) and each pair is separated by two six-membered rings around the nanotube. The number of atoms in these simulations is about 1000 (short tube with a length of 25 Å) and 2000 (long tube with a length of 50 Å). The spacing between two nanotubes is 18 Å and the smallest distance between a tooth atom and a tube atom is $\sim$4 Å. The gears should work well in vacuum since there is no drag to resist their rotation. The problem, however, is that heat generated by friction cannot be removed. The accumulated heat eventually causes the gears to slip. Figure 2 shows the adiabatic rotation dynamics of the short tube gears in vacuum.

Some observations can be made from figure 2. The gears were initially at a minimized energy state at 200 K. Input angular velocity was then increased linearly from

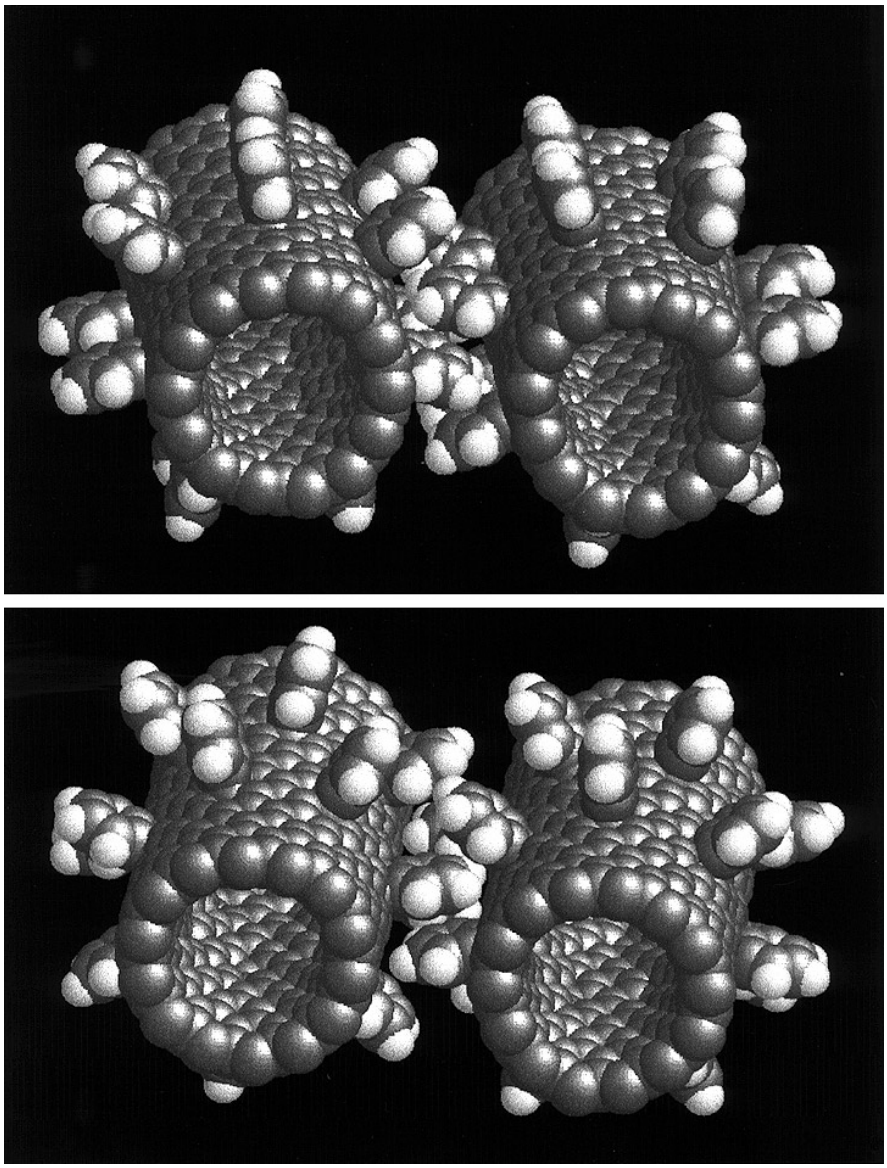

Figure 5. In-line (above) and off-line multiple rows of teeth gears.

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0 to 0.2 rpps (revolutions per ps) in the first 10 ps and then stayed at 0.2 rpps for up to 50 ps. Consequently, the gears started rotating with a linearly increasing rate from 0 to 0.05 rpps. During this period, heat accumulated and the temperature increased from 200 to 600 K. The gears worked well. But, heat generated from atomic friction accumulated and the temperature increased to $>$ 1000 K after 30 ps. At higher temperatures, input energy could not be effectively converted into rotational motion; the gears only wiggled and the measured rotation rate decreased. If the input rate was again increased from 0.2 to 0.3 rpps, the gears resumed rotation and the measured rate also increased. However, increasing temperature ($\sim$2000 K) forced the gears to return to the wiggling state with the measured rotation rate decreasing. At this high temperature, continuing to increase the input rate failed to rotate the gears. The critical temperature for gear operation is about 600–1000 K, as estimated from the current study. The gears cannot work well beyond this temperature. Note that no bond nor tooth breaking occurs up to at least 3000 K.

An interesting observation is that the input rate is not equal to the measured rate with hot end conditions. When the end atoms of a nanotube are given an angular velocity, strain and stress are induced between them and neighboring atoms. These atoms must move to release the strain. In the cold end conditions, end atoms are not allowed to move back in the direction of rotation; the neighboring atoms have to move forward and therefore the input rate should equal the measured rate. In contrast, hot end atoms can move back as neighboring atoms go forward and the input rate in this case is always larger than the measured rate, as shown in figure 2.

Table 1. Intergear energy (1000 eV/atom) and slip rate of gears.

Intergear potential	Energy (before slip)	Energy (after slip)	Slip rate, rpps
12 + 6 [12]	-1.0000 ± 012	-0.5250 ± 035	$0.10 \sim 0.12$
12 + 6 + Brenner [11]	-1.0100 ± 010	-0.5170 ± 038	$0.10 \sim 0.12$
exp +6 + columbic [13]	-0.9880 ± 016	-0.5100 ± 045	$0.10 \sim 0.12$

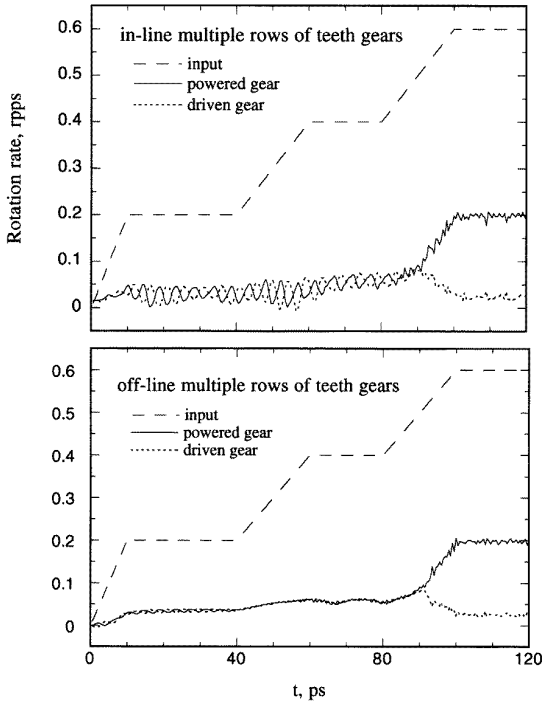

Figure 6. Rotation rate for in-line and off-line multiple rows of teeth gears. Notice the chattering in the in-line case.

3.2. Isothermal rotation dynamics of gears.

It is common sense to maintain constant kinetic temperature for gears to work. In MD simulations, constant temperature is often obtained by an artificial thermostat which controls temperature by a thermal conduction equation; not by a real cooling medium. Such a model system can provide information on isothermal dynamics in a constant temperature system without any coolant-gear molecular interactions. Figure 3 shows the isothermal rotation dynamics of the gear system in figure 1.

In the first 120 ps, the measured rotation rate of the two gears increases with increased input rate and the averaged values for the two gears are basically identical. A very interesting case can be made from the energy curve in figure 3. As the rotation rate increases centrifugal force stiffens the gears and the energy decreases. At the input rate of 0.4 rpps, the gear operation is remarkably more stable than in the rest of the simulation as seen from smaller fluctuations around 0.1 rpps. This is because of stabilization of larger centrifugal forces for the gear operation in that system energies reach minima as seen in figure 3. Beyond 0.1 rpps, a slip occurs as the rotation rate continues increasing or stays at a higher value for the powered gear and the rotation rate of the driven gear decreases. When the gears slip, intergear energy and bonded internal energy jump to a higher value. Obviously, this jump does not signify bond breaking nor tooth breaking because the energy change is small. Therefore, the gears should resume working if the input rate is reduced. It can be seen from figure 3 that the measured rotation rate and energies return to reasonable values when the input rotation rate decreases. When gears fail they slip rather than fragment (i.e. no bonds break). When the conditions that led to failure are removed, intermolecular forces will cause the gear teeth to straighten out and mesh properly, and the gears go back to a low energy state and start working again. This offers an operational advantage. A trial and error procedure can be used to establish operation conditions for *physical gears* without needing to worry about destroying them.

When the rotation rate approaches the critical value, 0.1 rpps, the benzyne molecular teeth start tilting. This tilting allows the gear teeth to slip at the expense of increasing both intergear and intragear energy. A rough estimation is that tilting at 20° will induce slip but the gear can still work when the tilt is up to about 10°. Relative to the energy of a stable tooth configuration, the tilting energy at 10° and 20° is 1.4 and 5.6 kcal mol^{-1}, respectively, from our quantum mechanics calculation [10]. These two values are represented by two dotted lines plotted in figure 4. Rotational kinetic energy of gear teeth is a function of the diameter of gear and rotation rate, as shown in figure 4. If the rotational kinetic energy is greater than the tilting energy at 20, major tilting and slip occurs. If the kinetic energy is less than the tilting energy at 10°, the gears will rotate steadily. Thus, figure 4 is divided into three zones by the two tilting energy values. Operation in the top zone is prohibited where the rotation rate is larger than 0.15 rpps and tilting is larger than 20. Operation in the middle zone can work but it is not as reliable as in the bottom zone. The operation curve in figure 4 has been supported by MD runs for the gear systems using short [14, 0] nanotubes. We also did MD runs for longer tubes (about twice as long) and the critical rotation rate of 0.1 rpps was found again, although it took more input energy and time to reach this value. The 0.1 value also holds for cold end gears.

We tested several force fields for gear simulations and some results are shown in table 1. Slip occurs because the molecular teeth tilt. To make sure that no reactive slip occurs, we did comparative MD runs for two cases: with and without Brenner's reactive potential for intergear interactions. No significant difference was observed for slip condition and energy values. Electrostatic interactions may also need to be taken into account. When two benzyne teeth come close, they try to maintain a displaced parallel configuration, even when slipping. This is similar to the

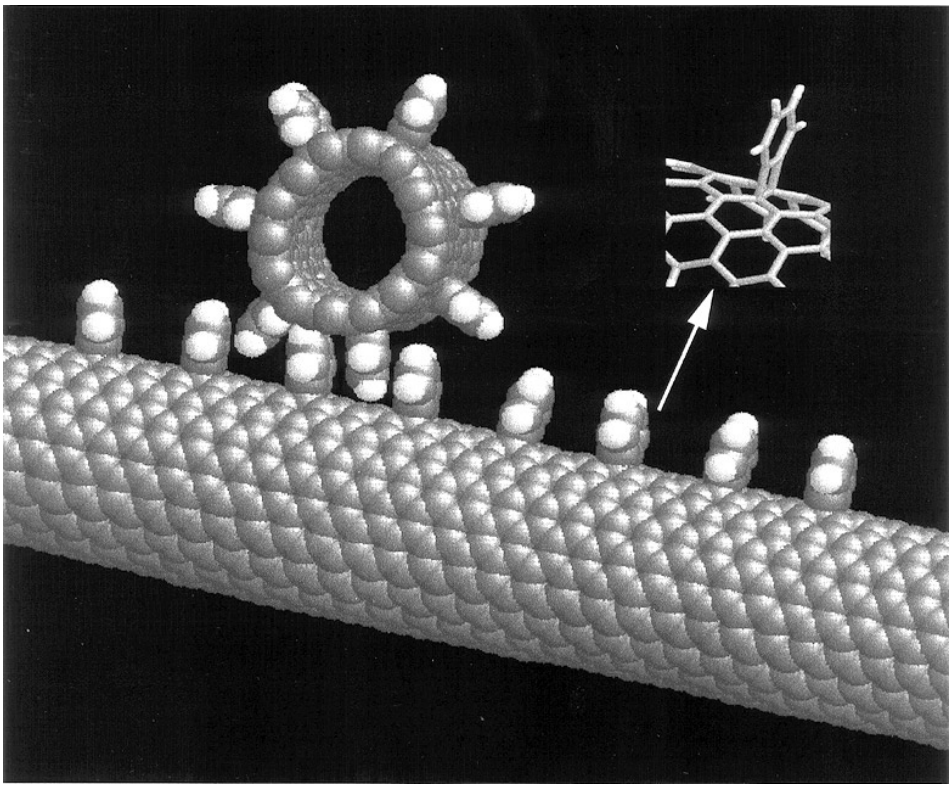

Figure 7. Gear and shaft system model. There are three rings between each benzyne tooth on the shaft, but only two rings between teeth in the gear.

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favorable interactions observed for benzene dimers [17]. It was found that the Buckingham (exp +6) force field plus electrostatic interaction terms was better at predicting the configuration and energy compared with Lennard–Jones 6–12 potential without the charge term. Therefore, we tested this case by placing partial charges on benzyne atoms. It turns out that these different force fields do not make significant differences in rotational dynamics. This is perhaps because mechanical motion is not as sensitive to force fields as local molecular configuration and conformation are. As a matter of fact, most force fields for the same types of atoms predict almost identical structures and properties for molecular systems in condensed state with difference only in detailed local structures.

3.3. More examples of operating gear systems

We have drawn a useful conclusion from the above studies. If gear temperature was less than 3000 K, a trial and error procedure could be used to determine gear operation conditions without fear of destroying the gears. Furthermore, if the tilting energy at several angles, say, 10° and 20°, was properly estimated and a rotation rate was chosen so that rotation energy was less than the tilting energy, gear systems should work well without any slip. Considering this point, we simulated operations of other types of nanotube-based gear systems.

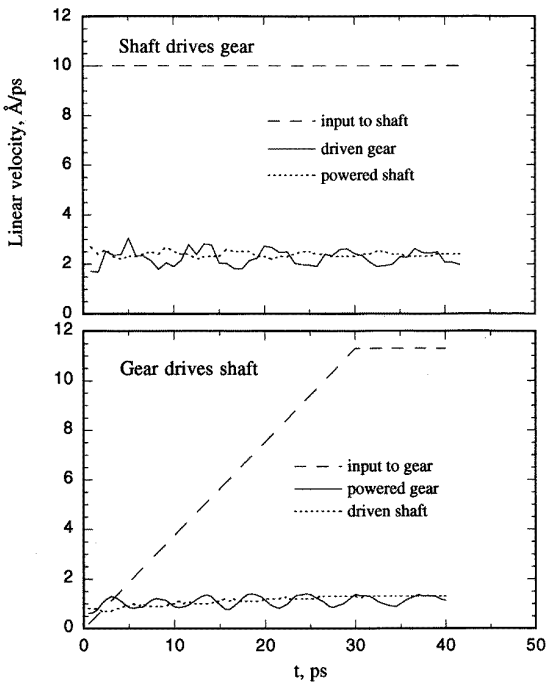

Figure 8. Velocity of gear and shaft configuration.

3.3.1. Multiple rows of teeth gears. Two types of gears with multiple rows of teeth are shown in figure 5. They

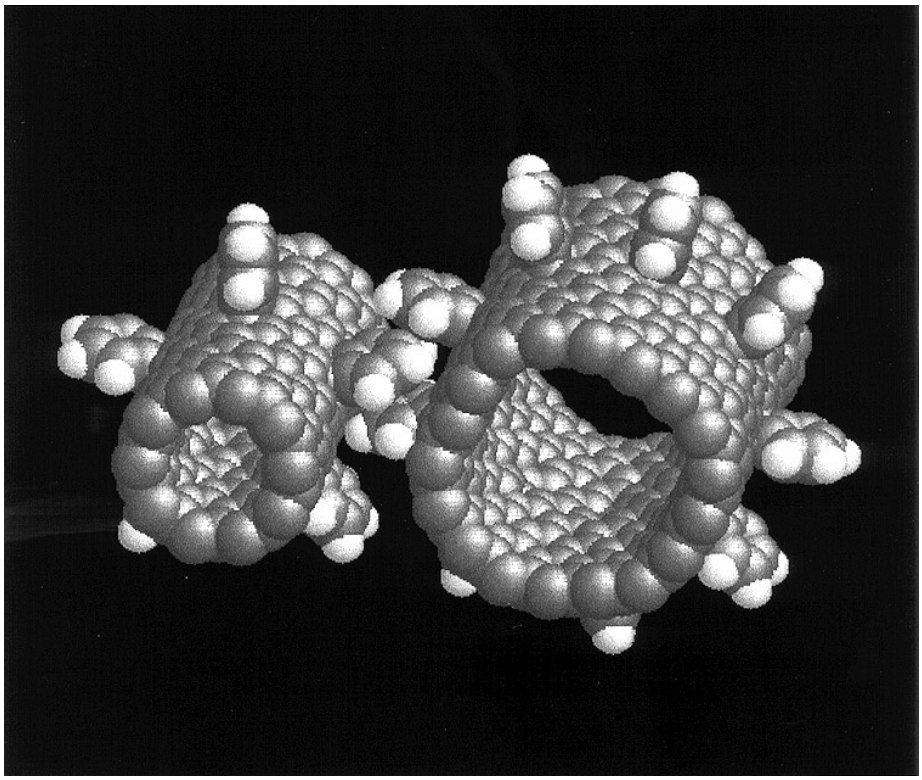

Figure 9. Small and large gear configuration.

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are identical in all geometry features to that in figure 1, but one more row of teeth was added. We call them the in-line multiple rows of teeth gears and the off-line multiple rows of teeth gears, with a separation between two rows of teeth of ∼7.0 and ∼7.3 Å. Operation curves at room temperature are shown in figure 6. The critical slip rate of 0.1 rpps was observed again. In addition, the ratio of input to measured rate was also the same as that of single row of teeth gears. As expected, operation of the off-line multiple rows of teeth gears, as indicated by the measured rotation rate, is smoother than in-line multiple rows of teeth gears and the single rows of teeth gears previously discussed. This is because gear teeth sometimes do not mesh properly and will occasionally exert counter-rotational forces on each other. In proper working conditions, the teeth will interface face to face. However, sometimes, particularly in the multiple rows of in-line teeth case, the teeth will interface in a T configuration. In this case, the vertical part of the T configuration will exert a counter-rotational force on the tooth representing the horizontal portion of the T configuration and the gears will tend to chatter.

3.3.2. Gear and shaft. This system is shown in figure 7. The gear is that shown in figure 1 with a [14, 0] tube and teeth separated by two hexagon rings. The shaft is made of a [9, 9] tube and teeth separated by three rings. The separation of the gear and shaft is 19.4 Å. Tooth face is normal to radial direction of nanotube [14, 0] for the gear, but in the axis direction of nanotube [9, 9] for the shaft. Two types of operations were performed. One was powering the gear to drive the shaft, converting rotational motion into translational motion. The other was converting translation of the shaft into rotation of the gear. In the latter case, a constant linear velocity was given to the atoms at one end of the shaft. Operation curves obtained from MD runs are shown in figure 8 with the angular velocity of the gear converted into linear velocity in Å ps^{-1}. We can see that the gear-shaft system works well in either case. However, it takes more input energy to convert these two types of mechanical motions compared with the case of one gear driving another gear. The ratio of input rate to measured rate is about 5 for the shaft driving the gear, and around 11 for the gear driving the shaft. Since the mass of the shaft is almost twice that of the gear, it takes more power for the gear to drive the shaft.

3.3.3. Small and large gears. This system is shown in figure 9. The nanotube is [18, 0] for the large gear and [10, 0] for the small gear with a same length (∼25 Å). The separation of two gears is ∼23. The ratio in diameter, number of atoms and mass is 1.8 with the smaller diameter being about 8 Å. Our simulations showed that this system could work and operation curves similar to the previous ones were obtained. Since the tube diameters in this system are different from those previously studied, the critical slip conditions and the ratio of rotation rates are not the same as before. Operation of the large gear driving the small one is easier and smoother than the small driving the large because

of the difference in mass. If the small gear is given a large acceleration, it does not drive the large one and instead bounces back and forth several times, like elastic collisions of a small ball between two boards.

4. Concluding remarks

This work has computationally suggested that nanotube-based gears can be made and operated. The gears will work well if the rotation rate is below 100 GHz, the temperature is lower than 600–1000 K and rotational energy is less than the teeth tilting energy at 20. The predominant mechanism of gear failure is slipping due to teeth tilting. Gears will resume functioning if the slipped gears are slowed down.

Some information that will be useful for future work can be extracted. The force field is not as sensitive to mechanical motion in nanodevices as to local molecular motion. This suggests that it may be possible to establish a set of force fields for fullerene nanomachines. The design space of all potential gears is quite large. This space can be at least partially parametrized by the diameter of the gears, length of the gears, distance between gears, temperature, rotation rate, angular acceleration, nearby molecules (we hypothesize that long-range forces will have some effect). Furthermore, the operating characteristics of the gears appears to change throughout this space. We have examined a few points in this design space and related slip conditions to input energy and tooth tilting energy. To design and build complex machines will require characterizing some substantial portion of this multidimensional design space.

Acknowledgments

We gratefully acknowledge Dr Don Brenner for providing his source MD code to this work. J Han and A Globus are the employees of MRJ, Inc at NASA Ames. G Deardorff is an employee of Stering Software, Inc. at NASA Ames. This work was supported by NASA Ames Research Center through contract NAS2-14303. Videos and atomic trajectory files in xyz format are available at http://science.nas.nasa.gov/Groups/Nanotechnology/publications/MGMS_EC1/simulation/data/index.html.

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