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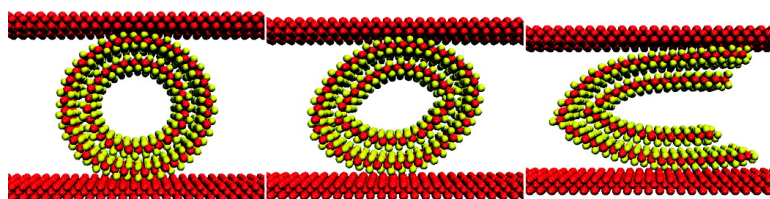
Letter

## Nanolubrication: How Do MoS-Based Nanostructures Lubricate?

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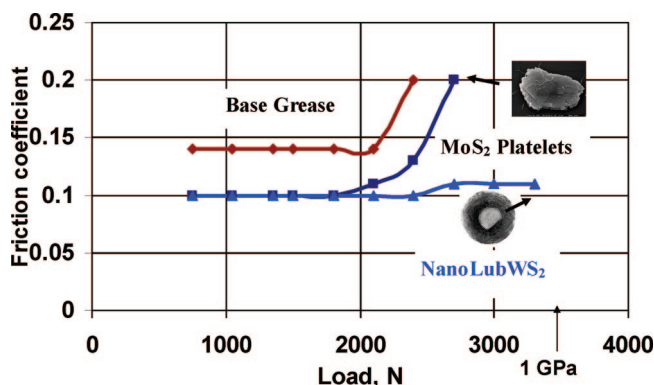
Nanolubrication: How Do MoS<sub>2</sub>-Based Nanostructures Lubricate?Milen Stefanov,<sup>†,‡</sup> Andrey N. Enyashin,<sup>†,§</sup> Thomas Heine,<sup>\*,||</sup> and Gotthard Seifert<sup>†</sup>*Physikalische Chemie, TU Dresden, 01062 Dresden, Germany, Institute of Catalysis, Bulgarian Academy of Sciences, Georgi Bonchev Str. 11, Sofia 1113, Bulgaria, Institute of Solid State Chemistry, Ural Branch of Russian Academy of Sciences, Pervomayskaya Str., 91, 620041 Ekaterinburg, Russia, and School of Engineering and Science, Jacobs University Bremen, 28759 Bremen, Germany**Received: September 15, 2008; Revised Manuscript Received: September 26, 2008*

Inorganic MoS<sub>2</sub> nanotubes under high pressure have been investigated at the atomistic scale using Born–Oppenheimer molecular dynamics simulations. We show that the low friction coefficient at high loads is not due to the ball-bearing effect. Instead the nanostructures burst under high loads and form nanoplatelets which attach themselves at the material surfaces of closest contact, effectively leading to local “nanocoating” which results in friction coefficients identical to those of lubricants based on MoS<sub>2</sub> platelets. The breakup process always starts from the innermost tube, which opens the possibility to tune the nanomaterials to be effective at well-defined loads.

Since prehistoric times the reduction of friction was one of the central topics of civil engineering whenever mobile parts have been involved in the design of transport means, mechanical tools, or machines. This problem is still present in modern technology, and various approaches have been developed to reduce the friction in systems containing mobile parts, as friction results in loss of mechanical energy, unwanted release of heat to the system, material fatigue, noise pollution, electrostatic charging, etc.

There are two standard procedures to reduce kinetic friction: one can reduce the kinetic friction coefficient, for example by adding a lubricant or by solid lubrication (coating), or one can replace parts which slide against each other by a mechanism which is only subject to rolling friction; the friction coefficient of the latter one is usually significantly lower than that of sliding friction. Both procedures are at least as old as prehistoric architecture and have probably already been applied when Stonehenge, the Mesopotamian cities, or the Egyptian pyramids were constructed. Two principal techniques were probably used: (i) replacement of sliding friction by rolling friction by usage of intermediates, like tree trunks, and (ii) insertion of a lubricant between two sliding materials, e.g., water or oil.

In modern times, the kinetic friction process is understood as toothing of surface features sliding against each other, usually on the micro- or even nanoscale. Hence, the sliding friction coefficient can be reduced by forming nearly ideal surfaces, and by the application of a lubricant which separates the surfaces, either by a liquid film (lubrication) or by particles which have a low friction coefficient (coating). At high loads, however, the lubricant is expelled from the locations of closest interface distance due to mechanical pressure and hence loses its



**Figure 1.** Friction coefficient as function of load. Figure courtesy of NanoMaterials, Ltd., Israel.

tribological properties, leading to an increase of the friction coefficient (Figure 1).

For a long time, d-transition metal dichalcogenides (TmS<sub>2</sub>, Tm = Mo, W, Nb, and Ta) have been known as excellent lubricants.<sup>1</sup> They not only reduce the friction coefficient but they also lubricate at higher loads than traditional lubricants as, for example, grease. These results were obtained in the last years through a long series of experiments, and found a realization in preparation of fluid or dry solid lubricants and self-lubricating metal coatings with nanostructured MoS<sub>2</sub> additives.<sup>2–4</sup> The general dependency of the friction coefficient on the load, however, is that of a standard grease-based lubricant.

The tribological properties of TmS<sub>2</sub> platelets or bulk powders can be improved by forming spherically or cylindrically shaped nanostructures. It has been claimed that the “bearing effect” is responsible for this improvement: the nanoparticles enter the intersurface area and act as a ball bearing when the surfaces are sliding against each other.<sup>5–8</sup> Besides, their closed shape avoids edges and results in a higher electronic stability, as dangling bonds are avoided and

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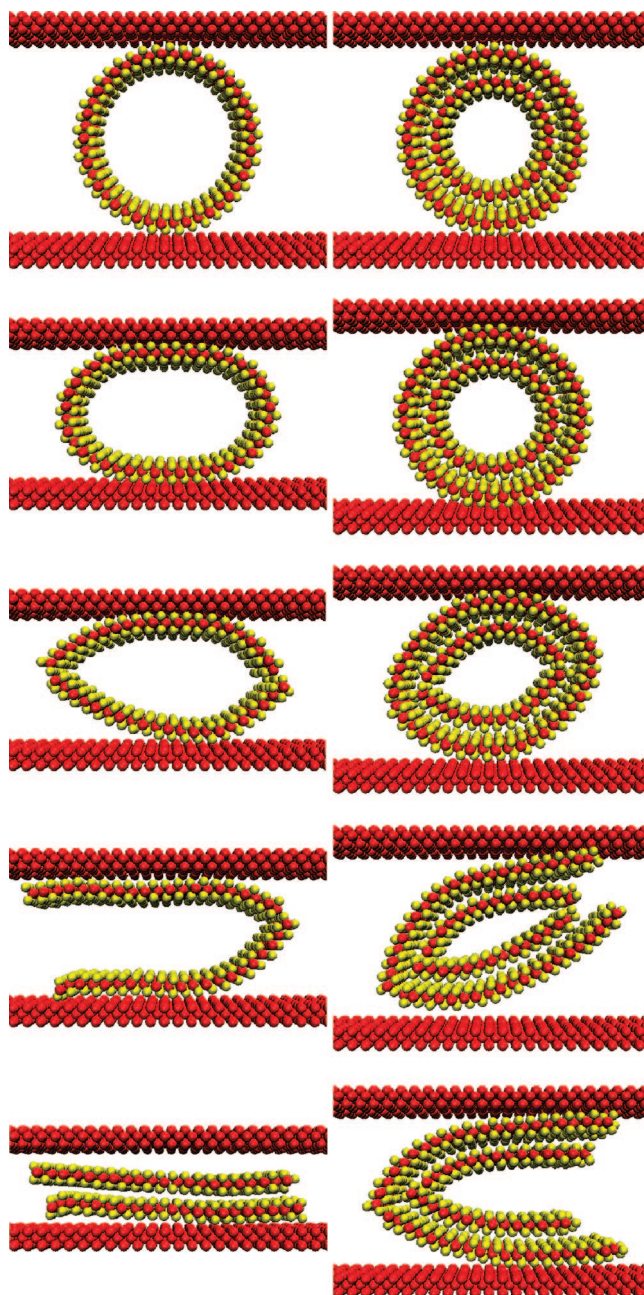
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hence the chemical resistance, for example against humidity and an oxidative atmosphere, is improved. If  $\text{WS}_2$  or  $\text{MoS}_2$  nanonions or nanotubes with diameters in the range of 10 to 100 nm are added to base grease, the dependency of the friction coefficient on the load is for lower loads that of the  $\text{TmS}_2$  platelets. Most remarkably, the friction coefficient remains low even at very high loads (Figure 1).

In this work the friction process at high loads is studied at the atomistic level using first principles computer simulations. We simulate the effect of high loads on spherical, defect-free  $\text{MoS}_2$  nanotubes of different diameters, chirality, and number of tube walls. These nanotubes have similar tribological properties as fullerene-like nanoparticles of the same stoichiometry; yet, they have better mechanical properties, are easier to simulate as their structure is well-defined at the atomic scale, and can be calculated employing periodic boundary conditions (along the tube direction) allowing smaller model systems. Two external grips put mechanical pressure and gradually squeeze the nanotubes, while we deliberately exclude chemical interactions between grips and nanotubes. As the tubes may undergo rearrangements in bonding, structure, and topology, the simulations are carried out using approximate density functional theory.<sup>9,10</sup> The external pressure is applied by designing solid molybdenum grips with frozen atomic positions which act through a Lennard-Jones potential with the nanotubes (QM/MM).<sup>11</sup>

First we studied the structural deformation of single, double, and triple-walled nanotubes under axial pressure. Individual snapshots of the simulations are given in Figure 2, and animations of the trajectories are available in the Supporting Information. The strain–stress curves of the systems are shown in Figure 3. Several remarkable trends can be found here: As expected, the strain–stress relation is steeper for smaller nanotubes, which is in agreement with the well-known inverse proportionality of the tube energy with respect to its diameter.<sup>12,13</sup> Normalized to the tube diameter, the tubes show nearly the same slope, which means that the strain–stress relation is essentially independent of the tube's chirality. In contrast to tensile strain–stress curves, the systems deviate from linearity toward higher stress values; that is, if the systems are deformed, it gets harder to deform them even stronger. The reason for this behavior is that the tubes form planar surface segments close to the grips which are connected with half-tubes (see Figure 2), so further compression is essentially equivalent with the compression of tubes with smaller diameters.

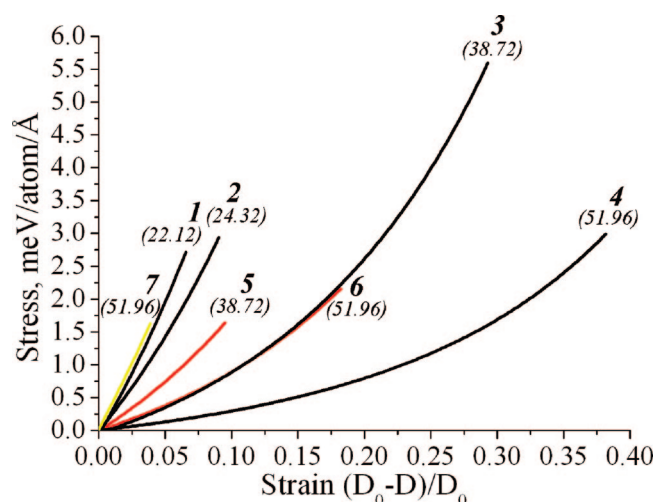
Further compression leads to irreversible deformation of the nanotubes: they break up and form platelets. At this point the strain–stress ratio is not well defined: The total energy drops, as the  $\text{MoS}_2$  fragments get planar and strain energy is released, even though no further work is necessary for the compression. This effect is partially compensated by the frustration energy, the energy which is released as the tubes are breaking apart and chemical bonds are broken. The breaking process is running on a short time scale (less than 1 ps), and more detailed interpretation of the trajectories from this point on is very speculative, as it mainly depends on the possibility of the system to distribute the released heat of the breakup, i.e., a stochastic process. The final products of this process are, however,  $\text{MoS}_2$  layers, attached to the two grips, at least by van der Waals interactions, in a face-to-face position which is ideal for lubrication. It might be meaningful to interpret this result as local coating of the grips.



**Figure 2.** Structural evolution of single-walled (21,21)  $\text{MoS}_2$  (on the left) and double-walled (14,14)@(21,21)  $\text{MoS}_2$  nanotubes (on the right) with the pressure growth (from top to bottom) under squeezing at 600 K between two  $\text{Mo}(001)$  planar grips. Cross sections of individual snapshots of the trajectories are shown. Animations showing the trajectory of the simulations are given as Supporting Information.

In the experiment,  $\text{MoS}_2$  nanostructures have been never observed as single-walled nanotubes or fullerenes. Therefore, we extended our investigations to double- and triple-walled nanotubes. Figure 3 shows that the strain–stress relation of multiwalled nanotubes is determined by the smallest, innermost tube. In all our simulations, the innermost tube determines the breaking process of the whole nanostructure; the tubes are breaking from inside to outside: While the innermost tube, that with the highest strain energy, bursts and unbends, it cracks the next-largest tube and so forth. The result of the process is, however, the same as for the single-walled nanotubes: At the end,  $\text{MoS}_2$  platelets are formed, partially attached to the grips, which will provide good lubrication at the position of closest contact of the materials sliding against each other.





**Figure 3.** Strain-stress relations of axially deformed MoS<sub>2</sub> nanotubes up to the burst for: 1, (22,0); 2, (14,14); 3, (21,21); 4, (28,28); 5, (14,14)@ (21,21); 6, (21,21)@ (28,28); and 7, (14,14)@ (21,21)@ (28,28) tubes. Tube diameters (in Å) are indicated in parenthesis.

The results of this study have various consequences for the interpretation of the experimental data (Figure 1): Our calculations suggest that the lubrication process at high loads is not determined by the ball-bearing effect. This is supported by the fact that the nanostructures break easily under mechanical pressure but also because the friction coefficient of MoS<sub>2</sub> platelets and nanostructures is identical for smaller loads. Also recent experiments<sup>8</sup> discuss that the lubrication mechanism is exfoliation, and not ball bearing. The excellent lubrication of nanostructures is hence interpreted as “nano-coating”, by attaching lubricating platelets to those parts of the material which are exposed most closely to each other.

The calculations also show that it might be possible to tune the mechanical properties of MoS<sub>2</sub> nanotubes “from inside”: As the innermost tube determines the mechanical properties, it might be possible to use templates to design nanotubes with well-defined axial stability.

We should point out that these simulations make severe approximations to the “real world” and the results need to be interpreted carefully: (i) Chemical interactions between tube and grips have been neglected. This only means that the sticking of the formed platelets to the grips must be even stronger. (ii) The subnanosecond time scale of the simulation indicates that the breaking process is very fast. We cannot comment on long-term effects like, for example, restructuring. (iii) We investigated inorganic nanotubes, but usually nanooxions are taken as lubricants. Previous investigations<sup>14</sup> showed that nanooxions are even less stable than nanotubes under external pressure, and the same conclusions are valid for those systems.

It should finally be noted that our simulations have no implications on established fact that fullerenes do show a ball-bearing effect.<sup>15,16</sup>

## Methods

All molecular dynamics calculations were performed using the density functional based tight-binding method (DFTB) applying periodic boundary conditions.<sup>12</sup> We employ the dispersion corrected modification (DC) of this method with the implementation of an empirical dispersion term of a Lennard-Jones potential parametrized in the framework of the universal force field (UFF).<sup>17</sup> Calculations have been carried out using an experimental version of the deMon code.<sup>18</sup>

**TABLE 1: Diameter,  $D_0$ , Elasticity Constant,  $k$ , and Critical Strain, When the Cracking of a MoS<sub>2</sub> Nanotube Occurs under Orthogonal Squeeze (MD DFTB Calculations at 600 K)**

MoS <sub>2</sub> nanotube	$D_0$ , Å	$k$ , eV·Å <sup>2</sup> /atom	$\epsilon_c$
(22,0)	22.12	567.32 <sup>a</sup>	0.066
(14,14)	24.32	517.70 <sup>b</sup>	0.090
(21,21)	38.72	293.21	0.293
(28,28)	51.96	126.87	0.383
(14,14)@ (21,21)	38.72	744.84	0.095
(21,21)@ (28,28)	51.96	728.34	0.240
(14,14)@ (21,21)@ (28,28)	51.96	3867.77	0.039

<sup>a</sup> 672.17 eV·Å<sup>2</sup>/atom and 27.1 Å at 300 K, respectively. <sup>b</sup> 427.83 eV·Å<sup>2</sup>/atom and 29.3 Å at 300 K, respectively.

The chirality classification of MoS<sub>2</sub> nanotubes was described by Seifert et al.<sup>12</sup> In the simulations we considered both single walled armchair (14,14), (21,21), and (28,28) and zigzag (22,0) nanotubes and multi walled (14,14)@ (21,21), (14,14)@ (21,21)@ (28,28) nanotubes. Multi walled tubes were formed such that the interlayer distance between coaxial tubes equals ~6.2 Å, which corresponds to the interlayer distance in the bulk 2H-MoS<sub>2</sub>. The quantum-mechanical part included only the nanoobject (a supercell of the (multiwalled) nanotube up to 1134 atoms), while the grip-nanotube interaction was described by the molecular mechanics potential. The grips contained six atomic Mo(001) planes, that is, 648 atoms with a grip area 9.45 Å × 113.4 Å, which were constrained during the MD runs. Simulations were carried out within the NVT ensemble (fixed number of particles, volume, and temperature,  $T = 600$  K), and the grips distance was lowered during the simulation. Technically, trajectories of 1 ps were carried out, if the average temperature and its standard deviation during this was within the thresholds of 10 K, then the grips were shifted by 0.1 Å, otherwise the equilibration was repeated until the criteria have been reached. The stress was determined as the negative of the first derivative of the total energy of the system  $E$  with respect to the diameter  $D$ , and the latter one was defined as the average distance between the Mo atoms of the opposite outer walls of a nanotubes which were in contact with the grips.

**Supporting Information Available:** The simulation of the breakup process of single-, double-, and triple-walled MoS<sub>2</sub> nanotubes is shown in three movie clips. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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