

Nanoscale superlubricity, peeling and fracture at carbon and silicon interfaces

Naruo Sasaki

Department of Engineering Science, University of Electro-Communications,
Chofu, Tokyo 182-8585, Japan

Control of friction is one of the most practical problems in our daily life, which covers almost all the areas from basic science to applied engineering. In this talk we discuss our recent numerical and experimental studies on nanotribology at nanoscale carbon and Si interfaces.

First we have experimentally developed the fullerene molecular bearings[1,2], measured peeling process of graphene[3], and performed the molecular mechanics simulations of nanoscale friction at the interfaces of the graphene/C₆₀ and graphene/graphene interface[4]. Anisotropy of friction of graphite/C₆₀ interface is found, where the maximum and minimum friction appears for the commensurate and other scan directions, respectively. It is clarified that the small rotation and elastic contact of C₆₀ molecules contribute to the ultralow friction. Similar anisotropy is also found during the peeling process at graphene/graphene interface during surface contact.

Next the nanoscale shear and fracture of the opposing Si tips are studied by molecular dynamics simulation. It is clarified that, under the high loading condition of several GPa, nanocontact region becomes amorphous[5]. During the shear process, the characteristic transition of the dynamics of the amorphous contact region occurs. First amorphous contact region slides at Si/Si interface. [Fig.1a] As the shear proceeds, the amorphous region becomes thinner and longer, and turns into nanowire.[Fig. 1b] The nanowire elongates until it breaks. The simulated contact diameter and angle are in good agreement with experimental one obtained by MEMS in TEM. Thus the dynamics of the amorphous contact region plays a major role in the shear process of opposing Si tips under the high loading condition, which can give us clue to understand one of the dynamics of the single real contact area.

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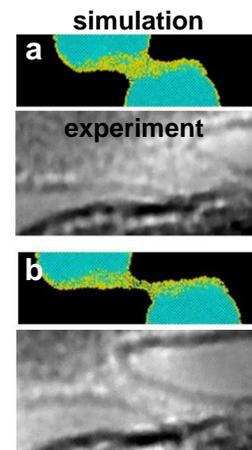


Figure 1: Simulated and measured amorphous contact regions of Si/Si interface.

Atomistic modeling friction on graphene: effects of hydrogenation, substrate roughness and electron-phonon coupling

Yalin Dong¹, Xiawa Wu², Ashlie Martini³

¹Department of Mechanical Engineering, the University of Akron, Akron, OH 44325

²Department of Mechanical Engineering, Purdue University, West Lafayette, IN 47907

³School of Engineering, University of California Merced, Merced, CA 95343

Thanks to the development of atomic force microscopy, many interesting tribological properties have been discovered on graphene from superlubricity and thickness dependence, to friction enhancement resulting from fluorination or hydrogenation. Due to the extreme difficulty to “see” what really occurs in the buried interface using experimental techniques, some of the underlying mechanisms remain unknown or controversial. We carry out molecular dynamics simulation to model single asperity friction to address these issues, and provide atomic level information to interpret related experimental observations obtained by atomic force microscopy. First, we perform simulations to model the friction on hydrogenated graphene, and reveal that the roughness induced by hydrogenation is the most likely origin of friction enhancement. Second, we study the effects of substrate roughness and electron-phonon coupling on thickness-dependent friction, and clarify their contributions to friction in general. Lastly, we briefly discuss how to use these principles we learned from our simulation to predict tribological properties of other materials.

Kinetic nanofriction: effect of temperature on the frictional mechanism of mobile molecules on a surface

Mehdi Jafary-Zadeh, Chilla Damodara Reddy, Yong-Wei Zhang

Institute of High Performance Computing (IHPC), A*STAR, Singapore 138632

To develop high-performance nano-electro-mechanical systems (NEMS) using bottom-up approaches, understanding frictional mechanisms of nanoscale building blocks is essential.¹ Such understanding allows us to quantify the frictional forces at single-atomic/molecular level, offering possibilities to precisely manipulate these building blocks by controlling their driving forces. Although nanoscale imaging and testing techniques, *e.g.* atomic force microscopy (AFM), are recently employed to measure *static nanofriction* of atomic/molecular adsorbates,² they are too slow to measure the *kinetic nanofriction* of the mobile adsorbates.³ On the other hand, Brownian motion of a single nanoparticle on a surface, which was recently found far below room temperature, poses an opportunity to study the kinetic nanofriction.³⁻⁶ Here, using prototype C₆₀/graphene system and employing large-scale molecular dynamics (MD) simulations, we study the variation of kinetic nanofriction coefficient with temperature. We show that the kinetic nanofriction coefficient decreases by increasing the temperature, and its temperature dependence follows an Arrhenius-form with two distinct regimes that have a crossover merely by changing the temperature. Moreover, we explain the mechanisms of interaction between the ad molecule and the substrate at these regimes. The C₆₀/graphene is a prototypical physisorbed system fascinating for fundamental studies of mass transfer and frictional phenomena at the nanoscale. Moreover, it is a promising system for various important applications such as nano-bearing, molecular spintronics and quantum computing. Our findings illustrate the important role of temperature in the performance of nanosystems and shed lights on the development of NEMS.

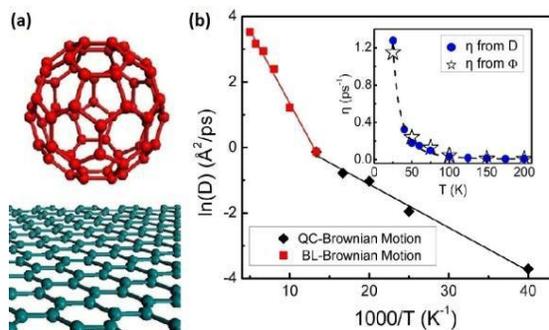


Figure 1 (a) Our computational model consists of a single C₆₀ molecule on top of a graphene sheet, *i.e.* C₆₀/graphene system. (b) The Arrhenius analysis of surface diffusion coefficient, D , indicates that in the temperature range of 25 K to 200 K, the C₆₀ ad molecule exhibits two distinct regimes of Brownian motion with a crossover at about 75 K. The inset of (b) shows the kinetic nanofriction coefficient, η , calculated from D as well as velocity

autocorrelation function, Φ , at different temperatures.

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Simulation of a Dental Tribological System at a Microscopic Scale

Christian Nutto¹, Sandra Sarmbe², Matthias Scherge¹, Claas Bierwisch¹

¹Fraunhofer IWM, 79108 Freiburg, Germany

²Fraunhofer IWM, 06120 Halle, Germany

For the investigation of abrasive processes in the field of oral hygiene, the complex interactions of dental care products with biological materials have to be considered. In the case of tooth-cleaning, toothpastes need an optimized cleaning efficiency to remove stains and biofilms from the teeth, which can be influenced by adding abrasives of various sizes, shapes and mechanical properties. In contrast, the concentration and material selection of the abrasives should be carefully chosen to avoid abrasion effects on the teeth. In order to understand the process of tooth cleaning and possible tooth wear, there is a need to investigate in detail how the abrasive particles interact with the toothbrush filaments in a cleaning contact. Up-to-now, due to the variability of the parameters, these data are hardly achievable.

The objective of this study was to investigate the interactions between toothbrush, toothpaste - including the abrasive grains - and human enamel during dental care. Therefore, the process of tooth cleaning is reduced to a tribological system of a single toothbrush filament, human enamel and different particle suspensions representing a mixture of toothpaste and water.

We have developed Smoothed Particle Hydrodynamic (SPH) simulations at a microscopic scale for the investigation of abrasive processes between a toothbrush filament, abrasive grains, and enamel. We focused on the induced stresses onto the enamel by varying process parameters, i.e., suspension viscosity, tilt-angle of filament and size of abrasive grains. The determined stresses are an indicator for the cleaning effectiveness of the abrasives but also for the wear risk on the enamel.

We can demonstrate how the variation of each of the parameters affects the interaction between all involved components. The results from our simulations at a grain-size scale support the interpretation of accompanying experiments.

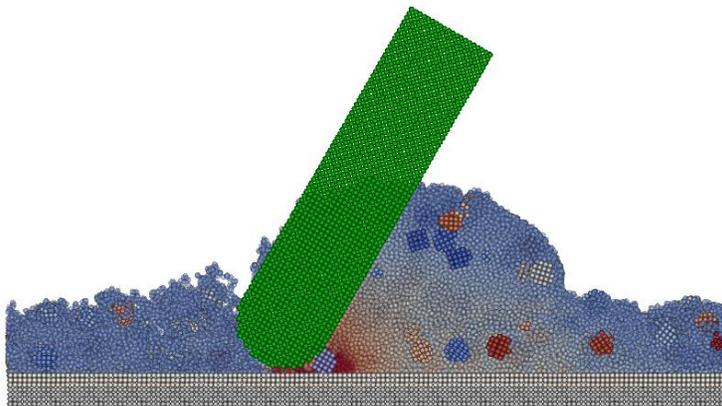


Figure 1 Numerical model of a toothbrush filament, enamel, and a toothpaste containing abrasive particles. The color scale shows the pressure distribution within the toothpaste at an instant of the abrasive process.

Nano scale contribution to features occurring at the macro scale in lubricated contacts

Philippe Vergne¹, Daniele Savio^{1,2}, Nicolas Fillot¹

¹ Université de Lyon, INSA-Lyon, CNRS, LaMCoS, UMR5259, F-69621, France

² SKF Aeroengine France, Valenciennes F-59309, France

Nowadays the thickness of the film separating two lubricated surfaces can decrease down to a few nanometers, thus becoming comparable with the size of the fluid molecules. Under such severe confinement, the continuum hypothesis upon which the traditional lubrication models are based may not be valid anymore. Understanding the properties of nanometer-thin lubricant films has thus been a major concern in the past 20 years, leading to the development of experimental and numerical methods capable of accessing quantities at the molecular scale. The current challenge consists to take into account the results in real-size contacts.

The integration of nano scale effects into the lubrication theory would allow unraveling the influence played by molecularly thin films on the global contact behavior. The main difficulty arises from the significant difference in scale between the atomistic simulation methods (for instance Molecular Dynamics) which are limited to some nanometers, and the existing continuous models for lubricated contacts of the order of one millimeter in size. A promising way to overcome this issue involves deriving the results of nano scale simulations through representative expressions, which can then be straightforwardly coupled to the equations of the classical lubrication theory in which a Navier-type boundary condition is imposed.

This multi-scale coupling strategy was successfully applied [1] to reflect the influence of wall-slip (quantified from MD simulations as a function of macro scale parameters like pressure, sliding velocity and thickness) onto a macro scale contact lubricated by a simple hydrocarbon fluid. The continuous problem was solved on the basis of a FE method solver [2]. This approach is now extended to more realistic situations in which firstly the wall-slip characterization was more extensively studied [3] and parameterized using atomistic simulations, and secondly the composition and thus the wettability of the bounding surfaces were considered as input parameters. According the different cases investigated, significant modifications of the film thickness profiles, fluid mass flow and friction were observed in the resulting thin films.

All in all we propose a way to bridge the gap between nano and macro scale simulations for lubricated contacts.

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Molecular dynamics study of automotive lubricants: linking molecular structure and friction

Michael Doig¹, Philip J. Camp¹, Chris P. Warrens²

¹School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Rd, Edinburgh, EH9 3JJ, UK

²BP Technology Centre, Pangbourne, RG8 7QR, UK

Lubricant oils are used to reduce friction and wear in a wide range of industrial and mechanical processes. Lubricant additives play a vital role in the oils' overall performance, particularly surface-active additives which can significantly affect the tribological properties of solid surfaces. However, there is insufficient understanding of the link between the atomic-level structure of tribofilms and the macroscopic properties such as friction, to direct the development of new lubricant formulations.

Using large-scale molecular dynamics simulations, we investigate a range of lubricated systems, studying the structural properties of surface-adsorbed tribofilms on metal-oxide surfaces, and how they vary with temperature, pressure, surface coverage and shear rate. Several important trends are identified linking molecular isomerism and architecture with the structure and stability of the adsorbed films. In addition, the simulation results are used to gain insight on recent experimental measurements of film structure [1]. Some examples of the systems studied include oleic acid and stearic acid films lubricated by squalane (see figure 1) [2], and hexadecylamine films lubricated by dodecane [3], both adsorbed on iron oxide surfaces.

The friction coefficients in these systems are computed and analysed with reference to the structure of the adsorbed films, to yield new insights on the intimate link between the molecular properties of lubricants and the macroscopic frictional properties of lubricated systems.

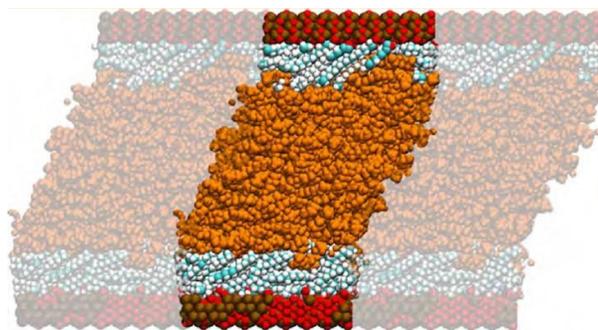


Figure 1: Lubricated system of oleic acid adsorbed on iron oxide lubricated by squalane base oil, under applied shear.

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Shear-induced amorphization of silicon crystals

Gianpietro Moras¹, Andreas Klemenz¹, Hiroshi Uetsuka²,
Michael Moseler¹, Lars Pastewka^{1,3}

¹Fraunhofer Institute for Mechanics of Materials IWM, Freiburg, Germany

²Asahi Diamond Industrial Co., Ltd., Ichihara, Japan

³Institute of Applied Materials - Reliability of Components and Systems IAM-ZBS,
Karlsruhe Institute of Technology, Karlsruhe, Germany

Phase transformations, and in particular amorphization, of crystalline silicon occur under contact loading [1]. The formation of amorphous silicon has been reported to occur during machining, indentation and scratching processes. However, little is known about the mechanisms leading to silicon amorphization under these loading conditions, where shear stress is present. Recently, thanks to the development of accurate reactive potentials for classical molecular dynamics simulations [2, 3], the atomic-scale mechanisms that lead to shear-induced amorphization of diamond, and the crucial role they play in the wear of diamond during mechanical polishing were unveiled [4]. Here, we report the results of reactive molecular dynamics simulations of silicon crystals upon sliding load and compare them to analogous results obtained for diamond crystals.

At temperatures higher than the melting temperature, a melting process starts at the silicon/silicon sliding interface. The thickness of the melted region grows rapidly and linearly in time, with a rate that depends on the difference between the actual temperature and the melting temperature for any applied normal pressure. For temperatures lower than the melting temperature, two different processes are observed for applied pressures ranging from 1 to 15 GPa. When the pressure is lower than the beta-tin transition pressure, and therefore the cubic diamond crystalline structure is stable, a thin (< 1 nm) amorphous region abruptly forms at the sliding interface. During the sliding process, the thickness of such region does not grow due to competing amorphization and recrystallization processes, and the sliding proceeds in a stick-slip-fashion. When the applied pressure exceeds the beta-tin transition limit, the thickness of the amorphous region grows in time and its growth rate increases at increasing applied loads, at odds with the apparently similar amorphization process observed for diamond crystals.

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Friction Process of Silicon Carbide under Water Lubrication: Quantum Chemical Molecular Dynamics Approach

Yoshihiko Kobayashi¹, Hiroki Murabayashi¹, Seiichiro Sato¹, Shandan Bai¹,
Yuji Higuchi¹, Nobuki Ozawa¹, Koshi Adachi², Jean Michel Martin³, Momoji Kubo¹

¹Fracture and Reliability Research Institute Graduate School of Engineering,
Tohoku University, Sendai, Japan

²Division of Mechanical Engineering, Tohoku University, Sendai, Japan

³Laboratoire de Tribologie et Dynamique des Systemes,
Ecole Centrale de Lyon, Lyon, France

Water lubrication has the characteristic of low environmental burden. When silicon carbide (SiC) slides in water, low friction coefficient is obtained experimentally. It is thought by experiments that chemical reactions during friction are important to gain low friction surface. Understanding of the mechanism is essential to improve friction characteristic. However, it is difficult to directly obtain atomic-scale dynamics during chemical reactions by experiments. In this study, our purpose is to reveal the chemical reactions of the SiC surface under water lubrication by our tight-binding quantum chemical molecular dynamics (TB-QCMD) method.

To reveal friction phenomena of SiC sliding in water environment, we performed friction simulation of SiC under water lubrication by our TB-QCMD method (Figure 1). Chemical reaction processes at frictional interface are shown in Figure 2. After 5 ps of the sliding under a pressure of 3 GPa, an OH⁻ ion was adsorbed on a Si atom of the SiC surface (Figure 2(a)). Moreover, after the O atom in the OH group also interacted with another Si atom of the SiC surface, a Si-O-Si bond was generated (Figure 2(b)). In addition, many Si-O-Si bonds were formed as friction time passed. Then, the growth of Si-O-Si bond chains was observed (Figure 2(c), and (d)). In experiment, SiO₂·n H₂O film is formed on the low friction surface of SiC under water lubrication. The generation of Si-O-Si bonds is initial process of the film formation. Therefore, we suggest that this growth relates to low friction property of SiC surface.

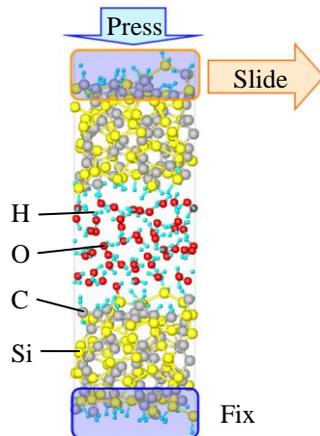


Figure 1: Friction simulation model of SiC films in water environment by TB-QCMD method.

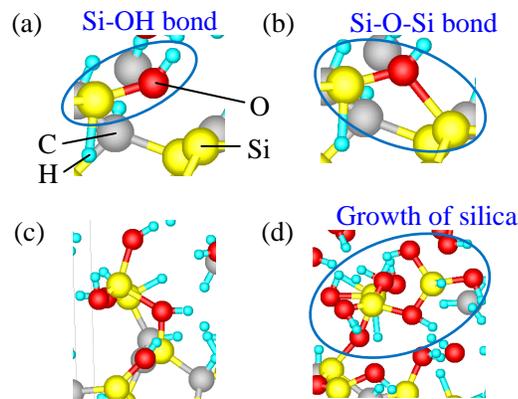


Figure 2: The reaction processes between H₂O and SiC films during friction under a pressure of 3 GPa with 50 water molecules at (a) 5.185 ps, (b) 5.190 ps, (c) 30.535 ps, and (d) 43.070 ps.

Polishing of Gallium Nitride: Quantum Chemical Molecular Dynamics Simulations

Kentaro Kawaguchi, Takehiro Aizawa, Yuji Higuchi, Nobuki Ozawa, Momoji Kubo

Fracture and Reliability Research Institute, Tohoku University, Sendai, 980-8579, Japan

Gallium nitride (GaN) is a next-generation semiconductor material with a wide band gap and high electron mobility. Although the atomic-level planar polished surface is essential for practical GaN devices, it is difficult to polish efficiently the GaN substrate because of its high hardness and chemical stability. The chemical mechanical polishing (CMP) is promising for efficient polishing of the GaN substrate. However, the detailed CMP mechanisms are unclear, and designing of the processes is difficult. In this study, in order to design the efficient and precise GaN CMP processes, we investigate the GaN CMP via our tight-binding quantum chemical molecular dynamics (TB-QCMD) method.

We use our TB-QCMD code “Colors” to investigate the CMP process of GaN(0001) surface by a SiO₂ abrasive grain in chemical solutions. We apply a pressure of 1.0 GPa on the SiO₂ abrasive grain and forcibly slid it with 50 m/s. All simulations are performed at a temperature of 300 K.

We perform CMP simulations of a GaN surface by a SiO₂ abrasive grain in aqueous H₂O₂ solution and aqueous NaOH solution to clarify the chemical reactions of each solution. We reveal that OH radicals and OH⁻ ions are adsorbed on the GaN surface in aqueous H₂O₂ solution and aqueous NaOH solution, respectively.

Moreover, we elucidate that Ga-N bonds of the GaN substrate in aqueous H₂O₂ solution are weaker than that in aqueous NaOH solution. Therefore, we suggest that the OH radicals are effective for efficient GaN CMP. To confirm the effectivity of OH radicals, we add one OH radical into the solution every 4.0 ps until 64.0 ps during polishing simulation under pure water environment. Fig. 1a shows a snapshot after 8 OH radicals are added.

The 8 added OH radicals are adsorbed on the GaN surface. Fig. 1b shows a snapshot after

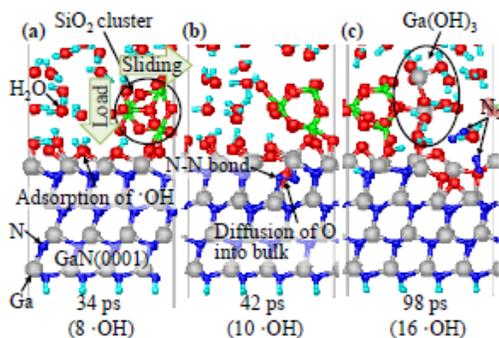


Figure 1: Snapshots of the GaN CMP simulation by a SiO₂ abrasive grain with 16 OH radicals

10 OH radicals are added. We observe the following oxidation reaction: the added OH radicals abstract H atoms from the adsorbed OH radicals, surface-adsorbed O atoms are generated, the surface-adsorbed O atom diffuses into the GaN bulk, and Ga-O bonds are generated. The N-N bond in the GaN substrate is generated due to the dissociation of Ga-N bonds by the oxidation reaction (Fig. 1b). Fig. 1c shows a snapshot after 16 OH radicals are added. The Ga atom of the first layer binds with 3 OH radicals and Ga(OH)₃ is desorbed

from the surface. The N₂ molecules are generated and desorbed from the surface due to the dissociation of Ga-N bonds by the generation of Ga-O bonds. We reveal that the GaN CMP process efficiently proceeds due to the oxidation reactions by the OH radicals.