Studies on the Use of Atomically Thin Films for Controlling Friction and Adhesion at Interfaces

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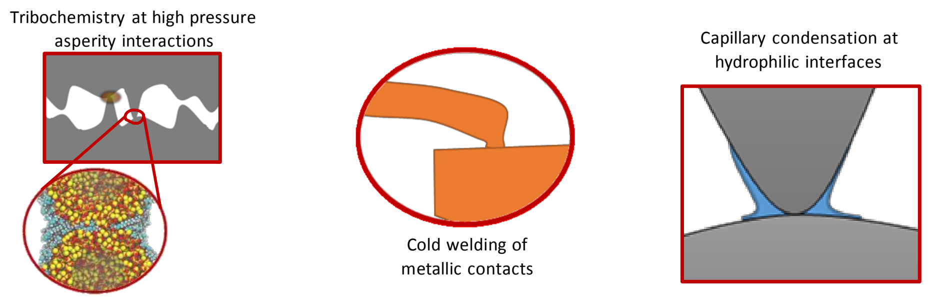
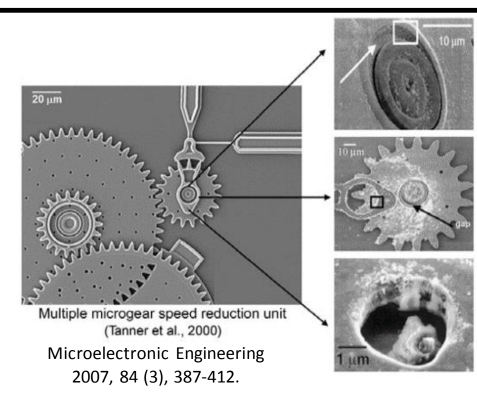
Introduction

Wear and energy dissipation resulting from friction between interfaces represents an enormous cost to society, approximately 1.5% of global GDP (~$200 billion annually in the U.S.) is lost due to surface wear and energy inefficiency. Furthermore, demanding applications like Microelectromechanical systems devices (MEMS) and space-based applications represent unique lubrication challenges that require the absolute best performance from surface coatings and lubricants. Understanding the atomic and molecular origins of friction and lubrication is therefore essential to overcoming these challenges and effectively controlling surface forces.





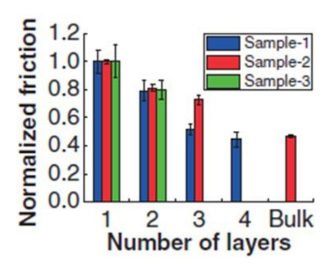
Microelectronic Engineering 2007, 84 (3), 387-412.

Due to their small size, restoring forces of MEMS devices are often insufficient to overcome surface forces like friction and adhesion, or the viscous drag associated with traditional lubricants. They represent one of the most challenging modern lubrication challenges.

In real tribological interfaces, the contact between sliding surfaces is often not atomically smooth. When polysilicon is used during MEMS fabrication, device surfaces typically exhibit nanoscale roughness on the order of 10 nm. It is critical for device operation and longevity that these asperities resist wear. Asperities between the surfaces interact with each other during contact and the high pressures formed at these asperity-asperity contacts dominate the adhesion, friction, and wear between the surfaces. To control adhesion and friction, surface lubricants such as self- assembled monolayers and 2D materials like graphene are ideal to reduce capillary condensation as well as reduce the friction at the interface. Graphene is also mechanically strong and can withstand high pressure contacts but easily delaminates from the surface known as "puckering". A detailed understanding of the mechanisms of these materials on rough surfaces is still needed to aid in optimizing and controlling the surface interactions for long lasting friction and wear reduction.

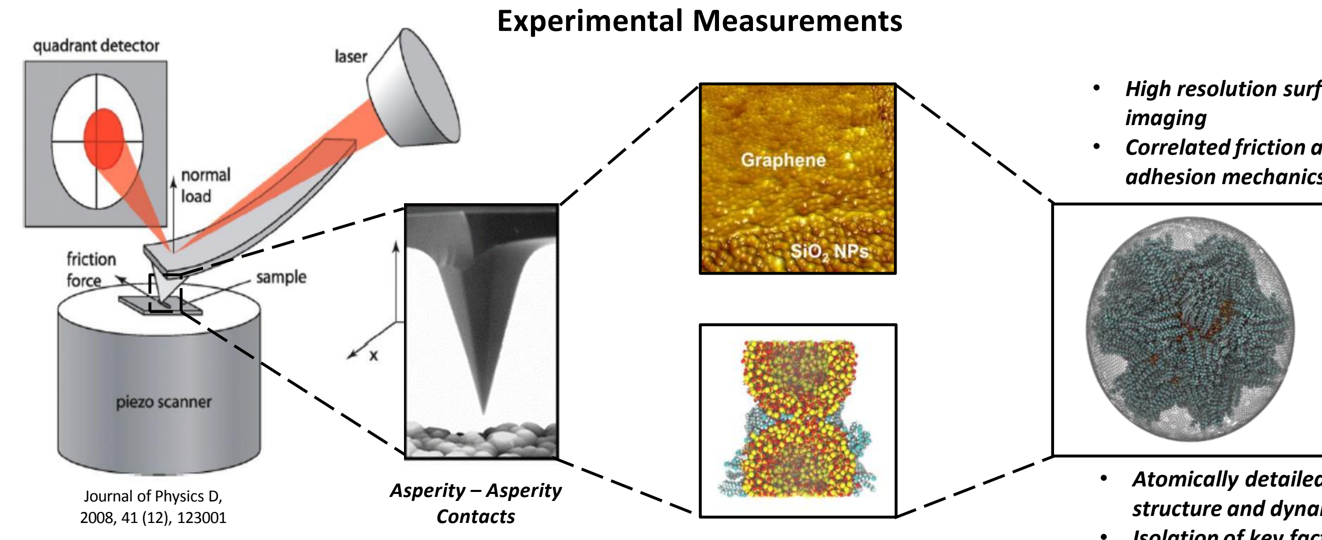
Much of the computation done for this research involved 256-way runs on the Eos cluster of the Texas A&M Supercomputing Facility using the LAMMPS MD software.

J.C. Spear, B.W. Ewers and J.D. Batteas, "2D-Nanomaterials for Controlling Friction and Wear at Interfaces," *Nano Today* **10** (2015) 301-314.



Science 2010, 328 (5974), 76-80. 4

Experimental Measurements



Journal of Physics D, 2008, 41 (12), 123001

Atomic Force Microscopy

Theoretical Calculations

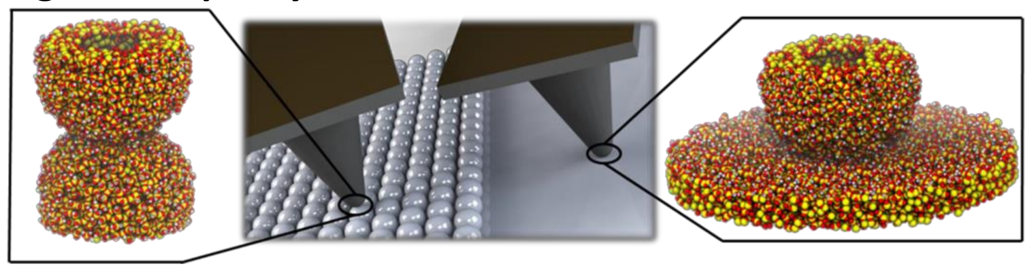
- *High resolution surface imaging*
- *Correlated friction and adhesion mechanics*

- *Atomically detailed structure and dynamics*
- *Isolation of key factors and variables*

To understand friction in atomically thick lubricants like graphene, a complete understanding of the structure and dynamics of these materials in sliding contacts is essential. To achieve this, we use Atomic Force Microscopy (AFM), complemented with atomistic Molecular Dynamics (MD) simulations. The high resolution measurement of surface forces like adhesion and friction that can be achieved with the AFM allows us to identify the critical phenomena which dictate the friction response of graphene, and through modeling and simulation we can identify the underlying mechanisms of these phenomena and how they are influenced by properties of the substrate and the graphene sheet.

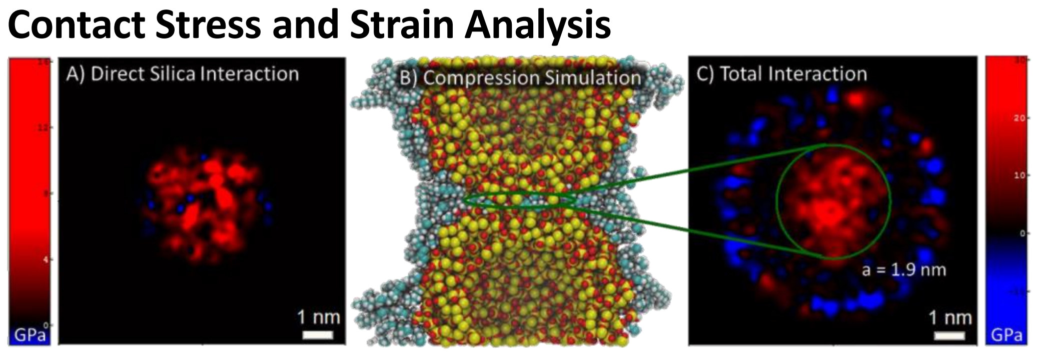
Modeling Contact and Sliding of Thin Films

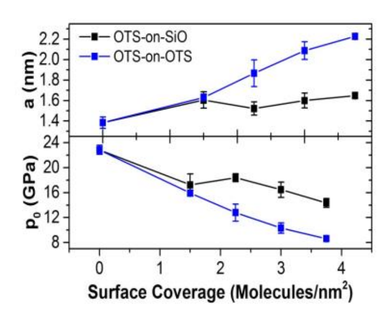
Simulating Nanoasperity Contacts



Molecular dynamics simulations employ silica nanoparticles and disks to simulate flat and curved surfaces similar to those used in experiment. This allows us to study the effects of surface morphology on the contact and friction response of surface coatings and boundary lubricants.

Contact Stress and Strain Analysis

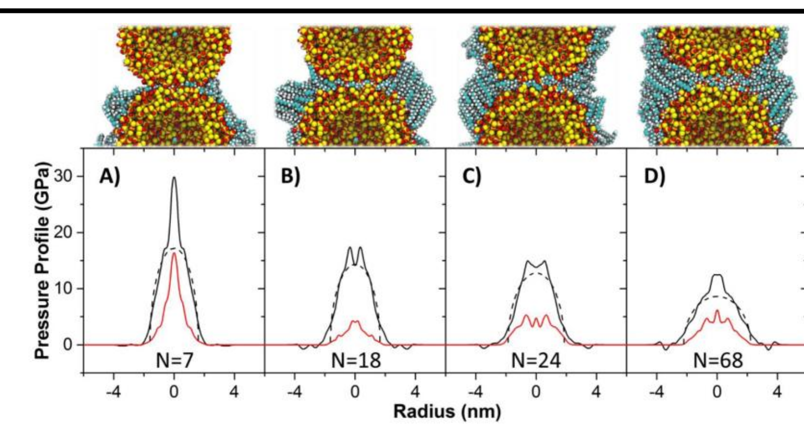




Simulation Setup Video

Pressure and strain mapping routines have been developed to determine in atomistic detail the distribution of these properties. Furthermore, it allows us to track the evolution of these properties with increasing lubricant density or changes in lubricant properties and configuration. For example, the evolution of contact area and peak stress can be evaluated as a function of film density on surfaces.

B.W. Ewers and J.D. Batteas, "Utilizing Atomistic Simulations to Map Pressure Distributions and Contact Areas in Molecular Adlayers within Nanoscale Surface-Asperity Junctions: A Demonstration with Octadecylsilane Functionalized Silica Interfaces," *Langmuir* **30** (2014) 11897-11905.

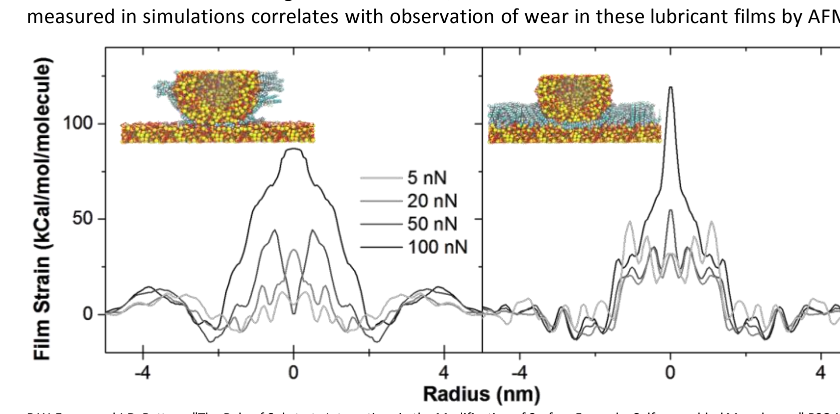


Stress Analysis and Effective Lubrication

Evaluation and decomposition of contact stresses between stresses imposed on the lubricant and the substrate can be used to guide the development of effective lubrication schemes. An effective lubricant should eliminate contact stresses at the substrate interface, minimizing pressure catalyzed tribochemistry and mechanical coupling of the sliding interfaces.

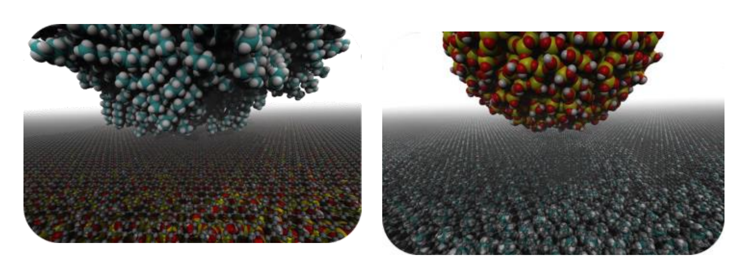
Strain Analysis and Tribochemical Wear

Isolating and evaluating strain in the lubricant film provides a guide to the point at which substantial tribochemistry can occur. For the OTS films considered here, the chemical bonds binding the molecules to the substrate have strengths of ~130 kCal/mol. Localization of the film strain at these magnitudes measured in simulations correlates with observation of wear in these lubricant films by AFM microscopy.



B.W. Ewers and J.D. Batteas, "The Role of Substrate Interactions in the Modification of Surface Forces by Self-assembled Monolayers," *RSC Advances* **4** (2014) 16803-16812.

Atomic Mechanisms of Friction in Graphene Films

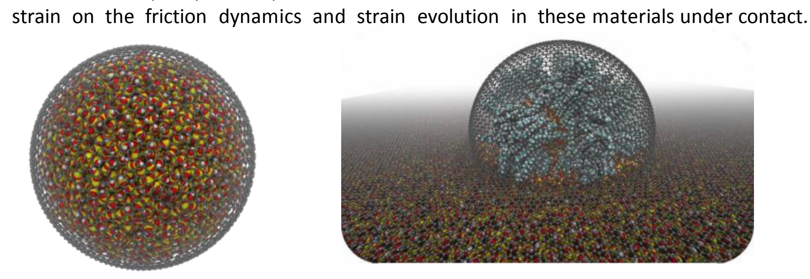


Surface Chemistry and Mechanics

The contact and sliding dynamics of graphene fundamentally depends on the interactions it has with the sliding interfaces. By varying the chemistry, morphology, and rigidity of the graphene's shearing and fixed interfaces, we can achieve a better understanding of how these interactions influence the behavior of graphene. Understands effects like puckering and wrinkling is possible, and the contribution of these effects to frictional dissipation can be isolated.

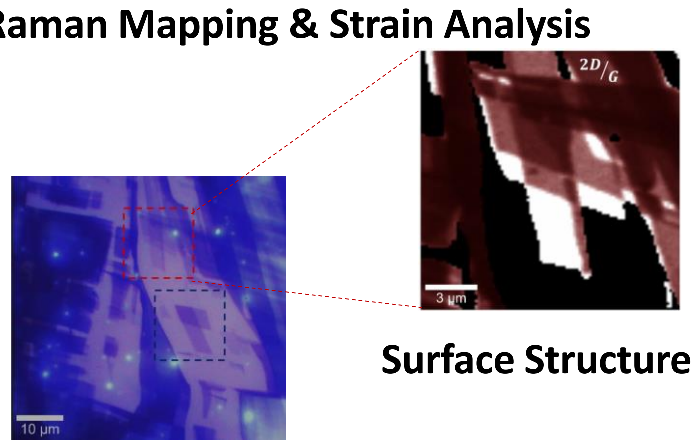
Friction of Graphene in Curved Geometries

We use two models of graphene on curved surfaces. Consistent with prior studies, a nanoparticle is used to simulate the nanoasperity morphology. The graphene sheet is applied either as a spherical structure with defects that alleviate curvature strain, or as typical graphene sheet placed across a nanoasperity. Comparison of these two situations isolates the influence of curvature strain on the friction dynamics and strain evolution in these materials under contact.

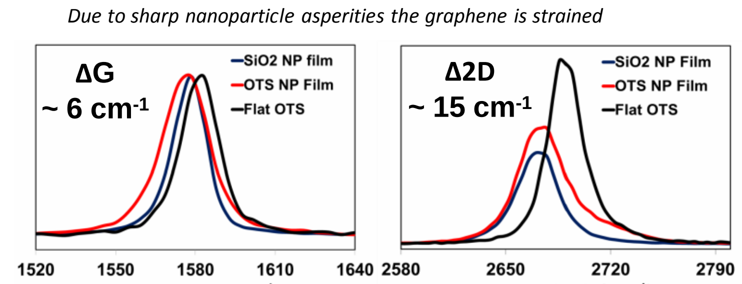


Friction and Adhesion of Graphene on Rough Surfaces

Raman Mapping & Strain Analysis



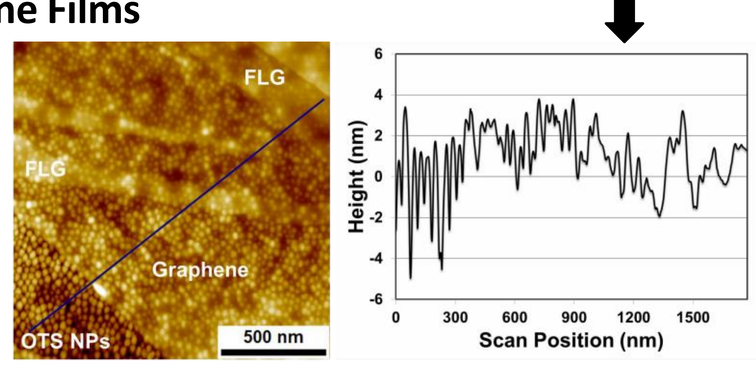
Due to sharp nanoparticle asperities the graphene is strained



Surface Structure of Graphene Films

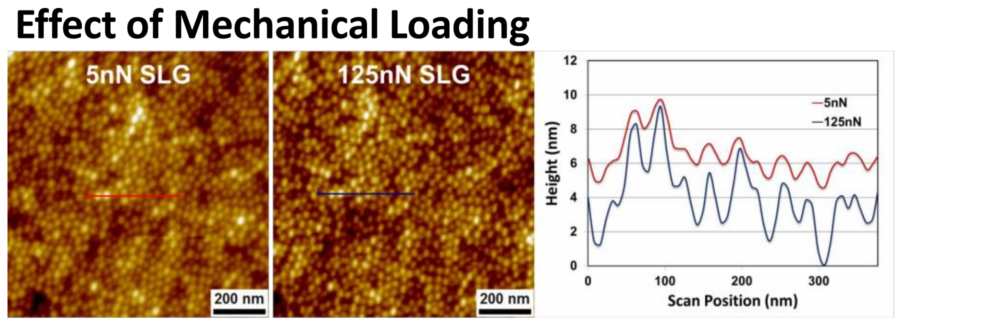
Analysis of the Raman spectra revealed small peak shifts attributed to biaxial strain in the graphene lattice due to the nanoscale roughness of the substrate as compared to graphene flakes on flat surfaces.

As layer thickness increases the bending stiffness also increases which results in a gradual reduction in the conformity and surface roughness as seen in the topography and line profile.



Graphene layers partially conform to nanoparticle substrates

Effect of Mechanical Loading

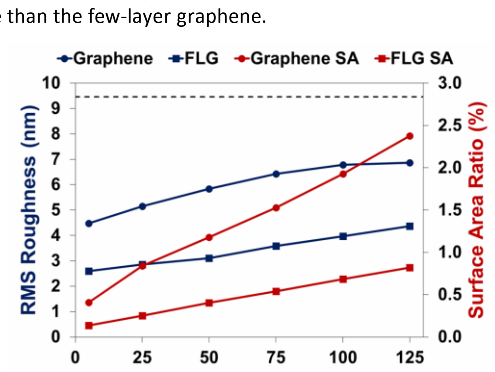


Conformity increases under increasing applied load

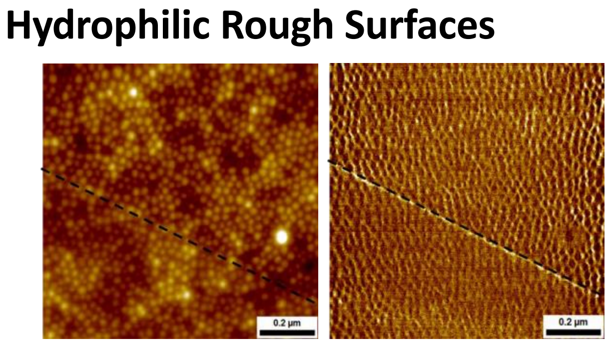
When external force is applied with the AFM tip, the conformity of the graphene flakes reversibly increased which can be seen in the increased roughness at higher loads. The roughness maximized at ~6.5 nm indicating full conformity (~9.5 nm) is not achieved due to the large strain requirement of the substrate geometry.

J.C. Spear, J.P. Custer and J.D. Batteas, "The Influence of Nanoscale Roughness and Substrate Chemistry on the Frictional Properties of Single and Few Layer Graphene," *Nanoscale* **7** (2015) 10021-10029.

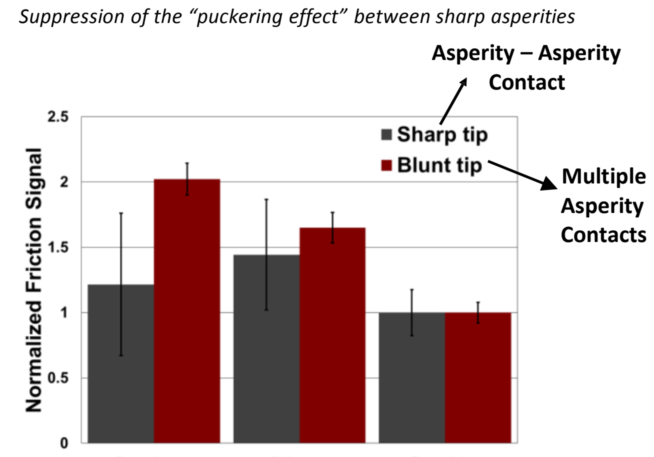
Topography images for single and few layer graphene both showed increased roughness with larger loads, however, comparison of the line profiles indicated graphene is stretched 1-2 nm more than the few-layer graphene.



Hydrophilic Rough Surfaces

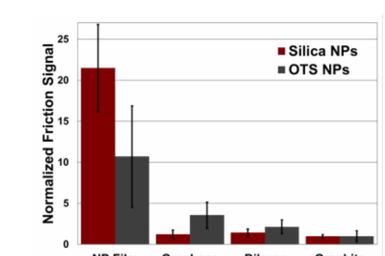


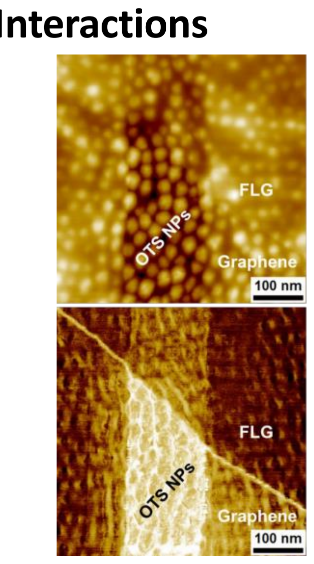
Suppression of the "puckering effect" between sharp asperities



Using a sharp AFM probe (~ 30 nm radius) there is not a significant change in friction between the graphene layers and bulk-like graphene, however, with a blunt probe (~ 130 nm) much larger than the asperities, the friction on graphene is 50% higher than the bulk. This implies a contact area dependence where the larger probe has a larger adhesion to the graphene over the surface as compared to the smaller probe.

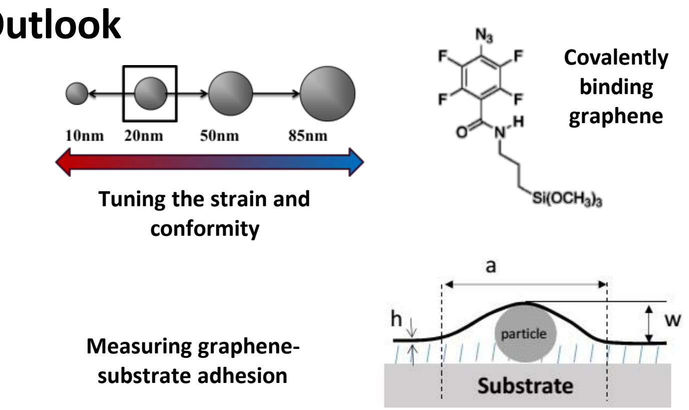
Hydrophobic Surface Interactions





A significant contrast between the nanoparticles modified with octadecyltrichlorosilane (OTS) and graphene layers can be easily seen in the AFM image In this case, the friction was not found to depend on the contact area of the probe.

Outlook



Acknowledgements

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