AmeriMech Symposium: ***Mechanical Behavior of 2D Materials - Graphene and Beyond***

April 4-6, 2016
University of Texas at Austin

Sponsored by the U.S. National Committee for Theoretical and Applied Mechanics (USNC/TAM) and National Science Foundation, this AmeriMech symposium is intended to promote interactions among active researchers in an area of contemporary interest in mechanics, material science, and physics.

Organizers:

Rui Huang - University of Texas at Austin

Kenneth M. Liechti - University of Texas at Austin

Symposium Program

Monday April 4:

8:30-10:00: Session I (Chair: Rui Huang)

1. **Huajian Gao (Brown Univ.), Topological Toughening of Graphene and Other 2D Materials**
2. **Nikhil Koratkar (RPI), Effect of Defects on the Intrinsic Strength and Stiffness of Graphene**
3. **Fatemeh Ahmadpoor (Univ. Houston), Nonlinear Elasticity and Thermal Fluctuations of Graphene**

10:00-10:30: break

10:30-12:00: Session II (Chair: Harold Park)

1. **Evan Reed (Stanford Univ.), The Role of Mechanical Constraints in Electromechanical and Structural Phase Change Properties of Two-Dimensional Materials**
2. **Teng Li (Univ. Maryland), Strain Engineering of 2D Materials**
3. **Deji Akinwande (UT Austin), Stressing Out 2D Materials under Extreme Pressures and Strains**

12:00-1:30: Lunch

1:30-3:00: Session III (Chair: Nanshu Lu)

1. **Harold Park (Boston Univ.), Electromechanics of Graphene Kirigami**
2. **Yong Zhu (North Carolina State Univ.), Probing Adhesion and Interfacial Shear Stress Transfer of Graphene**
3. **Ji Won Suk (Korea), Nanoscale Characterization of Adhesion Interactions of Graphene on Silicon Oxide**
4. **Zhenhai Xia (Univ. North Texas), Dynamics Adhesion and Self-cleaning of Gecko-Bioinspired Micromanipulators with Graphene Tips**

3:00-3:30: break

3:30-5:00: Discussions

6:00-9:00: Dinner at Tejas

Tuesday April 5:

8:30-10:00: Session IV (Chair: Yong Zhu)

1. **Philip Egberts (Univ. Calgary, Canada), Lubricating Properties of Graphene**
2. **Haitao Liu (Univ. Pittsburgh), Airborne Contamination of 2D Materials**
3. **Nanshu Lu (UT Austin), Wrinkling and Buckle Delamination of 2D MoS2 for Adhesion and Flexoelectricity Probing**

10:00-10:30: break

10:30-12:00: Session V (Chair: Jeffery Kysar)

1. **Kevin Turner (Univ. Penn), Interface Mechanics of Transfer Printing Processes for Semiconductor Nanomembranes and 2D Materials**
2. **H.B. Chew (UIUC), Nanoscale Mechanics of Plasma-Graphene Interaction and Its Effects on Patterning**
3. **Ken Liechti (UT Austin), Adhesion and Fracture of Graphene for Roll-to-Roll Transfer**

12:00-1:30: Lunch

1:30-3:30: Session VI (Chair: Pradeep Sharma)

1. **Jeffery Kysar (Columbia Univ.), Multiscale Modeling of Two-Dimensional Materials: Stiffness, Strength and Reliability**
2. **Scott Bunch (Boston Univ.), Blister Testing Atomic Membranes: A Route Towards Understanding 2D Materials**
3. **Yong-Wei Zhang (IHPC, Singapore), Mechanical Properties of 2D Materials**
4. **Boris Yakobson (Rice Univ.), Predictive Modeling in 2D Materials: Morphology, Dislocations, Grain Boundaries**

3:30-4:00: break

4:00-5:00: Discussions

6:00-9:00: Dinner (on your own)

Wednesday April 6:

8:30-10:00: Session VII (Chair: Kenneth Liechti)

1. **Jonathan R. Felts (Texas A&M), Chemical Kinetics on Graphene Using Local Stress and Heat**
2. **Jianliang Xiao (Univ. Colorado Boulder), Programmable Localized Wrinkling of Thin Films on Shape Memory Polymer Substrates**
3. **Seung Ryul Na (UT Austin), Self-healing of Molybdenum Disulfide and Silicon Oxide**

10:00-10:30: break

10:30-12:00: Session VIII (Chair: Yong-Wei Zhang)

1. **Chris Marianetti (Columbia Univ.), An Interatomic Potential for Graphene Derived from First-Principles**
2. **Alireza Ostadhossein (Penn State Univ.), Atomistic Scale Simulations of 2D Layer Materials Using ReaxFF**
3. **Rui Huang (UT Austin), Thermomechanical and Interfacial Properties of Graphene – A Few Challenges for Modeling**

12:00-1:30: Lunch

1:30-3:00: Discussions

Abstracts

Topological Toughening of Graphene and Other 2D Materials

Huajian Gao
School of Engineering, Brown University

It has been claimed that graphene, with the elastic modulus of 1TPa and theoretical strength as high as 130 GPa, is the strongest material. However, from an engineering point of view, it is the fracture toughness that determines the actual strength of materials, as crack-like flaws (i.e., cracks, holes, notches, corners, etc.) are inevitable in the design, fabrication, and operation of practical devices and systems. Recently, it has been demonstrated that graphene has very low fracture toughness, in fact close to that of ideally brittle solids. These findings have raised sharp questions and are calling for efforts to explore effective methods to toughen graphene.

Recently, we have been exploring the potential use of topological effects to enhance the fracture toughness of graphene. For example, it has been shown that a sinusoidal graphene containing periodically distributed disclination quadrupoles can achieve a mode I fracture toughness nearly twice that of pristine graphene. Here we report working progresses on further studies of topological toughening of graphene and other 2D materials. A phase field crystal method is adopted to generate the atomic coordinates of material with specific topological patterns. We then perform molecular dynamics simulations of fracture in the designed samples, and observe a variety of toughening mechanisms, including crack tip blunting, crack trapping, ligament bridging, crack deflection and daughter crack initiation and coalescence.

Effect of Defects on the Intrinsic Strength and Stiffness of Graphene

Nikhil A. Koratkar
Department of Mechanical, Aerospace and Nuclear Engineering and Department of Materials Science and Engineering, Rensselaer Polytechnic Institute

It is important from a fundamental standpoint and for practical applications to understand how the mechanical properties of graphene are influenced by defects. I will show that the two-dimensional elastic modulus of graphene is maintained even at a high density of sp^3-type defects associated with the oxygenation of graphene. Moreover, the breaking strength

of defective graphene is only ~14% smaller than its pristine counterpart in the sp^3-defect regime. By contrast, we find a significant drop in the mechanical properties of graphene in the vacancy-defect regime. We also provide a mapping between the Raman spectra of defective graphene and its mechanical properties. This provides a simple, yet non-destructive methodology to identify graphene samples that are still mechanically functional. By establishing a relationship between the type and density of defects and the mechanical properties of graphene, this work provides important basic information for the rational design of composites and other systems utilizing the high modulus and strength of graphene. I will end the talk by discussing possibilities for future research such as how this work could be extended to other 2D materials beyond graphene as well as possibilities to control the mechanical properties of graphene by defect engineering.

Nonlinear Elasticity and the Thermal Fluctuations of Graphene

F. Ahmadpoor[1], P. Wang[2], R. Huang[2], P. Sharma[1,3]

[1]*Department of Mechanical Engineering, University of Houston*
[2]*Department of Aerospace Engineering and Engineering Mechanics, University of Texas at Austin*
[3]*Department of Physics, University of Houston*

The study of statistical mechanics of thermal fluctuations of graphene---the prototypical two-dimensional material---is rendered rather complicated due to the necessity of accounting for geometric deformation nonlinearity in its deformation. Unlike fluid membranes such as lipid bilayers, coupling of stretching and flexural modes leads to a highly anharmonic elastic Hamiltonian. Existing treatments heavily draw on analogies that exist in the high-energy physics literature. In this study, using a variational perturbation method, we present a "mechanics-oriented" novel treatment of the thermal fluctuations of graphene, fully accounting for deformation nonlinearities, and evaluate their effect on the effective bending stiffness. We compare the results from our approach to both molecular dynamics simulations as well as other analytical methods in the literature.

The Role of Mechanical Constraints in Electromechanical and Structural Phase Change Properties of Two-Dimensional Materials

Evan J. Reed
Department of Materials Science and Engineering, Stanford University

Some of the most dramatic engineering feats accomplished with layered materials are enabled by properties that emerge only at the single or few-layer limit and are not found in bulk forms. I will discuss our efforts to elucidate useful emergent properties of monolayer and few-layer materials, including our predictions and several recent experimental observations of substantive electromechanical coupling in the form of piezoelectric [1] and flexoelectric-like effects,[2] unlike their bulk forms. Single-layers of some transition metal dichalcogenide compounds have the potential to exist in more than one crystal structure, leading to intriguing phase change application possibilities. By developing electronic structure-based computational approaches, we have discovered that mechanical deformations,[3] electrostatic gating, and temperature changes all independently have the potential to control phase changes in some specific 2D materials and their alloys.[4] I will discuss essential aspects of mechanical thermodynamic constraints for 2D materials, and contrast with those of 3D materials.

[1] K.-A. N. Duerloo, M. T. Ong, and E. J. Reed, “Intrinsic Piezoelectricity in Two-Dimensional Materials,” *J. Phys. Chem. Lett.*, vol. 3, no. 19, pp. 2871–2876, Oct. 2012.
[2] K.-A. N. Duerloo and E. J. Reed, “Flexural electromechanical coupling: a nanoscale emergent property of boron nitride bilayers.,” *Nano letters*, vol. 13, no. 4, pp. 1681–6, Apr. 2013.
[3] K.-A. N. Duerloo, Y. Li, and E. J. Reed, “Structural phase transitions in two-dimensional Mo- and W-dichalcogenide monolayers,” *Nature Communications*, vol. 5, Jul. 2014.
[4] K.-A. N. Duerloo and E. J. Reed, “Structural Phase Transitions by Design in Monolayer Alloys,” *ACS Nano*, Dec. 2015.

Strain Engineering of 2D Materials:

Programming morphology and properties of graphene and derivatives by stretching, folding, and rolling

Teng Li
Department of Mechanical Engineering, University of Maryland

The morphology and properties of 2D materials are strongly tied to their lattice structure. The highly malleable structure and amenable surface chemistry of atomically thin 2D materials open up fertile opportunities to tailor the morphology and properties of 2D materials via simple mechanical deformation, such as stretching, folding and rolling. Ever maturing techniques of 2D material synthesis and functionalization further promise such tailoring of morphology and properties in a programmable manner. In this talk, three case studies of strain engineering of graphene and derivatives will be presented:

- We demonstrate strong coupling of electro-mechanical properties of graphene and graphene-based hetero-structures by tuning charge carrier dynamics through mechanical strain. The graphene electro-mechanical coupling yields very large pseudomagnetic fields for small strain fields, up to hundreds of Tesla, which offer new scientific opportunities unattainable with ordinary laboratory magnets. Such strain-induced pseudomagnetic fields can enable on-demand and reversible formation of quantum dots in graphene [1]. We further reveal a viable approach to achieving programmable uniform pseudomagnetic fields of extreme intensity by a simple uniaxial stretch [2].
- Atomically thin graphene makes it a potential candidate material for nanoscale origami, a promising bottom-up nanomanufacturing approach to fabricating nano-building blocks of desirable shapes. Inspired by recent progresses on functionalization and patterning of graphene, we demonstrate hydrogenation assisted graphene origami (HAGO), a feasible and robust approach to enabling the formation of unconventional carbon nanostructures [3]. We demonstrate reversible opening and closing of a HAGO-enabled graphene nanocage via an external electric field, a unique and reversible mechanism that is crucial to achieve molecular mass uptake, storage and release. HAGO holds promise to enable an array of novel carbon nanostructures of desirable functionalities by design.
- Rolling up a monolayer graphene results in a spiral multilayer nano-structure, termed carbon nanoscroll (CNS). CNSs are topologically open and thus have tunable interlayer space and inner core size, distinct from MWCNTs, which consists of several coaxial graphene cylinders and thus is topologically closed. The open and highly tunable structure of CNSs, combining with the exceptional mechanical and electronic properties inherited from the basal graphene, has inspired potential applications such as hydrogen storage medium, water and ion channels, nano-oscillators, and nanoactuators. Enthusiasm aside, feasible and reliable fabrication of high quality CNSs remains as a significant challenge. To this end, we demonstrate two viable approaches to fabricating CNSs: (a) by CNT-initiated rolling of graphene [4] and (b) by hydrogenation-enabled rolling of graphene [5].

References:

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[5] S. Zhu, T. Li, *Hydrogenation enabled scrolling of graphene*, **Journal of Physics D: Applied Physics**, 46, 075301 (2013)

Stressing Out 2D Materials under Extreme Pressures and Strains

Deji Akinwande
Department of Electrical and Computer Engineering, University of Texas at Austin

Two-dimensional (2D) nanomaterials have attracted broad interest owing to their outstanding properties that includes electronics, photonics, and mechanics. In this work, we discuss the current progress in the basic studies of 2D materials under strain and pressure. We find that strain or pressure engineering can be used to tune the opto-electro-mechanical properties including electronic phase transitions, structural phase transition, bandgap tuning, direct to indirect gap transition, and 2D to 3D reconfiguration. In the extremes of pressure, superconductivity emerges at low temperatures. Our investigation covers several members of the 2D family including transitional metal dichalcogenides, black phosphorus and 2D heterostructures.

Electromechanics of Graphene Kirigami

Harold Park
Department of Mechanical Engineering, Boston University

Graphene's exceptional mechanical properties, including its highest-known stiffness (1 TPa) and strength (100 GPa) have been exploited for various structural applications. However, graphene is also known to be quite brittle, with experimentally-measured tensile fracture strains that do not exceed a few percent. In this work, we introduce the notion of graphene kirigami, where concepts that have been used almost exclusively for macroscale structures are applied to dramatically enhance the stretchability of both zigzag and armchair graphene. Specifically, we show using classical molecular dynamics simulations that the yield and fracture strains of graphene can be enhanced by about a factor of three using kirigami as compared to standard monolayer graphene. We further demonstrate that this enhanced ductility in graphene may open up interesting opportunities in coupling to graphene's electronic behavior. Specifically, our results show that the pristine kirigami behaves as coupled quantum dots with a clear control of the conductance and I-V characteristic by the tensile load. Current is reduced when the segments of kirigami are simply distorted but rises again due to electron confinement by strain barriers created when carbon bonds are stretched. In the presence of strong phase-breaking scatterers the effect of the deformation is washed out.

Probing Adhesion and Interfacial Shear Stress Transfer of Graphene

Yong Zhu

Department of Mechanical & Aerospace Engineering, North Carolina State University

Interfacial mechanics between graphene and substrate such as adhesion and friction plays a critical role in the morphology and functionality of graphene-based devices. Here I will present our recent work on adhesion and interfacial shear stress transfer of graphene. In the first part, I will present a new method that can measure adhesion energies between ultraflat graphene and a broad range of materials using atomic force microscopy (AFM) with a microsphere tip. In our experiments, only van der Waals force between the tip and a graphene flake is measured. The Maugis-Dugdale theory is employed to calculate the adhesion energy. The ultraflatness of monolayer graphene on mica eliminates the effect of graphene surface roughness on the adhesion, while roughness of the microsphere tip is addressed by the modified Rumpf model. Adhesion energies of monolayer graphene to SiO2 and Cu are obtained as 0.46 and 0.75 Jm^{-2}, respectively. In the second part, I will present the nonlinear mechanical response of monolayer graphene on polyethylene terephthalate (PET), which is characterised using *in-situ* Raman spectroscopy and AFM. While interfacial stress transfer leads to tension in graphene as the PET substrate is stretched, retraction of the substrate during unloading imposes compression in the graphene. Two interfacial failure mechanisms, shear sliding under tension and buckling under compression, are identified. Using a nonlinear shear-lag model, the interfacial shear strength is found to range between 0.46 and 0.69 MPa. The critical strain for onset of interfacial sliding is ~ 0.3%, while the maximum strain that can be transferred to graphene ranges from 1.2% to 1.6% depending on the interfacial shear strength and graphene size. Beyond a critical compressive strain of around −0.7%, buckling ridges are observed after unloading. In addition, the interfacial shear stress transfer is investigated by a cohesive zone model integrated with a shear-lag model. Strain distribution in the graphene flake is assumed to behave in three stages in general, bonded, damaged, and debonded, as a result of the interfacial stress transfer. By fitting the cohesive-shear-lag model to our experimental results, the interface properties are identified including interface stiffness, shear strength, and mode II fracture toughness.

References:

T. Jiang and Y. Zhu, "Measuring Graphene Adhesion using Atomic Force Microscopy with a Microsphere Tip", Nanoscale 7, 10760-10766 (2015); T. Jiang, R. Huang, Y. Zhu, "Interfacial Sliding and Buckling of Monolayer Graphene on a Stretchable Substrate", Advanced Functional Materials 24, 396-402 (2014); G. Guo and Y. Zhu, "Cohesive-Shear-Lag Modeling of Interfacial Stress Transfer between a Monolayer Graphene and a Polymer Substrate", Journal of Applied Mechanics 82 (3), 031005 (2015).

Nanoscale Characterization of Adhesion Interactions of Graphene on Silicon Oxide

Ji Won Suk
School of Mechanical Engineering, Sungkyunkwan University, Republic of Korea

Large-area graphene grown by chemical vapor deposition on metals needs to be transferred onto target substrates for further uses. In addition to its other properties, the characteristics of the interactions between large-area graphene and substrates are critical for practical and reliable applications of graphene. The adhesion energy of graphene with other materials such as silicon and copper has been investigated by mechanical delamination at the interfaces. Additionally, in this work, the interaction of graphene was examined over smaller spatial domains by nanoindentation. The graphene surface placed on silicon oxide was indented with a diamond indenter under displacement control. The force profiles provided the adhesive interactions between the probe and the graphene during approach and withdrawal. Based on these force profiles, traction-separation relations were extracted by using continuum analysis.

Dynamics Adhesion and Self-cleaning of Gecko-Bioinspired Micromanipulators with Graphene Tips

Zhenhai Xia
Department of Materials Science and Engineering, University of North Texas

Geckos have the extraordinary ability to keep their sticky feet from fouling while running on dusty walls or ceilings. Such adhesion and self-cleaning ability stems from the hierarchical structures of gecko toes, consisting of millions of micro-fibrils, called setae; these branches further into hundreds to thousands of nano-sized platelet-shaped pads, called spatulae. Inspired by the unique setal structure and their dynamic effect, we fabricate artificial setae using synthetic microfibers. These artificial setae or micromanipulators have a micro-pad at their tips, on which a layer-by-layer gluing of 3 layers of wrinkled graphene multilayers was made. The wrinkled graphene layers on the micro-pad, mimicking gecko spatulae on a seta, increase the surface compliance and contact area for further enhancement in adhesion. The gecko-inspired micromanipulators can easily pick up, transport, and drop off microparticles for precise assembling by simply tuning the pull-off velocity. The dynamics adhesion of the micromanipulators was measured under different pull-off velocity, and the adhesion and self-cleaning mechanisms are analyzed. The results demonstrate that the self-cleaning and micromanipulation capabilities based on the distinctive dynamic effect of gecko spatular nano-pads are robust and efficient in synthetic bio-inspired adhesives as well.

Lubricating Properties of Graphene

Philip Egberts
Department of Mechanical and Manufacturing Engineering, University of Calgary, Calgary, Alberta, Canada

Single asperity friction experiments on graphene, as well as other atomically thin films, have shown that single layers of atoms can dramatically reduce friction when compared to the substrate materials. In particular, the low adhesion and the high tensile modulus typically measured on graphene makes it an ideal solid lubricant for a variety of applications, including nano/microelectromechanical (N/MEMS) system, magnetic storage, and other industrial applications. However, a number of factors have been shown to significantly influence the ability of graphene to reduce friction, including the number of graphene layers used, the adhesive properties of the underlying substrate, and chemical functionalization of the surface. In this study, the lubricating properties of graphene will examined, specifically exfoliated graphene on silicon wafers and chemical vapour deposition (CVD) grown graphene on both polycrystalline copper foils and single crystals of platinum. Additional factors, such as environmental exposure, surface topographical structure, and surface energies will be discussed in terms of their influence on the ability of graphene to lubricate a surface. Atomic scale mechanisms of lubrication will be discussed by combining experimental atomic force microscopy results, atomistic simulations, and analytical friction theories.

Airborne Contamination of 2D Materials

Haitao Liu
Department of Chemistry, University of Pittsburgh

Graphitic materials (e.g. graphene) are long believed to hydrophobic. However, our recent work showed that a clean graphitic surface is in fact mildly hydrophilic; the hydrophobicity is due to airborne hydrocarbon contamination. Hydrocarbon contamination of other 2D materials and its impact on their properties will be discussed.

Wrinkling and Buckle Delamination of 2D MoS_2 for Adhesion and Flexoelectricity Probing

Nanshu Lu
Department of Aerospace Engineering & Engineering Mechanics, University of Texas at Austin

Although wrinkle and buckle-delamination of thin films are often considered to be failures in microelectronics, they could be harnessed as a convenient method for metrology. Transferring 2D materials on pre-stretched soft elastomers can lead to wrinkled and buckle-delaminated structures. While wrinkle and buckle-delamination topology can be accurately probed by atomic force microscope (AFM), the step-edge thickness measured by AFM tip scanning across the edge of a 2D flake on a soft elastomer is not reliable. Wrinkling based metrology is employed to accurately determine the flake thickness and buckle-delamination based metrology is applied to determine the flake-substrate adhesion. The adhesion energy between 2D MoS_2 and Sylgard 184 10:1 polydimethylsiloxane (PDMS) is measured to be 18 mJ/m^2. In addition, wrinkled 2D materials generates large local curvature at the peaks and valleys of the wrinkle, which provides an opportunity to probe the flexoelectric behaviors in 2D materials, which is still under debate. Using a piezoresponse force microscope (PFM), we supplied voltage across the thickness of the monolayer MoS_2 and measured the resulted displacement. Curvature dependent piezoresponse has been observed and we are now in the process of rationalizing the data.

Interface Mechanics of Transfer Printing Processes for Semiconductor Nanomembranes and 2D Materials

Kevin T. Turner
Department of Mechanical Engineering & Applied Mechanics, University of Pennsylvania

Semiconductor nanomembranes and 2D materials are often grown or otherwise produced on a donor substrate and must then be transferred to a different substrate for functional devices to be realized. Soft-stamp microtransfer printing, wafer bonding-based transfer processes, and roll-to-roll transfer schemes are all being pursued as scalable approaches for achieving transfer. Success in all of these transfer processes generally requires that a crack be controllably propagated along specific interfaces. In microtransfer printing, a crack must be propagated along the nanomembrane-donor substrate interface during retrieval and then a crack must subsequently be propagated along the stamp-nanomembrane interface to achieve printing. This talk will: (1) review transfer processes for nanomembranes and 2D materials with a focus on process mechanics, (2) discuss fracture mechanics models that elucidate key factors in achieving transfer and enable the design of robust transfer processes, (3) present experimental results that illustrate the use of mechanics for designing and enhancing microtransfer printing processes.

Nanoscale Mechanics of Plasma-Graphene Interaction and Its Effects on Patterning

H.B. Chew
Department of Aerospace Engineering, University of Illinois at Urbana-Champaign

Graphene is the lightest and strongest known material, and is also an ideal thermal and electrical conductor. Despite its unique properties, graphene has to be patterned to achieve its full engineering and nanotechnological potential. Recent experiments show that a monolayer of graphene deposited on an SiO2 substrate and subjected to hydrogen plasma treatment either undergoes (a) selective etching from the edges of the graphene sheet while leaving the basal plane intact, or experiences (b) etching of both the edges and basal plane of the graphene sheet which results in the formation of nanoscale holes in graphene. The plasma-etched holes in (b) can be either circular or hexagonal, suggesting that the etching process can be isotropic or anisotropic. Here, we model the hydrogen-plasma etching of monolayer graphene on SiO2 substrates across the range of plasma energies using scale-bridging molecular dynamics simulations. Our results uncover distinct etching mechanisms, operative within narrow hydrogen-plasma energy windows, which fully explain the differing plasma-graphene reactions observed experimentally. Specifically, our simulations reveal very sharp transitions in the etching mechanisms with increasing hydrogen ion energy: selective edge etching at ion energies of ~1 eV, isotropic basal plane etching at ion energies of between 2 and 5 eV, and anisotropic etching at ion energies > 7 eV. Understanding the complex plasma-graphene chemistry and the relationship to plasma process parameters opens up a means for controlled patterning of graphene nanostructures.

Adhesion and Fracture of Graphene for Roll-to-Roll Transfer

Kenneth M. Liechti and Seung R. Na
Department of Aerospace Engineering & Engineering Mechanics, University of Texas at Austin

Dry transfer of graphene has been an integral part of its history from the earliest days when scotch tape was first used to exfoliate graphene from graphite [1]. This approach produces relatively small flakes with single or multiple layers. Chemical vapor deposition of graphene on thin (~35 μm) large area copper foils [2-4], and related metal foils such as commercially available Cu-Ni foils, [5] produces large area graphene, up to meters in the in-plane dimension [6]. Graphene has also been grown on copper film (~ 1 µm thick) [7] that has been deposited on silicon wafers.

No matter which approach to the deposition of large area graphene is taken, the same problem remains: transferring the graphene to its destination substrate for the myriad of applications that are currently being considered. Some applications may require intermediate carrier films to be used, so several contact and separation events can be expected. In most cases, the adhesive interactions that are involved in contact and separation are assumed to be van der Waals in nature, but the details could vary significantly depending on the contact pair and environmental effects [8]. The strongest interactions may be between graphene and its seed metal; interactions between graphene and target substrates are expected to be weaker but may be modified by surface functionalization. Doubts about being able to meet the challenge of dry transfer have led to so called "wet transfer" where the seed copper foil is etched away [9] or an electrochemical process [10] that generates bubbles at the graphene/copper foil interface and separates the graphene from the foil. Yoon *et al*. [11] were the first to demonstrate that graphene could be mechanically separated from its seed copper layer.

This presentation will review our efforts to effect dry transfer of graphene from seed copper foil [12] and film [13] using rate effects. At the same time, it was possible to extract the strength, range and fracture energy of the interactions between graphene and the seed copper. Interesting differences in these properties were attributed to distinctions in the roughness of the surfaces of the copper foil and film. The interactions between graphene and silicon oxide will also be discussed [8]. In all three cases, the interaction strengths are lower and ranges are longer than expected for van der Waals forces.

Another issue related to roll-to-roll transfer of graphene is the possibility that graphene will crack under any tension that is applied to the copper foil. We will report on tension tests conducted in an SEM microscope where graphene cracking was observed. Analysis of the underlying shear interactions allowed the toughness of the graphene as well as the shear strength of the interaction to be estimated.

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Multiscale Modeling of Two-Dimensional Materials: Stiffness, Strength and Reliability

Jeffrey W. Kysar
Department of Mechanical Engineering, Columbia University

The focus of this talk is on the mechanical properties of graphene. We will discuss methods to isolate two-dimensional materials via mechanical exfoliation and subsequently to make single crystal specimens via nanofabrication methods. An atomic force microscope or a nanoindenter is used to indent monatomically thin freestanding circular specimens of graphene. The experimental results suggest the mechanically exfoliated single crystal materials to be free of defects. Thus, the breaking strength of graphene represents the intrinsic strength, or the maximum stress that a material can support in the absence of defects. We develop a multiscale nonlinear anisotropic elastic constitutive theory and implement it into the finite element method to validate the multiscale model against experiments. We will discuss graphene grown by Chemical Vapor Deposition (CVD) using industrially scalable processes. The CVD grown graphene is polycrystalline, yet upon optimization of the CVD parameters, the strength of the polycrystalline graphene can achieve a very high fraction of the intrinsic strength of defect-free single crystal graphene. We discuss the development of multiscale models to predict the strength of grain boundaries in the polycrystalline graphene and implement the results in the form of a cohesive zone to model the effects of grain boundaries on the rupture strength in polycrystalline graphene.

Blister Testing Atomic Membranes: A route towards understanding 2D materials

J. Scott Bunch
Department of Mechanical Engineering and Division of Materials Science and Engineering, Boston University

Imagine a sheet of paper only one atom thin with atomic bonding similar to diamond. Graphene, a single layer of graphite, is such a structure. It is the first two dimensional atomic crystal and consists solely of carbon atoms covalently bonded in a hexagonal chicken wire lattice. This unique atomic structure gives it remarkable electrical, mechanical, and thermal properties. Moreover, graphene represents only one of a whole class of 2D materials that include metals, insulators, and semiconductors. It is the mechanical properties of these wondrous materials that fascinate our group the most. They are the thinnest materials in the world and impermeable to standard gases. We suspend 2D materials over microcavities etched in silicon dioxide and utilize this remarkable gas impermeability to apply a pressure difference across the membrane. This results in a pressurized blister test that allows us to introduce controlled biaxial strain in the membrane. In this talk, I will focus on our recent experimental results utilizing the pressurized blister test on molybdenum disulfide, MoS_2, to measure its Young's modulus and adhesion energy to silicon oxide and using biaxial strain to tune its electronic band structure.

Mechanical Properties of 2D Materials

Yong-Wei Zhang
*Institute of High Performance Computing, A*STAR, Singapore*

Recently, 2D materials, such as graphene, MoS2, silicene, phosphorene et al, have drawn a great deal of attention due to their remarkable electronic, thermal, magnetic, optical and mechanical properties. Understanding the structural and mechanical properties of these 2D materials is critically important for the development of 2D materials-based electronic, optoelectronic and sensing devices and also their reinforced composite materials.

We report our recent research work on the mechanical properties of graphene, silence, MoS2, phosphorene, and their chemically functionalized nanostructures using different simulation methods, such as molecular dynamic simulations, density functional tight-binding simulations, and first-principles calculations, focusing on the following aspects: 1) the mechanical properties of their edges and implications; 2) the effect of atomic defects on the failure mechanisms and behaviors; and 3) the effect of chemical functionalization on the mechanical properties.

Predictive Modeling in 2D Materials: Morphology, Dislocations, Grain Boundaries

Boris I. Yakobson
Department of Materials Science & NanoEngineering, Department of Chemistry, and the Richard E. Smalley Institute, Rice University

It is of great interest and importance for materials design to uncover, through computational and theoretical modeling, the following relationships: {basic atomic interactions → structure/morphology (including defects) → functionality (including electronic)}. We will discuss recent examples from low-dimensional materials, where we seem to achieve satisfactory degree of understanding, mostly focusing on nucleation and islands shapes of graphene, h-BN, metal dichalcogenides MX_2 [1], grain boundaries and dislocations [2] including the nanoscale electromagnetism of the latter, heterojunctions [3], if time permits—catalysis [4], and even predictive 2D boron synthesis [5].

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Chemical Kinetics on Graphene Using Local Stress and Heat

Shivaranjan Raghuraman and Jonathan R. Felts
Department of Mechanical Engineering, Texas A&M University

Here we investigate the chemical dynamics of local graphene oxide reduction through the application of local temperature and stress using a heated atomic force microscope (AFM) tip. Specifically, a silicon AFM cantilever with an embedded Joule heater applies both local stress and heat to chemically functionalized graphene surfaces during tip sliding. The friction of the graphene sheet depends linearly on percent chemical group surface concentration, so monitoring friction force during chemical reduction provides an *in situ* measure of chemical functionality on the surface over time. We first demonstrate bond cleavage of oxygen, fluorine, and hydrogen from graphene using solely force from the AFM

tip. We then investigate the application of local temperature and force during tip sliding on graphene oxide. Monitoring friction over time for tip temperatures between 310 – 355 ˚C and loads < 40 nN provides the kinetics of the reduction process. Calculating reaction rate as a function of temperature assuming a first order reaction provided an activation energy for bond scission of 0.7 ± 0.3 eV, where measurement noise contributed significantly to error and precluded determination of reaction order. In an effort to reduce measurement time and error, friction was measured as a function of load during linear temperature ramps of the tip heater. Such a measurement is analogous to thermogravimetric analysis (TGA) or temperature programmed desorption (TPD), which is governed by

$$\frac{df}{dT} = \frac{v}{\beta} f^n e^{-\frac{(E_a - \sigma V_a)}{kT}} \qquad \text{(eqn 1)}$$

where β is the temperature ramp rate, ν is an exponential pre-factor, f is the measured friction, n is the order of the reaction, E_a is activation energy for bond removal, σ is stress at the tip-surface contact, V_a is the activation volume of the reacted molecules, k is Boltzmann's constant, and T is temperature. Numerically curve fitting the solution to this equation with the measured friction response provided an activation energy of 0.62 ± 0.07 eV, an activation volume of 40 ± 10 Å^3, a reaction order $n \sim 1$, and a pre-exponential factor between $10^1 - 10^4$ s^{-1}. It was further shown that applied force nearly linearly reduces the observed activation barrier. Quantitatively, the results are at odds with many theoretical and experimental works showing that graphene oxide reduces via a 2nd order recombination reaction with activation energies significantly exceeding 1 eV. We propose an alternative reduction mechanism where the local temperature rise at the tip promotes diffusion of molecules under the tip. This mechanism is physically intuitive, as adsorbed species can no longer contribute to friction once excited above the diffusion energy barrier. Further, the measured pre-exponential factor depends on the time required for a molecule to diffuse over the scan area, resulting in values of 10^{-1}-10^4 s^{-1}, quantitatively agreeing with experimental observation. Thus, we showed that heated AFM tips can simultaneously drive and measure chemical reactions on 2D surfaces, provide quantitative measures of the kinetics of those reactions, and induce reactions which would otherwise not be possible during bulk processing. Such exquisite thermomechanical control over local surface chemistry will impact nanofabrication efforts and fundamental studies of surface chemistry.

Programmable Localized Wrinkling of Thin Films on Shape Memory Polymer Substrates

Jianliang Xiao

Department of Mechanical Engineering, University of Colorado Boulder

Wrinkling of stiff thin films on soft substrates has many promising applications and has attracted researchers' attention for years. As a class of smart material, shape memory polymers (SMPs) can remember different shapes and can recover to their permanent shapes under appropriate stimuli, such as heat, humility, and electrical field. SMPs show attractive properties in fabricating surface wrinkling due to the shape memory effect, low cost, and convenience in processing. Using pre-programmed heat responsive SMPs as substrates, we demonstrate a self-assembly fabrication method for programmable localized surface wrinkling. Different from global wrinkling in most of previous studies, locally heating the thin film-substrate system causes localized recovery in the SMP substrate, and thus induces localized thin film wrinkling. The wrinkle pattern shows good sinusoidal profile, with wavelength and amplitude decreasing gradually with the distance from the heating source. The surface wrinkle area can also be tuned by controlling heat input. We have also demonstrated spatially tunable optical gratings by using this method. This study can find potential applications in programmable optical gratings, surface property control, and other demanding applications.

Self-healing of Molybdenum Disulfide and Silicon Oxide

Seung Ryul. Na[1], Youngchan Kim[2], Changgu Lee[2], Ji Won Suk[2], Kenneth M. Liechti[1]

[1]*Department of Aerospace Engineering & Engineering Mechanics, University of Texas at Austin*

[2]*School of Mechanical Engineering, Sungkyunkwan University, Republic of Korea*

The transition metal dichalcogenides (TMDC) are atomically thin semiconductors in the form of MX_2 consisting of a transition metal (M) atom and chalcogen (X) atom. The usefulness of two-dimensional TMDC has been proven in various nanoelectronics, photoelectronics, nanotribology and energy applications. Also, bulk crystals of TMDC can be formed from several monolayers, whose interfaces are bound by weak interactions such as van der Waal forces. Mechanically exfoliated graphene using the scotch tape method and synthesized graphene by chemical vapor deposition (CVD) on copper foil or film are the first reported two-dimensional materials studied in various fields. Now, the molybdenum disulfide (MoS_2) monolayer is of interest due to high electrical mobility, mechanical strength, and low-friction properties.

Recently, MoS_2 field-effect transistors (FETs) coupled with micromechanical cleavage technique have been demonstrated with excellent on/off ratios and mobility higher than 200 cm2/Vs. Also, not only wafer scale MoS_2 growth but also device fabrications were demonstrated with CVD-grown MoS_2 assisted by a polymer support. Many of these applications require that the adhesive behavior of MoS_2 be characterized for reliability assessments or transfer. Currently, our understanding regarding the adhesion interaction of MoS_2 to other substances is limited despite all the other achievements associated with MoS_2 in the field of nanoelectronics.

The adhesion energy and interaction of two-dimensional materials can be characterized by taking advantage of the fracture mechanics concepts, which was actively used in the field of graphene research. For example, a micro-blister experiment, a macro scale blister experiment, a double cantilever beam fracture experiment (DCB), a Mode I fracture wedge experiment, and scratch test have all been used to evaluate the adhesion energy and interactions of graphene to seed and target substrates. In this study, we focused on the adhesion energy as well as the adhesion interactions between silicon oxide and MoS_2 using double cantilever beam fracture experiments.

MoS_2 was uniformly grown on the thermally grown silicon oxide surface of a silicon strip by CVD. It was bonded to a second silicon strip with an epoxy. The silicon/epoxy/MoS_2/silicon laminates were loaded as double cantilever beam specimens and the MoS_2/silicon interface was separated under displacement control while the load was monitored *via* a load cell. The fractured surface was examined by X-ray photoelectron spectroscopy (XPS), Raman spectroscopy as well as scanning electron microscopy (SEM) and atomic force microscopy (AFM). The clean separation of the MoS_2 monolayer from the original silicon oxide surface was clearly demonstrated.

Simple Euler beam theory was adopted to evaluate the adhesion energy between MoS_2 and silicon oxide. Furthermore, the adhesion strength and interaction range were estimated by the finite element method using traction-separation relations for the interface between MoS_2 and silicon oxide. The key parameters of the traction-separation relation were obtained by an iterative approach based on the force-displacement response and fracture resistance curve of that interface. Furthermore, self-healing behavior was observed during the experiments. The adhesion interactions of the healed interface were noticeably different from the original response of the MoS_2 and silicon oxide interface.

An Interatomic Potential for Graphene Derived from First-Principles

Chris Marianetti
Department of Materials Science and Engineering, Columbia University

Here we use density-functional theory to compute an interatomic potential for graphene, including all anharmonic interactions up to at least fourth order. We generate all group-theoretically allowed terms within a hexagon via the recently-developed slave mode expansion. This expands the potential in terms of the normal modes of overlapping hexagons,

while obeying the space group symmetry and homogeneity of free space. We further introduce the notion of cooperative modes, which combine strain and q=0 phonons to yield the same pure mode amplitude on each hexagon. Within the cooperative subspace, cooperative modes allow for arbitrarily-precise meshing to directly compute energies, or calculation of the anharmonic coefficients via finite-difference. We demonstrate the power of our approach in the context of strained graphene, which is known to have a novel strain-driven soft mode at the K-point. We identify the dominant anharmonic terms which drive the soft K mode, and study the role of finite temperatures using molecular dynamics and Monte-Carlo simulations.

Atomistic Scale Simulations of 2D layer Materials Using ReaxFF

Alireza Ostadhossein[1], Peng Zhao[1], Hui Yang[1], Sulin Zhang[1], Adri van Duin[2]

[1]*Department of Engineering Science & Mechanics, Pennsylvania State University*

[2]*Department of Mechanical & Nuclear Engineering, Pennsylvania State University*

The discovery of graphene was the moment of the birth of an emerging research realm of two-dimensional (2D) materials. However, the ever-increasing demand of electronic and chemical industries for novel materials with superior structural, thermal and electrical properties has stimulated extensive scientific efforts to develop and synthesis of new ‘graphene-liked’ 2D-structures. Of the various proposed materials, transition metal dichalcogenides (TMDCs), such as MoS_2 and WS_2 and 2D-transition metal carbide/nitride, so called MXene, have been recognized as one of the promising candidates. TMDCs with high direct band-gap exhibited excellent properties which has potential applications in next generation nanoelectronics, optoelectronics, and flexible devices. Recent experimental advances confirm the possibility of further tuning the electronic properties of these materials through the fabrication of single-layer hetrostructures consisting of 2H (semiconducting) and 1T (metallic) phases. Furthermore, titanium carbides MXenes, synthesized via selective extraction of Al from MAX phases, present very attractive electrochemical properties such as high specific capacitance in aqueous electrolytes, high electroconductivity exceeding than that of graphene and its hydrophilic surface. In this study, a new reactive ReaxFF force field parameterization has been performed to describe the mechanical and thermal behavior of MoS_2 and $Ti_{x+1}C_xT_x$ 2D-phases. Influence of defects, e.g. vacancies, grain boundaries and ripplocations on the mechanical and thermal properties of all-MoS_2 layers were also examined. This new ReaxFF interatomic potential is employed to study the behavior of functional MXene and the structure of the confined inter-layer water intercalated with metal ions. Our atomistic simulations along with the new force field developments provides a reliable tool to model the structural and interfacial behavior of two classes of 2D-layer materials.

Thermomechanical and Interfacial Properties of Graphene: A Few Challenges for Modeling

Rui Huang
Department of Aerospace Engineering & Engineering Mechanics, University of Texas at Austin

In this talk I will present my perspectives on modeling thermomechanical and interfacial properties of graphene and a few challenges to be resolved in future works. First, for the basic mechanical properties such as in-plane elasticity, theoretical strength, and bending modulus of monolayer graphene, the first-principle calculations based on density functional theory have produced well-accepted results, in good agreement with experiments. However, for most atomistic simulations using empirical force fields, the in-plane elasticity is not well predicted quantitatively. Next, the effects of temperature on the mechanical properties of monolayer graphene are discussed, largely based on molecular dynamics simulations. Here challenges exist to correctly predict the thermal expansion or contraction over a wide range of temperatures and to understand the potentially temperature and size-dependent mechanical properties due to entropic effects of thermal rippling. The effects of temperature on the strength and fracture toughness are not well understood as well. Finally, even more challenges exist to model the interactions between graphene and other materials, including the effects of temperature, moisture, and surface roughness. Both adhesive and frictional interactions are important for understanding a variety of surface morphologies (wrinkles, bubbles, cracks) of graphene with potential impacts on other physical properties.