

Figure 1. (a) Equilibrated boundary lubrication system at start of simulation. Color denotes atomic charge, blue-positive, red-negative. (b-d) Boundary lubrication system through simulation progress.

### Innovation

Today, modeling and simulation often drive innovation by allowing material insight with reduced experimental times and costs. The development of this work will provide a boundary lubrication model for the furthered fundamental understanding of tribochemical reactions that can drive innovative tribological solutions for the US Army. This model will also provide a toolset that can be extended to study other materials and lubrication regimes, and elicit useful tribological metrics that can direct future experiments.

	(\$M)	PE	Project	18
FY18-FY20	0.08	61101	91A	0.08

Date: 12 DEC 18

POC: Talia Marie Sebastian

### Problems/Questions

Boundary lubrication presents the most severe conditions for lubricants to control. In these regimes, high load and/or low speed are often supported by the surface asperities (i.e., roughness) of the mating materials. These surface asperities however also participate in the lubrication process, and can drive several beneficial chemical reactions, to include the formation of protective tribofilms that reduce friction and prevent wear. To date, the formation of graphene tribofilms on rough surfaces is not well characterized, and thus its full tribological knowledge and potential unknown.

### Theoretical Basis for Research

Graphene, known for its superior mechanical, electrical, optical, and thermal properties, has seen increasing tribological interest over the past decade for its superior lubricity and corrosion inhibiting abilities over traditional lubricants. Despite this, additional studies have demonstrated these tribological properties to weaken with physical and chemical changes in the material. These studies often focus on defects incurred through synthesis, as opposed to those incurred through lubrication, and thus this work aims to further expand the tribological knowledge of graphene under dynamic boundary lubrication conditions.

### Relevance to Org Mission

Research, development, and standardization of fluids, lubricants, and fuels works to create tribological solutions that simplify life-cycle logistics, improve reliability, availability, and maintainability of military ground systems, and reduce energy footprint.



# U.S. ARMY RESEARCH, DEVELOPMENT, AND ENGINEERING COMMAND

*In-House Laboratory Independent Research (ILIR) FY18*

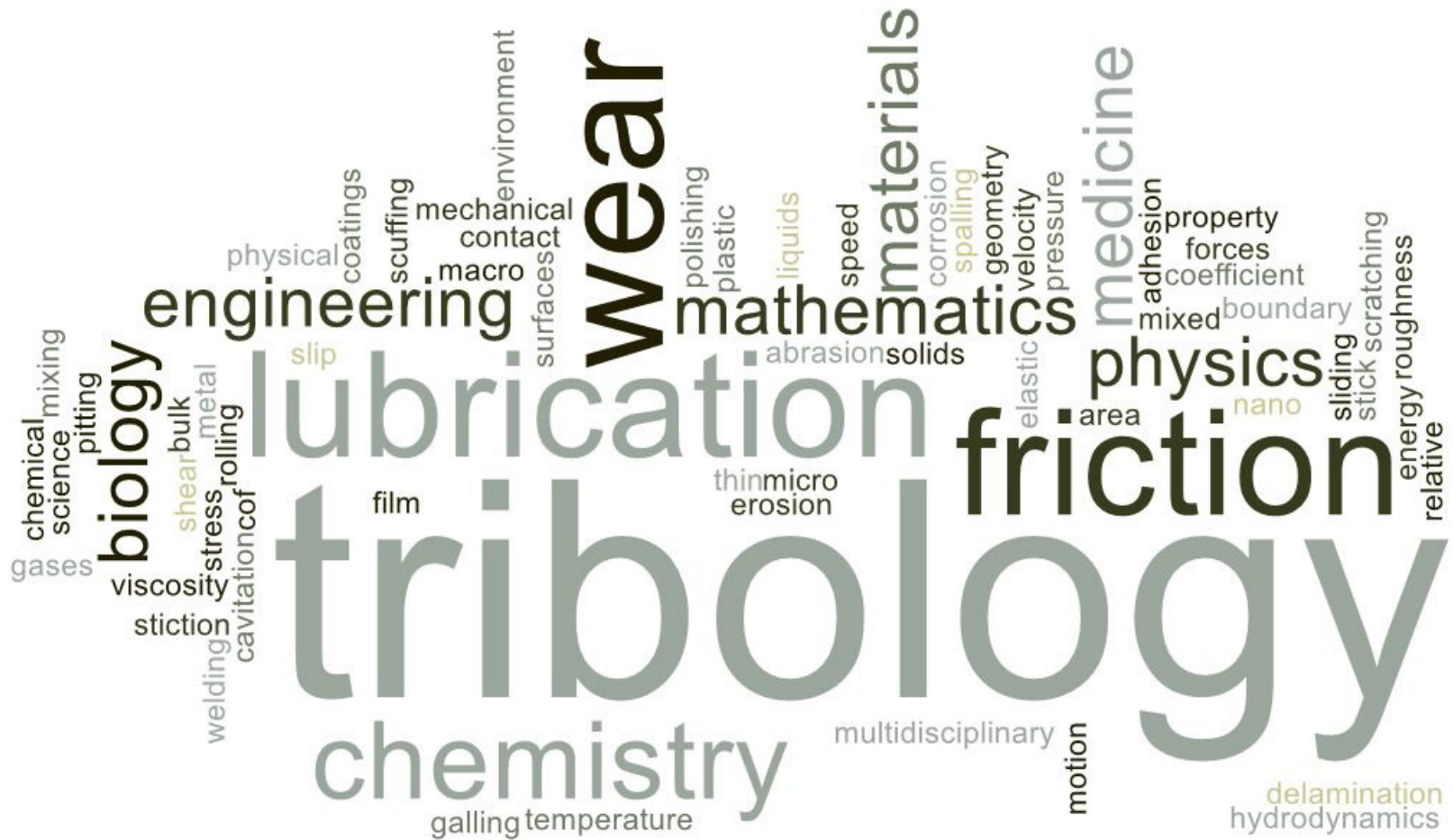
*Exploring Graphene's Potential for Enhanced Chemical Reactivity Induced by Regions of Local Conformational Deformation on Rough Iron Surfaces: Kinky Chemistry Applied*

Talia Marie Sebastian, PhD

Chemist

Ground System Performance Fluids (GSPF)

DISTRIBUTION A. Approved for public release; distribution unlimited.





## Tribological Strengths

- *Low friction due to lamellar stacking structure*
- *Wear suppression due to mechanical strength*
- *Reduces corrosion and oxidation due to chemical stability*

## Tribological Behavior

- *Number of layers*
- *Stacking of layers*
- *Substrate adhesion*
- *Defects or modifications*

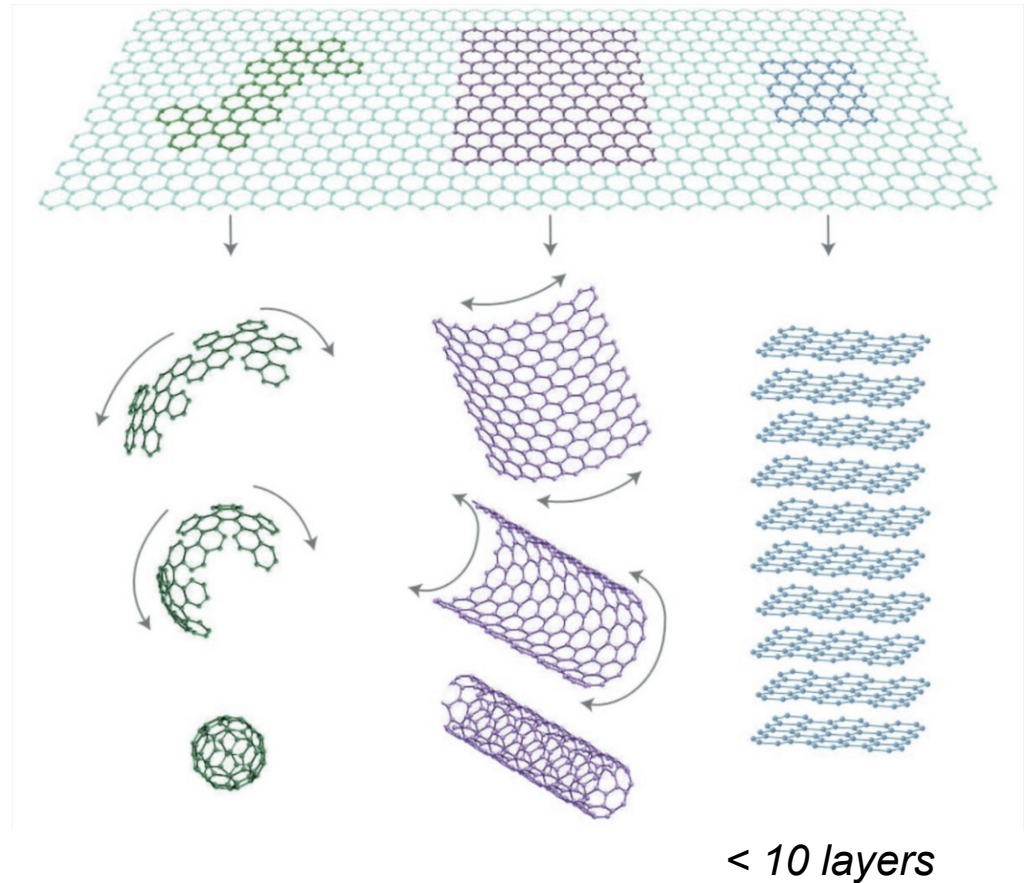




TABLE 1

**Overview of macroscale tribological properties of widely used solid lubricants.**

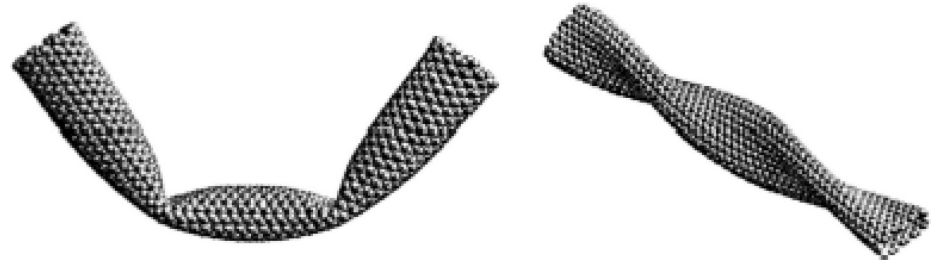
Solid lubricant coating	Deposition methods	Coating thickness ( $\mu\text{m}$ )	Typical friction coefficient	Wear/friction mechanism
<b>Graphite</b>	Evaporation, pyrolysis	0.2–5	Dry: 0.5–0.6; Humid: 0.1–0.2	Interlayer shear and water intercalation
<b>Diamond like carbon (near frictionless carbon)</b>	Sputtering (rf and dc), ion-beam, PECVD	1–3	Dry: 0.001–0.05; Humid: 0.2–0.3	High chemical inertness and repulsive forces due to hydrogen termination
<b>Tetrahedral amorphous carbon</b>	Ion beam, cathodic arc, pulsed laser	0.01–1	Dry: 0.7; Humid: 0.1	Tribochemically induced surface reaction and termination of top carbon atoms
<b>Ultrananocrystalline diamond</b>	MPCVD, HFCVD	0.5–1.5	Dry: 0.05–0.13; Humid: 0.007–0.1	Tribochemically induced reaction with H, O, or OH
<b>MoS<sub>2</sub> and WS<sub>2</sub></b>	Sputtering (rf and dc), thermal evaporation CVD, ALD	0.2–2	Dry: 0.02–0.06; Humid: 0.15–0.25 initial and increasing	Interlayer shear and transfer film formation
<b>Graphene/graphene oxide</b>	CVD, chemical and mechanical exfoliation	0.001–0.002	Dry: 0.15–0.2; Humid: 0.15–0.2	Interlayer shear and prevention of tribocorrosion

Adapted: Berman, et al. 2014. Materials Today.



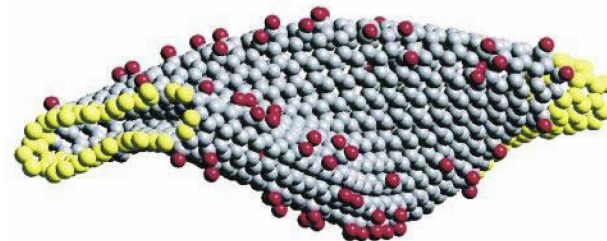
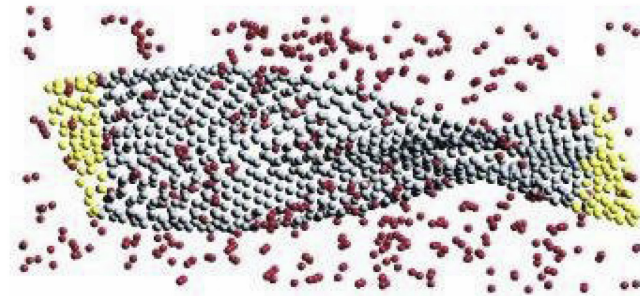
## Kink Promoted Chemistry

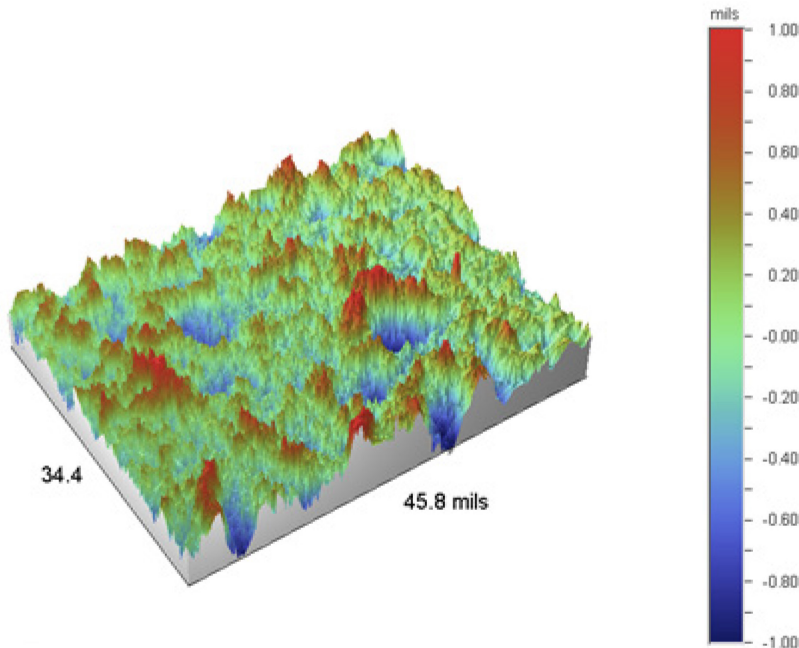
- *Controlled functionalization*
- *Kinks and ridges*
- *Static and classical trajectory simulations*



## Results

- *Nonlinear distortions disrupt  $sp^2$  conjugation resulting in loss of  $p$ -orbital spatial overlap*
- *Shift in hybridization to  $sp^2 - sp^3$  intermediate*
- *Increase in local energy due to partial radical character in  $\pi$ -bonding electrons*
- *Enhanced chemisorption*





### Surface Stats:

Ra: 0.23 mils      Rq: 0.30 mils      Rt: 2.61 mils

## SURFACE PREPARATION

Please contact Sandstrom Products Company for substitute surface preparations if recommended steps cannot be followed.

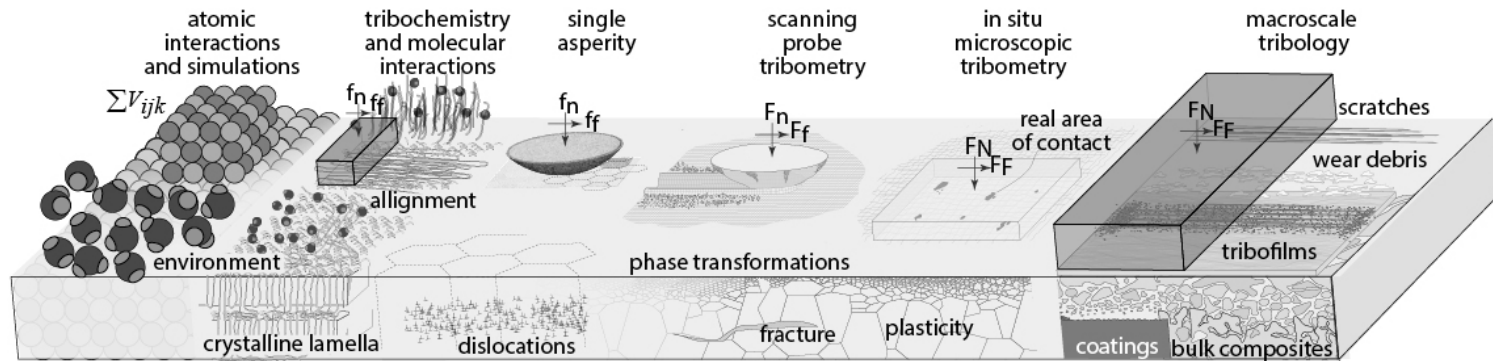
**Application on steel.** Pre-clean surface with aliphatic naphtha or any other EPA compliant cleaner that sufficiently cleans surface to pass ASTM F22. Abrasive blast surface with 180-220 grit aluminum oxide (25-50 RMS optimum). Phosphate IAW MIL-DTL-16232 (weight should be 11-22 g/m<sup>2</sup>), type M, class 3 (optimal performance) or type Z, class 3.

**Application on stainless steels.** Pre-clean surface with aliphatic naphtha or any other EPA compliant cleaner that sufficiently cleans surface to pass ASTM F22. Abrasive blast surface with 180-220 grit aluminum oxide (25-50 RMS optimum). Passivate surface with ASTM A967, types nitric 1, nitric 2 or nitric 3, as applicable.

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**Application on copper and copper alloys.** Pre-clean surface with aliphatic naphtha or any other EPA compliant cleaner that sufficiently cleans surface to pass ASTM F22. Abrasive blast surface with 180-220 grit aluminum oxide (25-50 RMS optimum). Form a black oxide finish on surface.



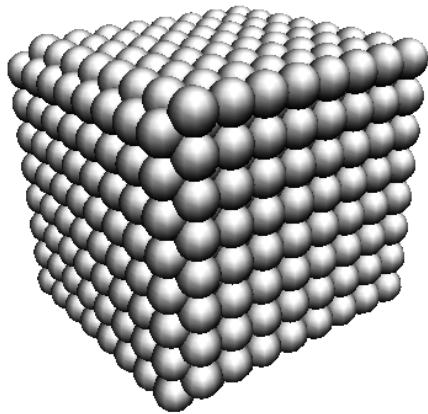
Nano

Micro

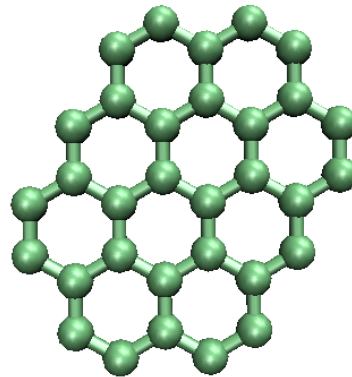
Macro



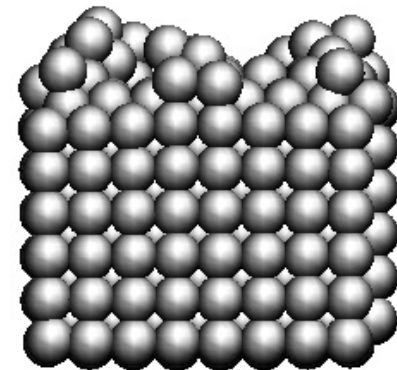
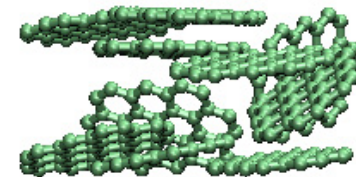
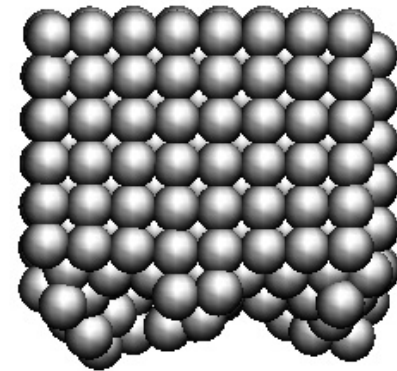
Explore the effects of surface roughness/defects on graphene's tribological behavior in boundary lubrication conditions.



- $\alpha$ -iron (bcc)
- $a_0$  2.87 Å at 300 K
- 8 x 8 x 8 cube



- zig zag
- $a_0$  2.46 Å at 300 K
- 10 count
- 23 x 23 x 10 Å box



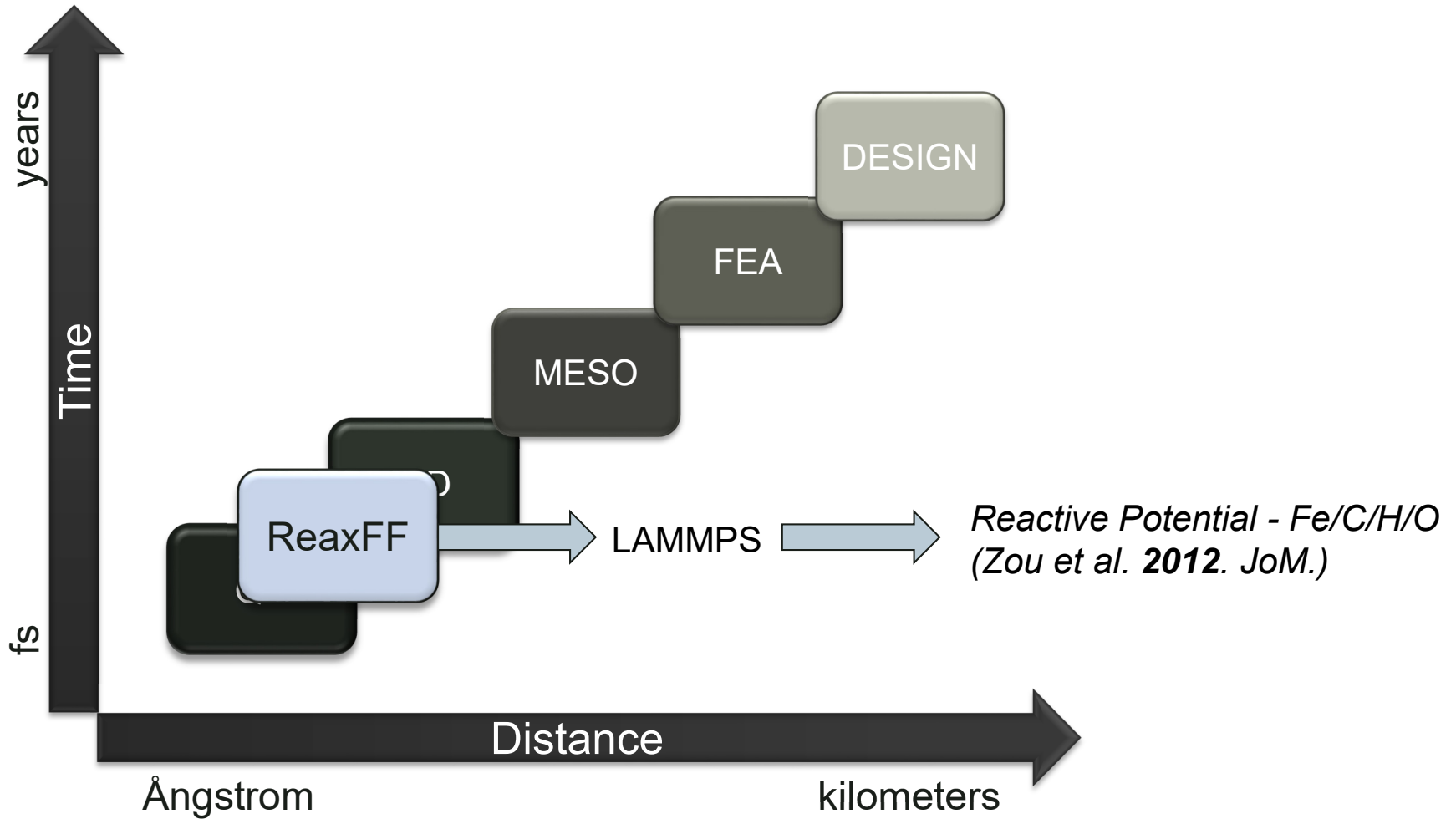


Parameters



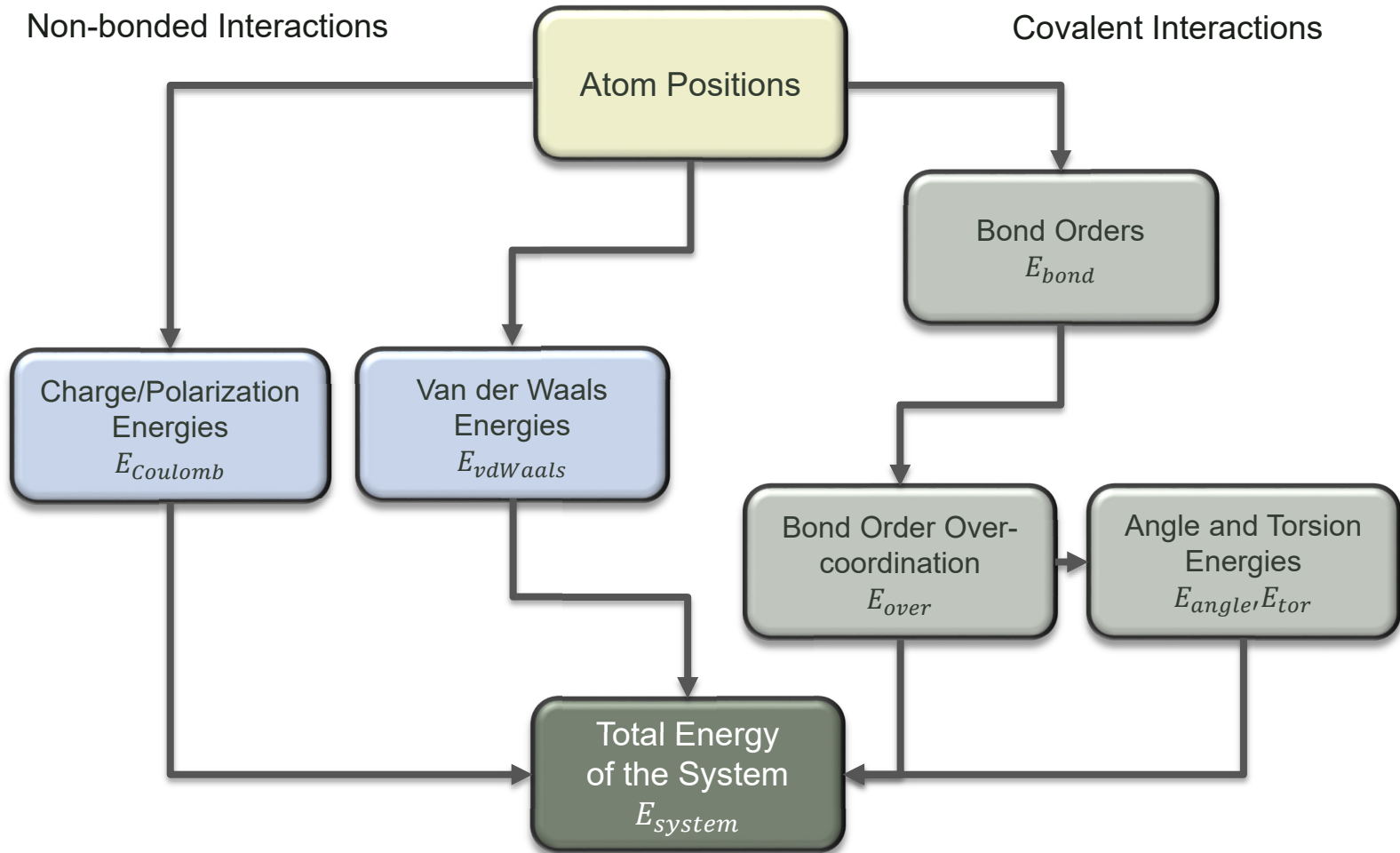
- *NVE*
- *Load – constant*
- *Shear – constant*
- *Temperature – 300 K*
- *Timescale – 2 ns*







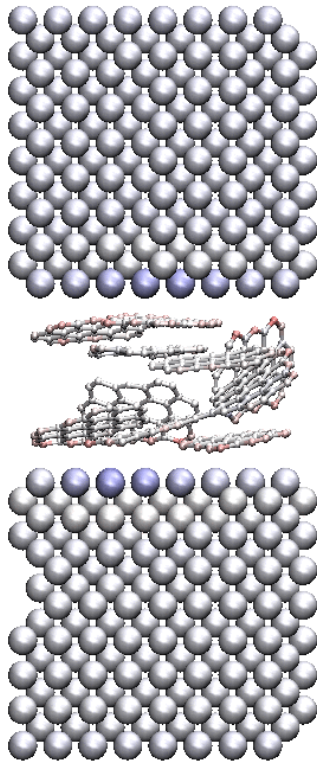
$$E_{system} = E_{bond} + E_{over} + E_{angle} + E_{tor} + E_{vdWaals} + E_{Coulomb} + E_{Specific}$$



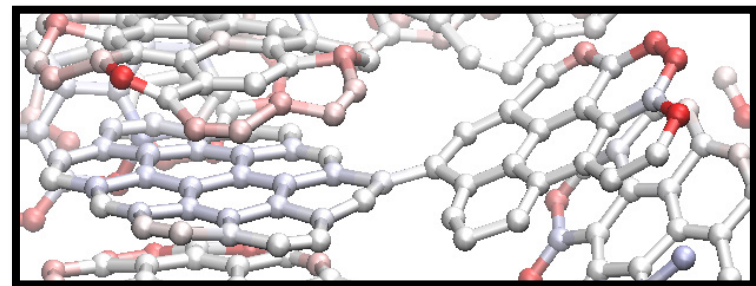
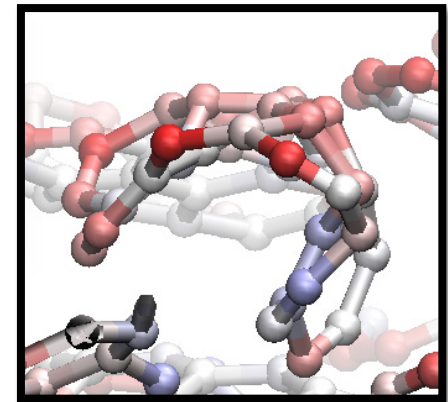
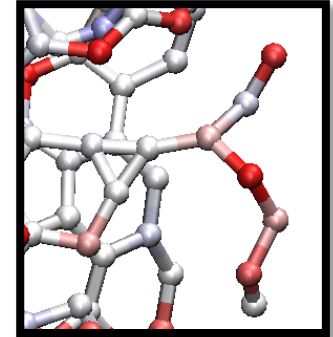
Adapted: Russo and van Duin. 2011. Nuclear Instruments and Methods in Physics Research B.

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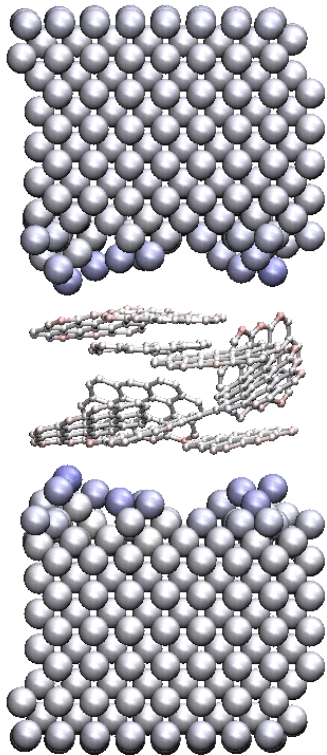
## Graphene Platelets on Pristine Fe Surfaces



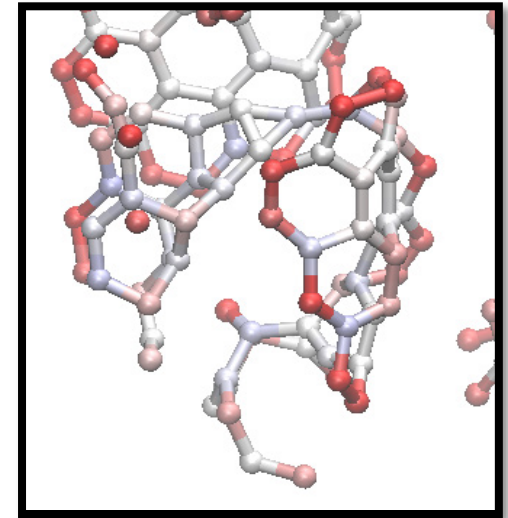
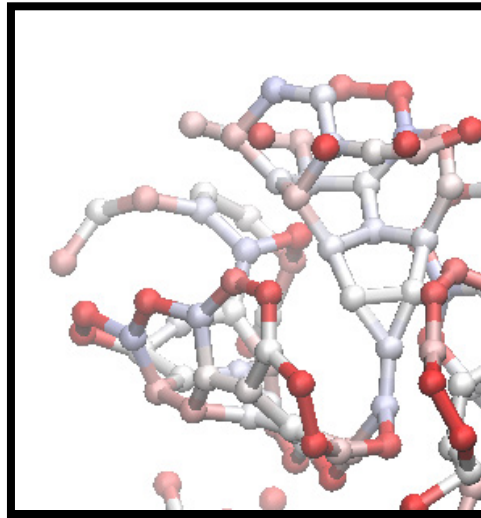
- *Sequestering and entrainment of stationary Fe*
- *Dimerization*
- *Charge transfer through the basal plane*
- *Platelet folding*
- *Platelet ring opening*
- *3, 5 - ring formations in platelet*



## Graphene Platelets on Rough Fe Surfaces



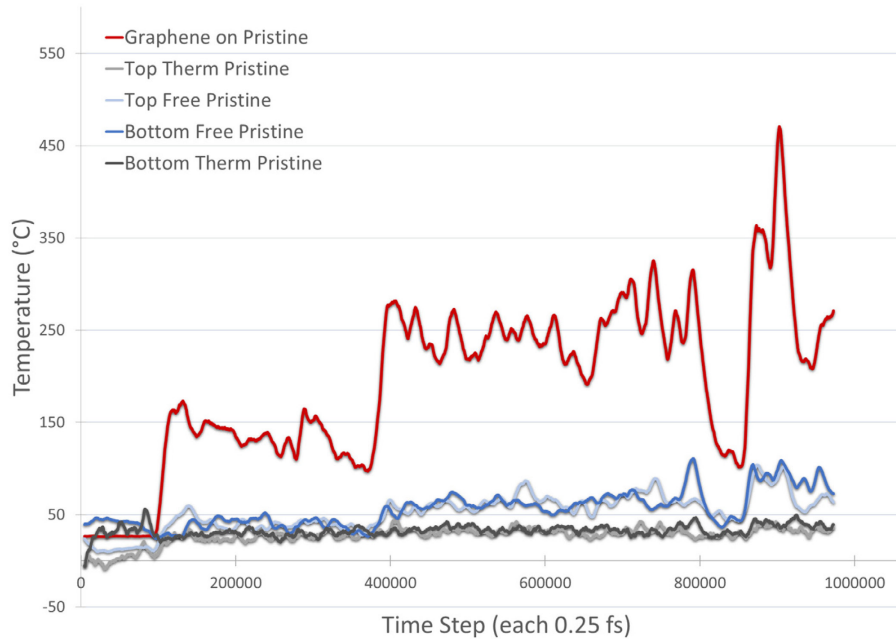
- Cage like formations



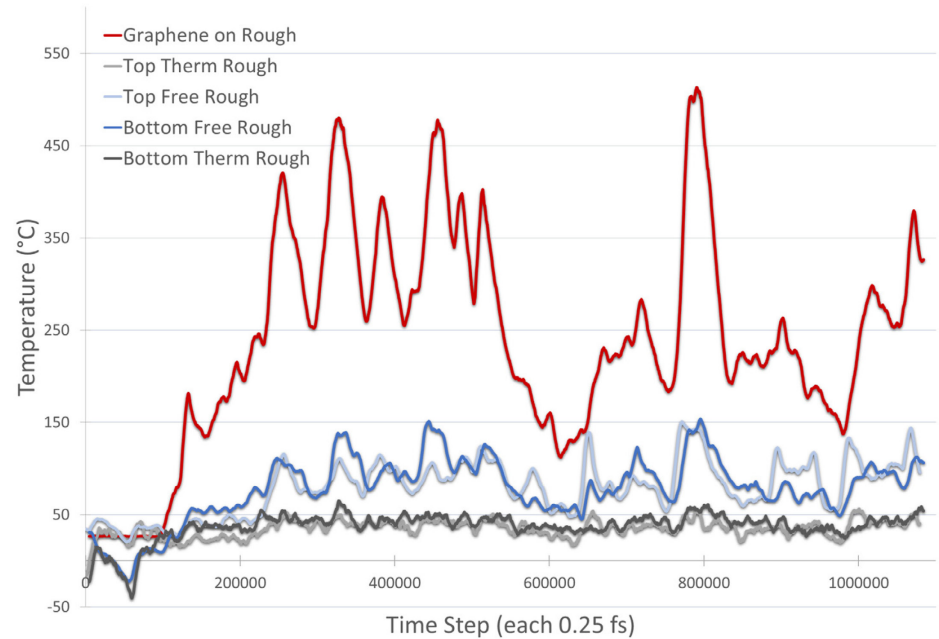


## Graphene Platelets on Pristine and Rough Fe Surfaces

### Temperature Mapping Pristine Fe Surfaces

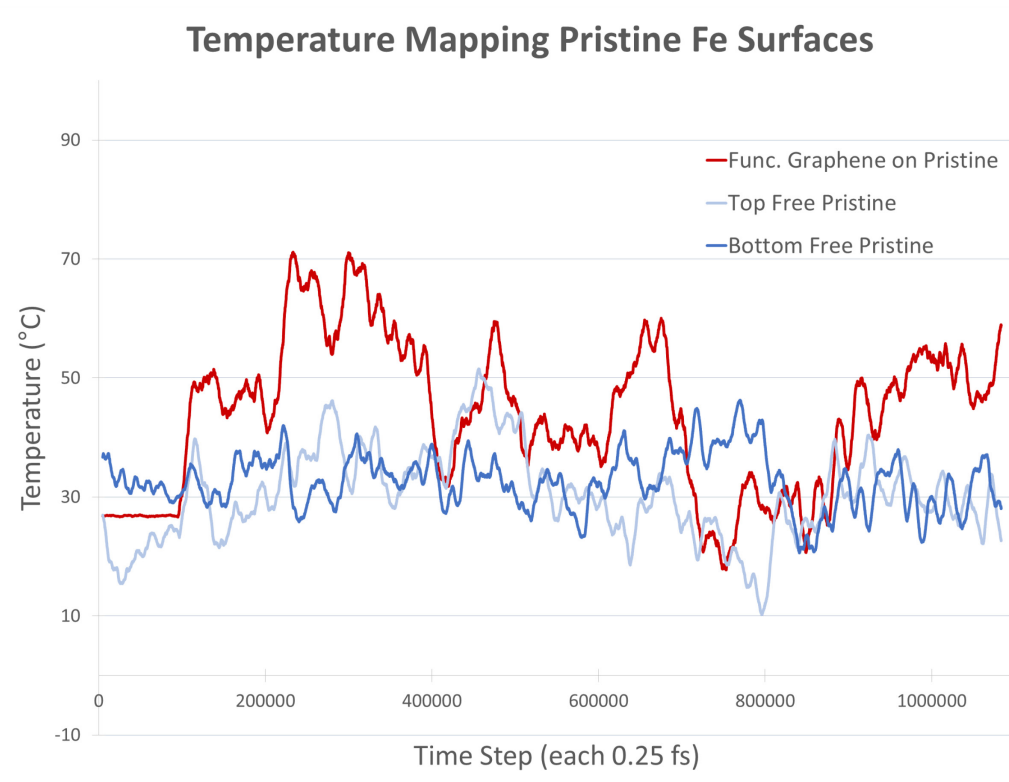
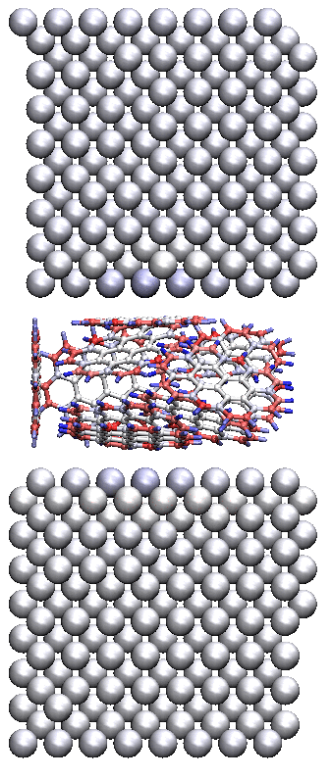


### Temperature Mapping Rough Fe Surfaces



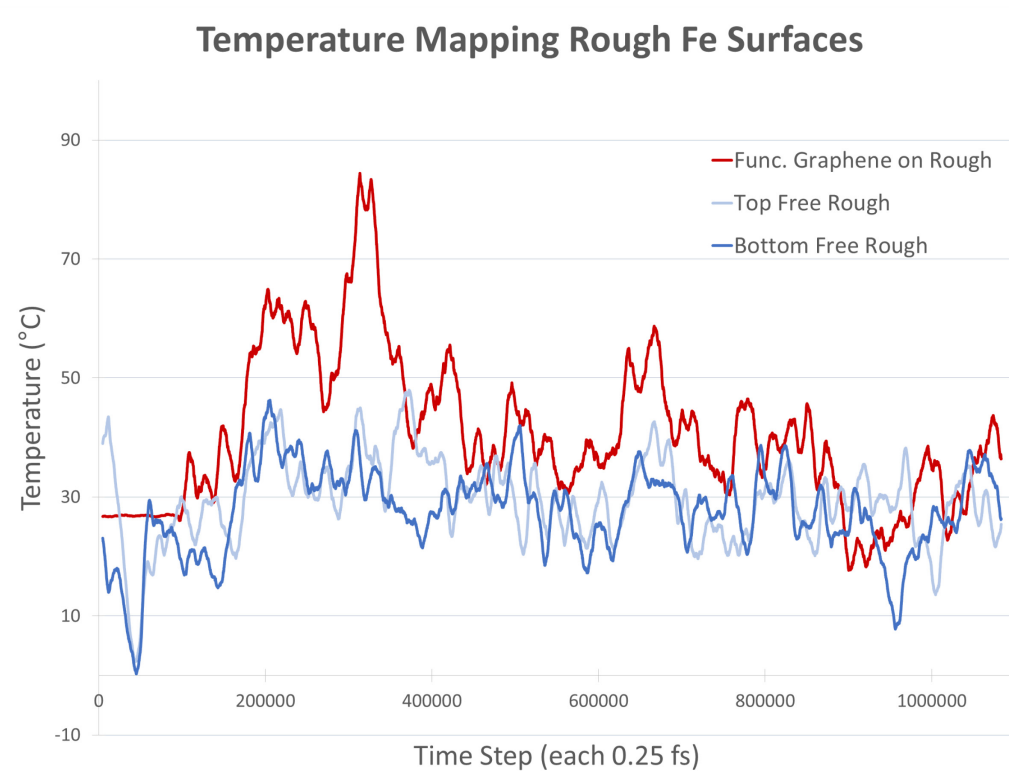
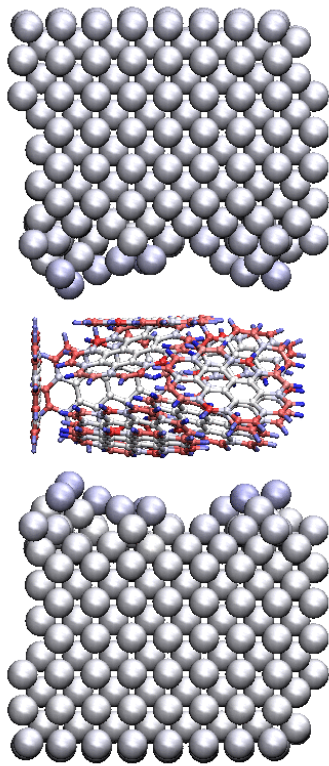


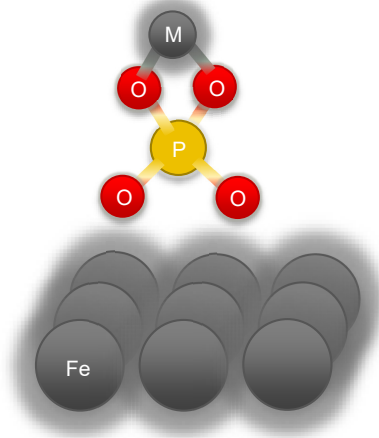
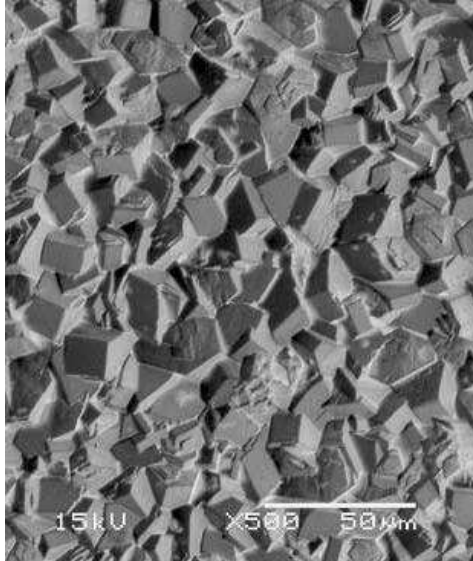
## Functionalized Graphene Platelets on Pristine Fe Surfaces





## Functionalized Graphene Platelets on Rough Fe Surfaces





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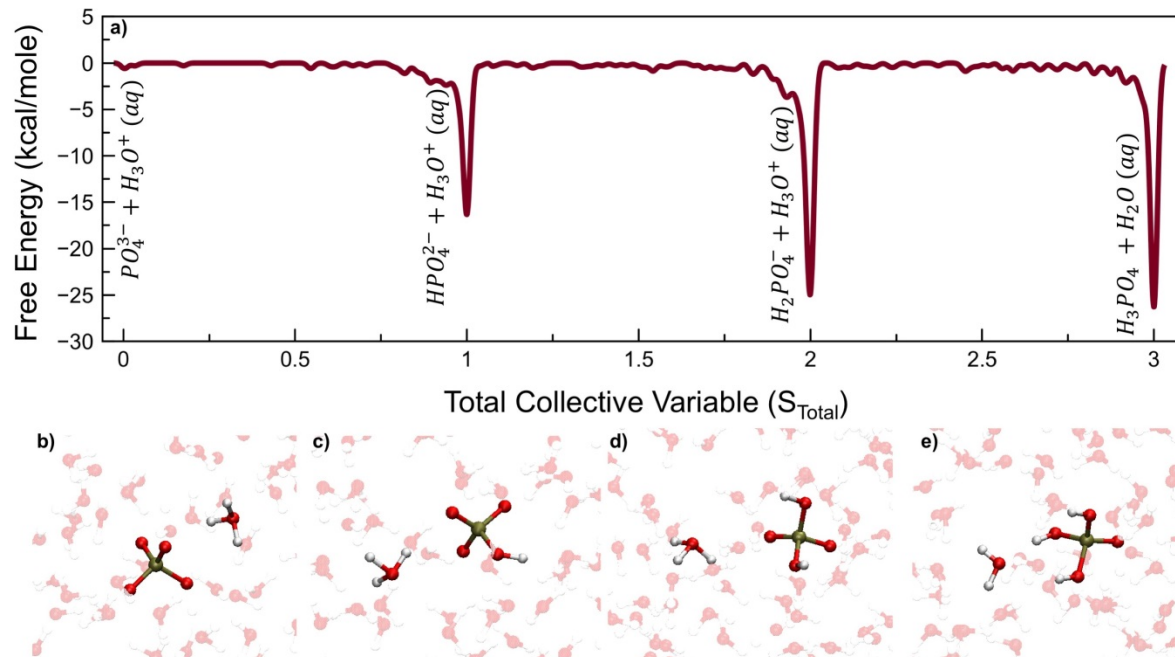
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## Development of Fe/O/P/M (M=Zn, Mn) ReaxFF Potential





### *ILIR FY19*

#### *Current status*

- *Updated model to compute analytical output (forces, velocities, temperature mapping\*)*
- *Testing hydrogen environment(s\*)*

#### *Future work*

- *Test additional environments (oxygen, water, hydrocarbon)*
- *Test additional load regimes*
- *Test additional sliding regimes\**



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*Adrianus van Duin, PhD, Pennsylvania State University, Professor*