

Multi-Scale Simulation of Interfacial Phenomena and Nano-Particle Placement in Polymer Matrix Composites

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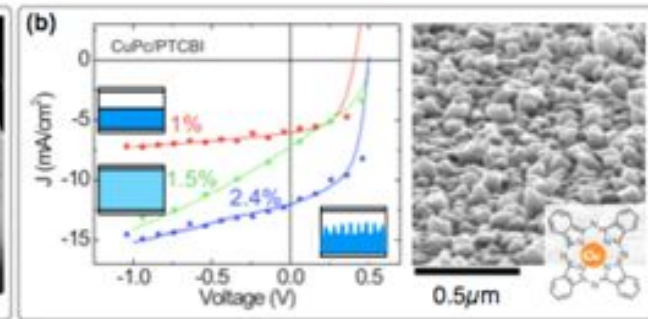
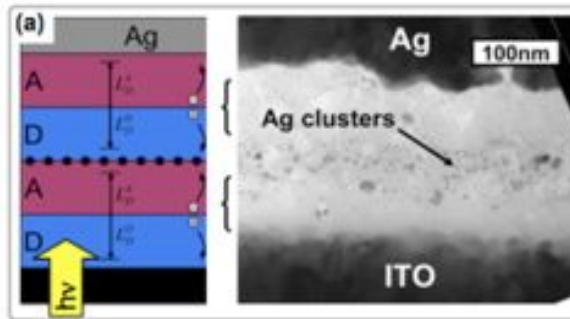
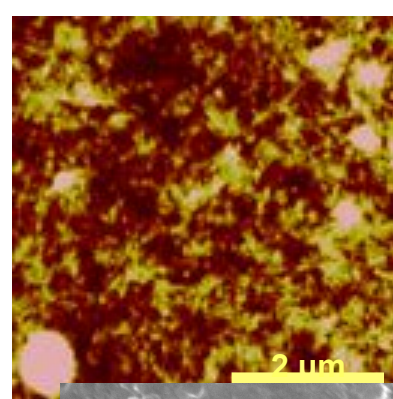
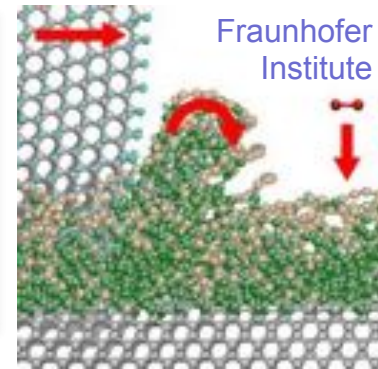
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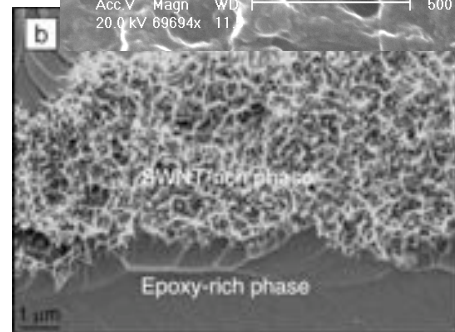
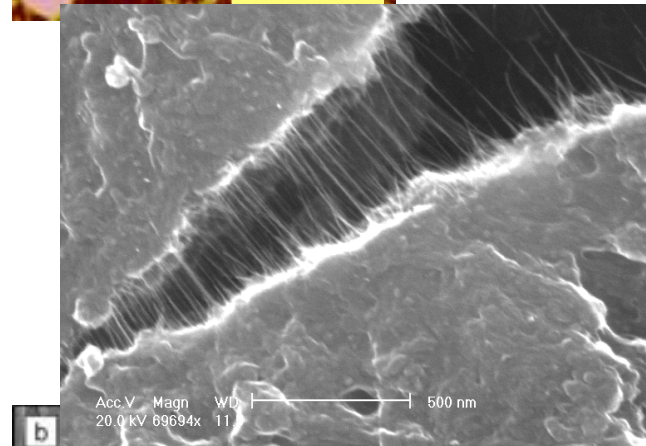


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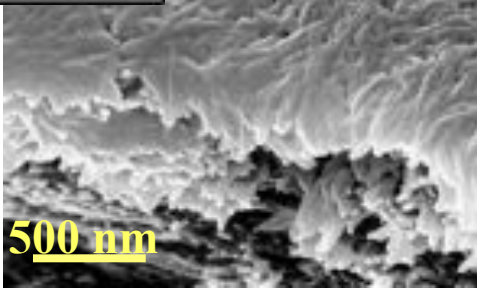
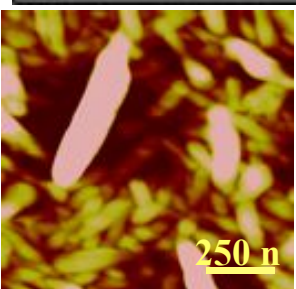
Interfaces: Cradle of Materials Functionality



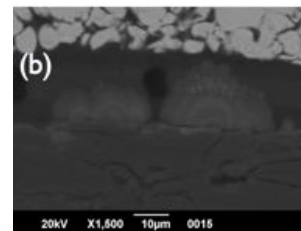
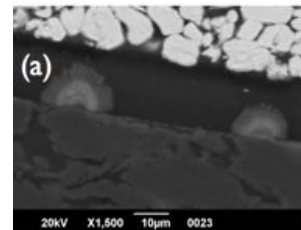
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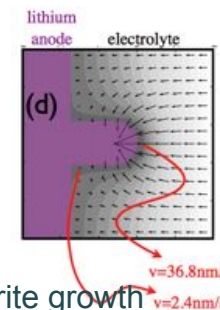
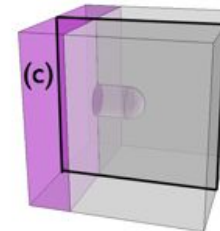
K.I. Winey, *et al.*, MRS Bulletin **32**, 348 (2007))



P. Podsiadlo *et al.* Biomacro. **6**, 2914 (2005)



Battery Anode: dendrite growth
E. Garcia, Purdue U.



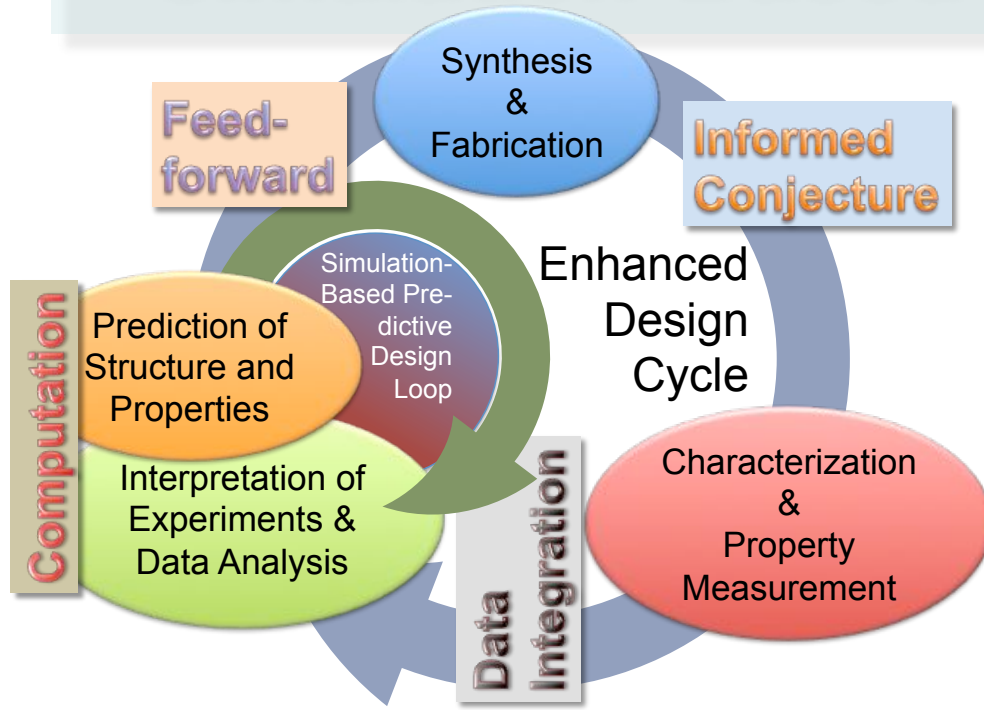
A. Tuteja, UM



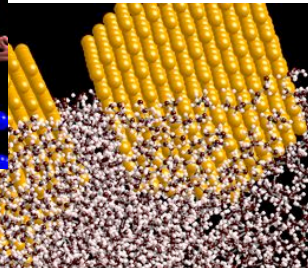
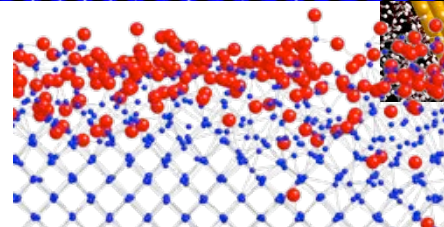
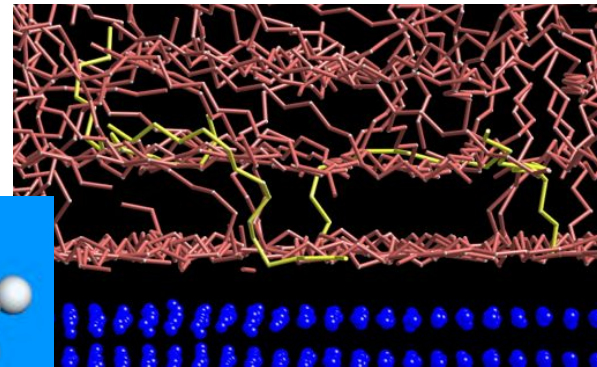
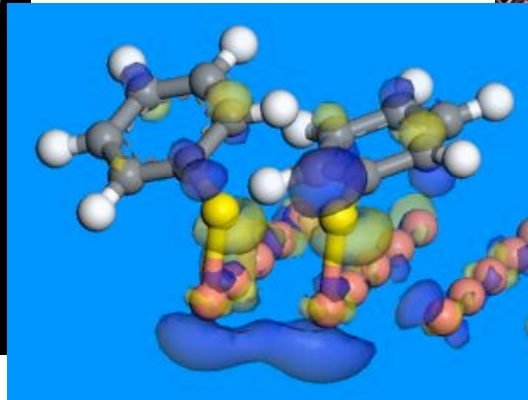
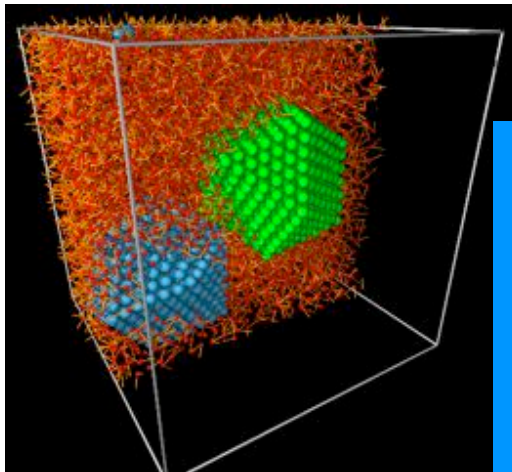
MEMS
Sandia National Labs



Simulation-Based Predictive Design



- ❑ Generate realistic structural models of interfacial regions by reproducing reactions and transport phenomena that underlie their formation
- ❑ Predict properties of these models
- ❑ Identify governing factors



Outline

❑ Simulation Approach

- ❖ Accurate force field models

❑ Generating Realistic Structures

- ❖ Types of Structure Formation Processes

❑ Structural Ubiquities

- ❖ Surface Patterning
- ❖ Pronounced Layering
- ❖ Densification of Polymer Near Interface
- ❖ Formation of Gaps and Voids

❑ Property Prediction & Analysis of Governing Principles

- ❖ Interfacial Strength Models
- ❖ Thermal Boundary Resistance

❑ Summary and Outlook

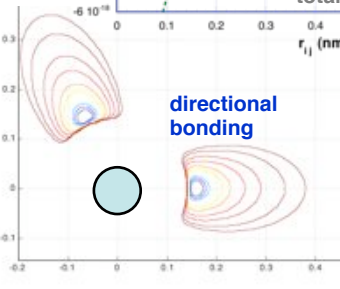
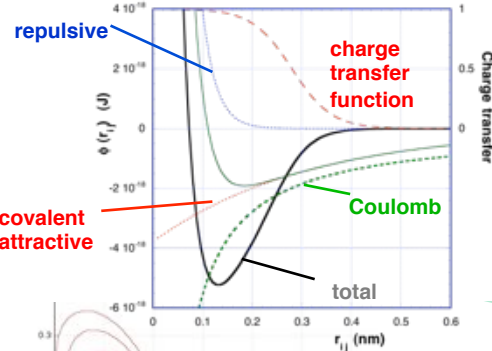
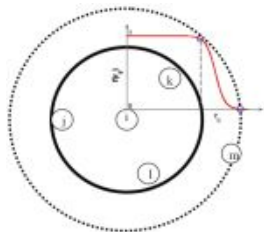


Simulation Framework

- ❑ Realistic structural models that account for nano-scale features are needed to predict interfacial properties
- ❑ Models generated using reactive molecular dynamics simulations
- ❑ Accurate description of atomic interaction models

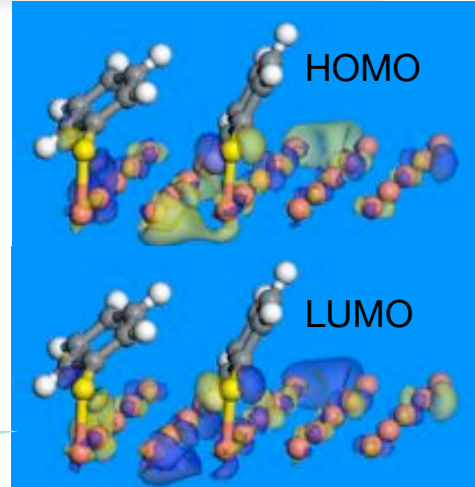
Reactive force field

variable coordination & coordination-dependent angular constraints



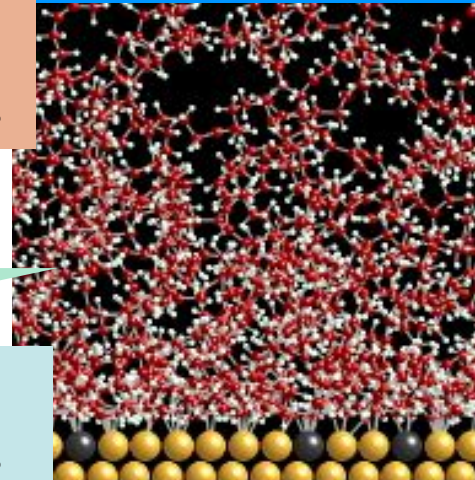
Density Functional Theory Calculations

Local structure; Force field parameterization



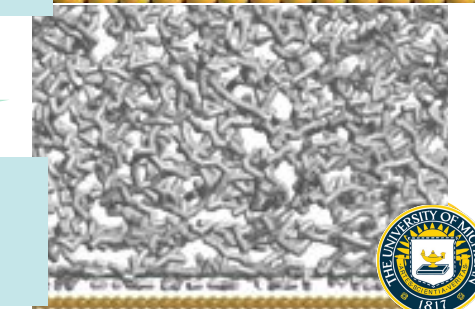
Reactive Molecular Dynamics Simulations

Extended structure; Reaction Mechanisms; Predict Thermo-mechanical properties

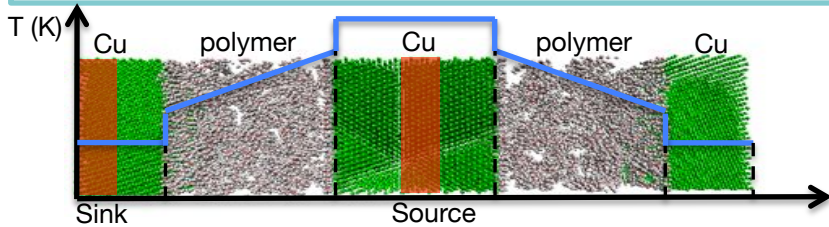


Coarse-Grain Particle Dynamics Simulations

Accelerated simulation of structural evolution



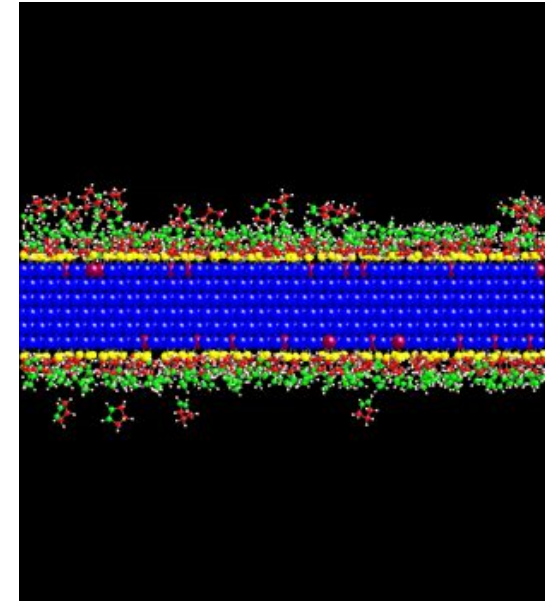
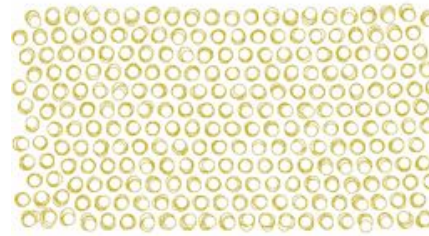
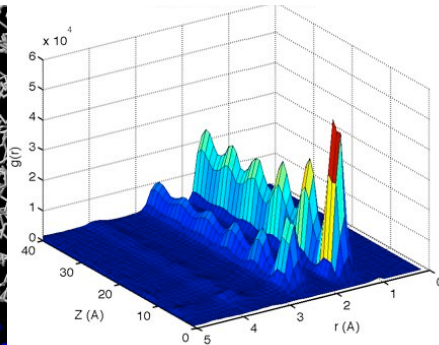
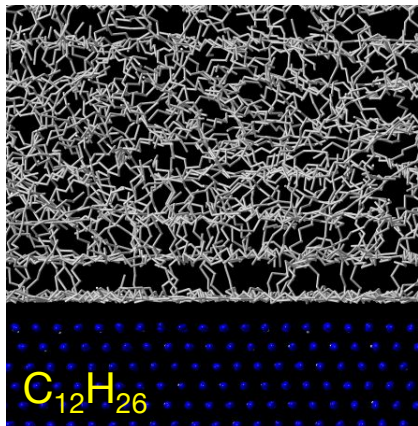
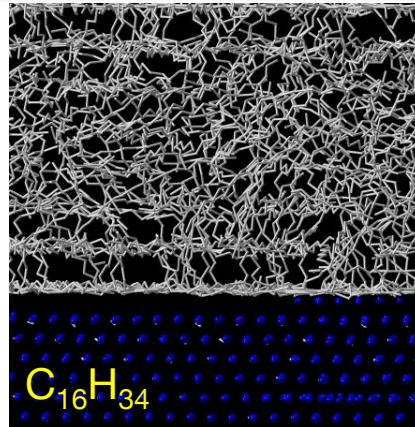
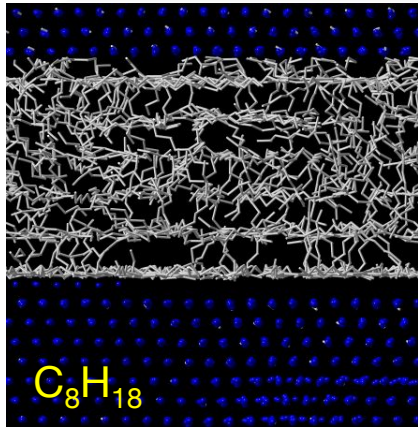
Validation, Verification and Interpretation



Generating Realistic Structural Models of Interfaces

Vapor deposition

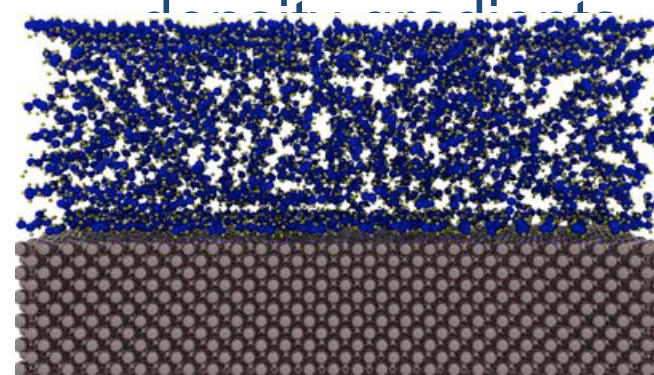
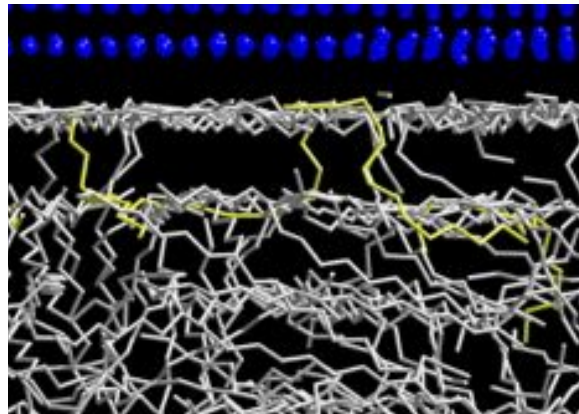
In situ polymerization



Adhesive forces
can cause local

- ❖ Pronounced layering of polymer near interfaces affects mechanical properties

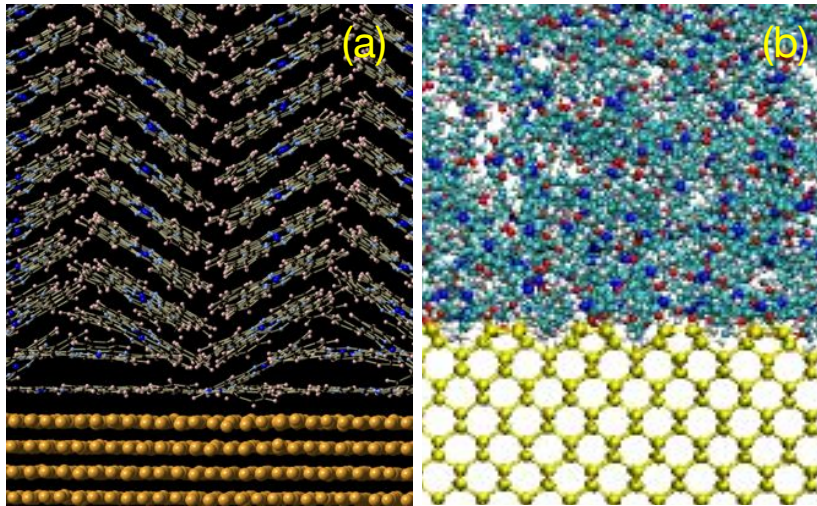
- ❖ Polymer chains span layers in “staircase” pattern



Generating Realistic Interfacial Structures

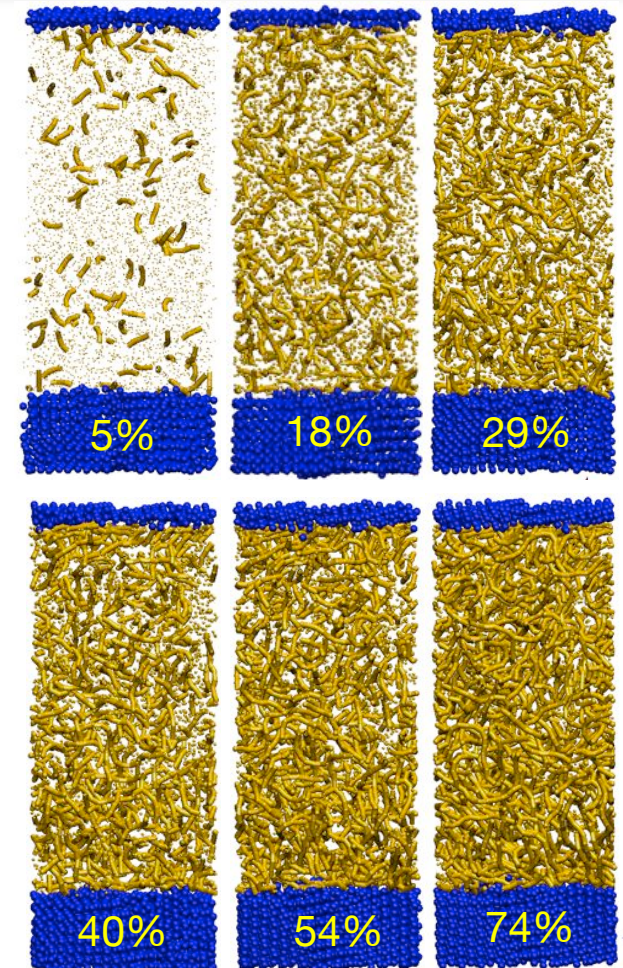
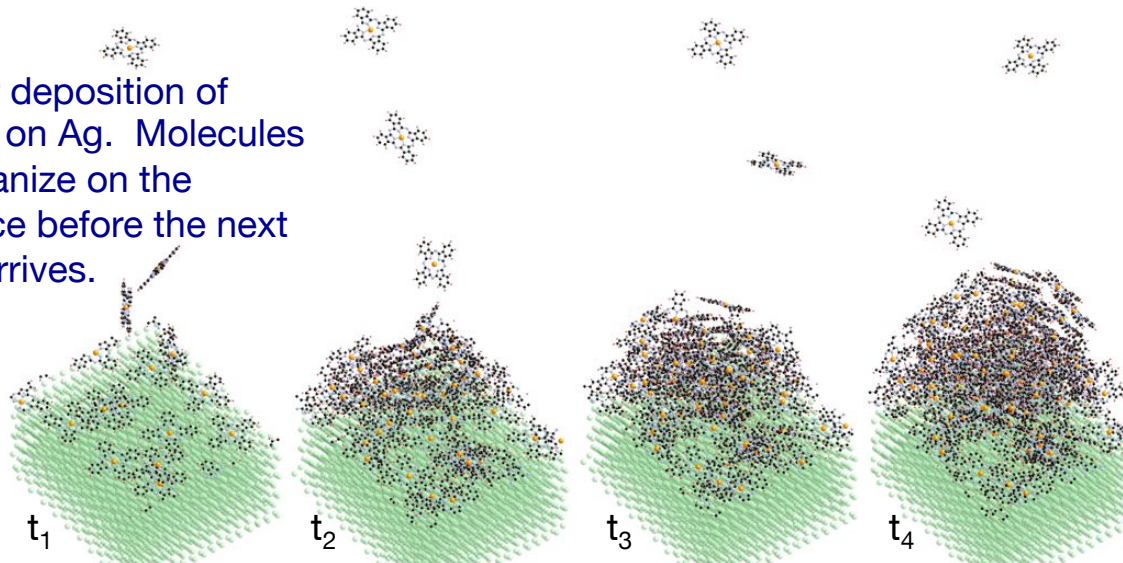
Three methods proved successful:

1. Juxtaposition of truncated bulk structures followed by relaxation
2. Simulation of the deposition process of thin layers
3. Simulation of the polymerization process near a substrate.



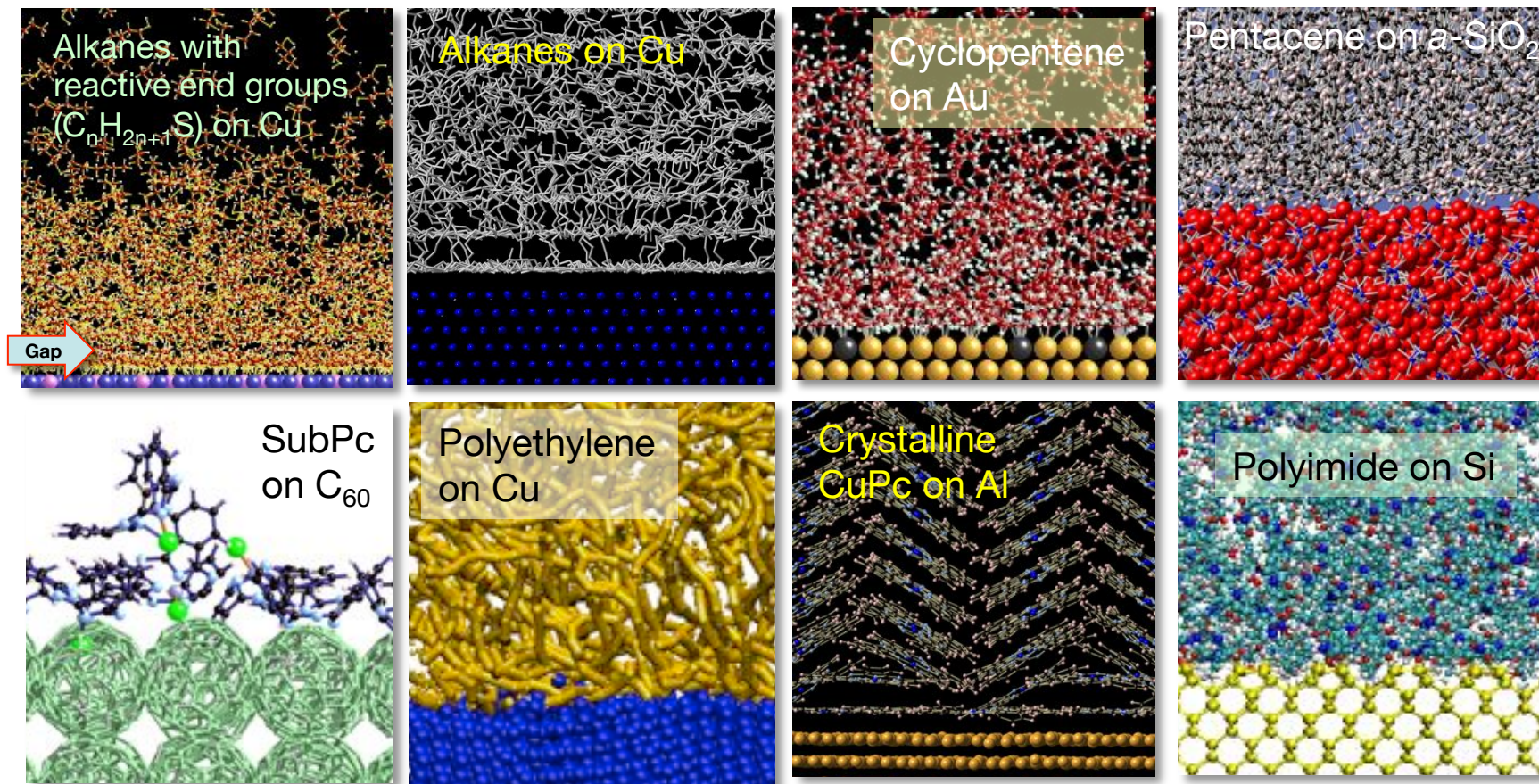
Interface between: (a) CuPc single crystal and Ag;
(b) polyimide and Si obtained via phase juxtaposition

Vapor deposition of CuPc on Ag. Molecules reorganize on the surface before the next one arrives.



Polymerization of polyethylene in the gap between two Cu surfaces at various degrees of cure. Simulation involves a heuristic bonding scheme.

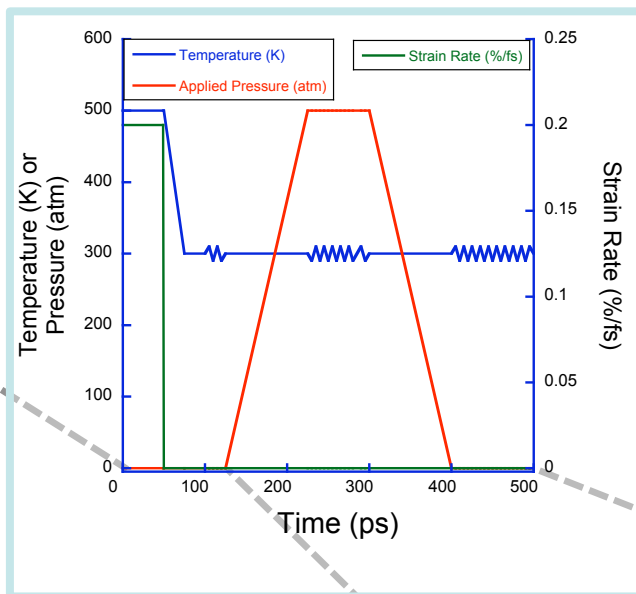
Materials Simulation Repertoire



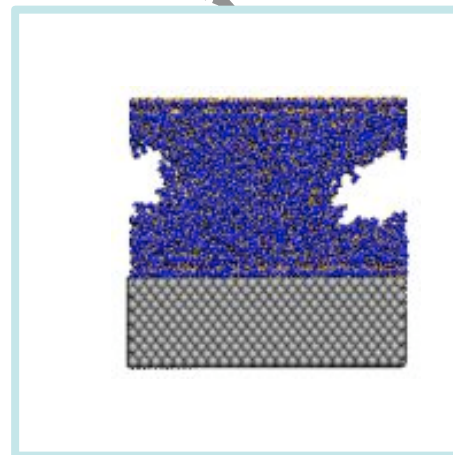
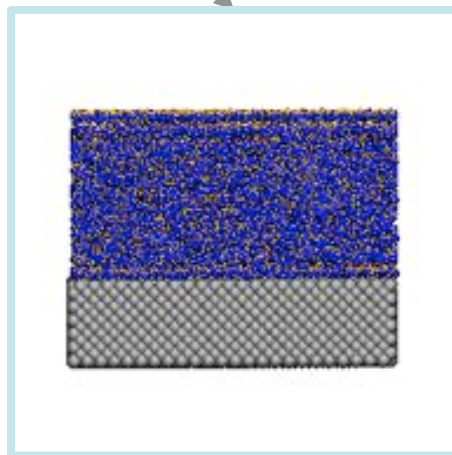
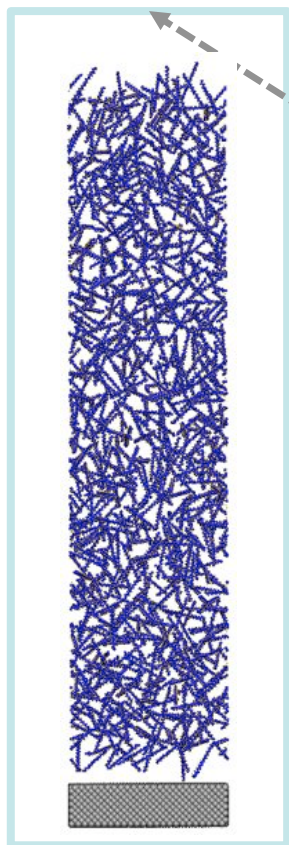
Systematic exploration of the chemical nature and structural complexity of interface systems

- ❖ Force field optimization based on the results from first-principles quantum mechanical calculations
- ❖ Development and verification of the structure generation strategy
- ❖ Property prediction and validation with known experimental data
- ❖ Structural analysis and identification of structure property correlations

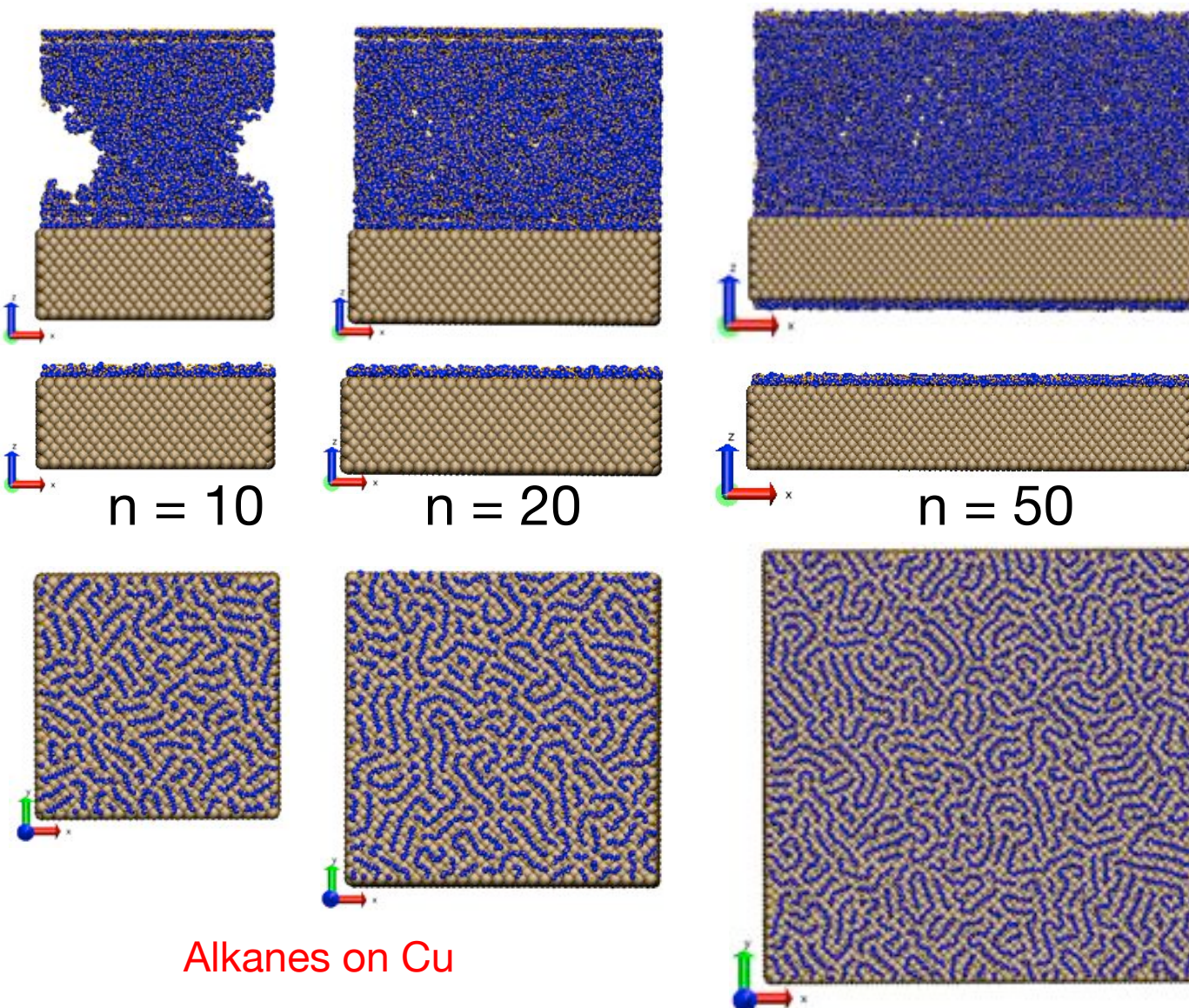
Alkane/Metal: Simulation Details



- ❑ Structure generated with random linear alkanes near fcc [100] surface
- ❑ Target thickness of 50 Å
- ❑ NPT phase required for structural stability

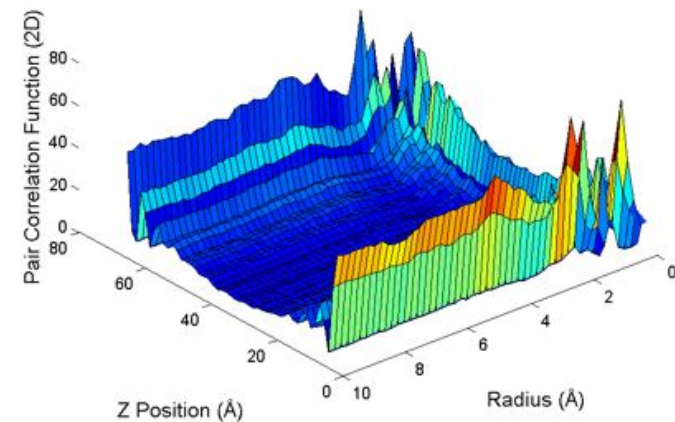
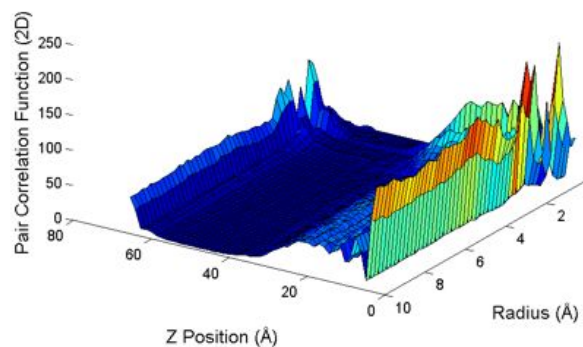
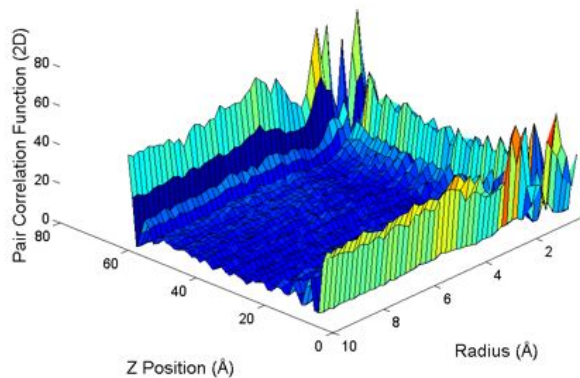
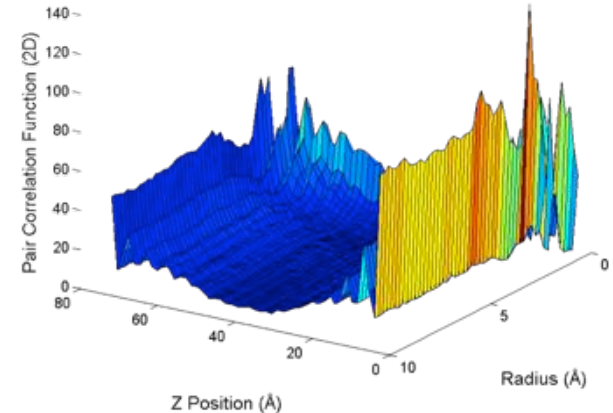
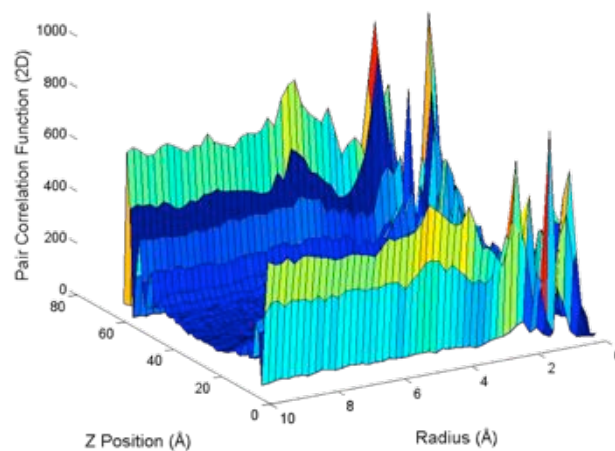
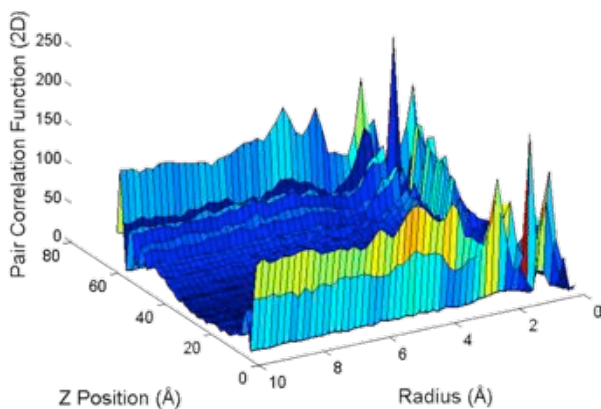


Surface Patterning – Chain Length



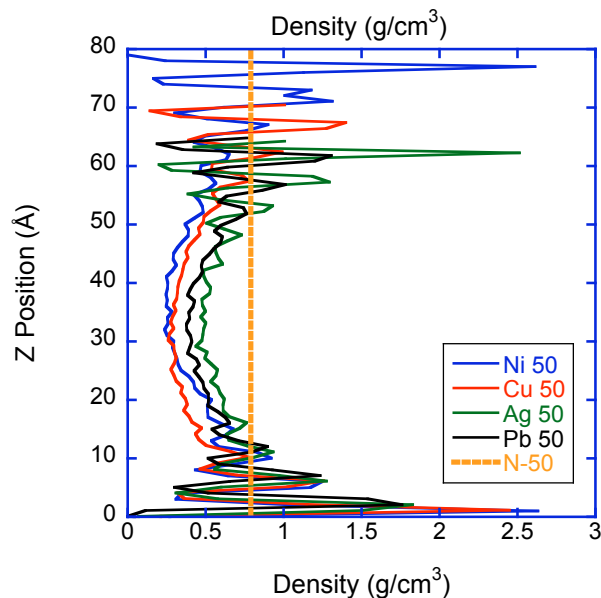
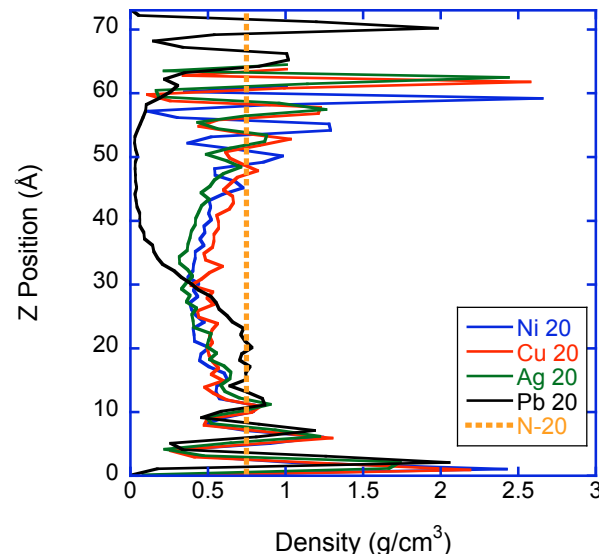
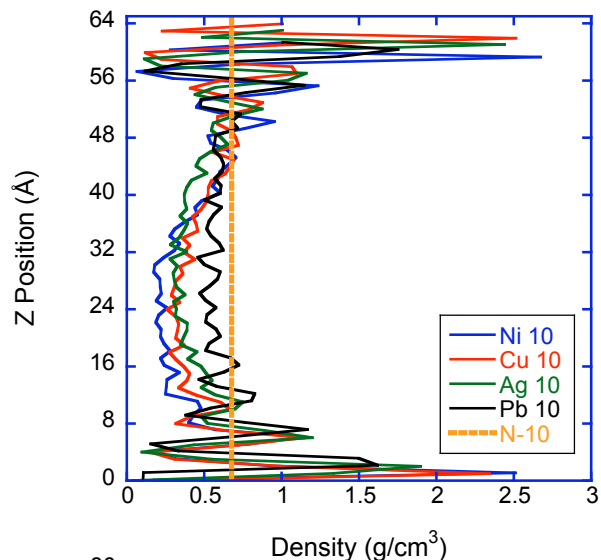
- ❖ Alkanes of length n
- ❖ Chain segments in direct surface contact are shown
- ❖ Pattern no longer change appearance beyond threshold n

2D Pair Correlation Functions



- ❑ Slice projected into 2 dimensions before pcf calculated
- ❑ Normalized according to overall average number density
- ❑ Upper: Nickel Lower: Lead Left to Right: $n=10$, $n=20$, $n=50$

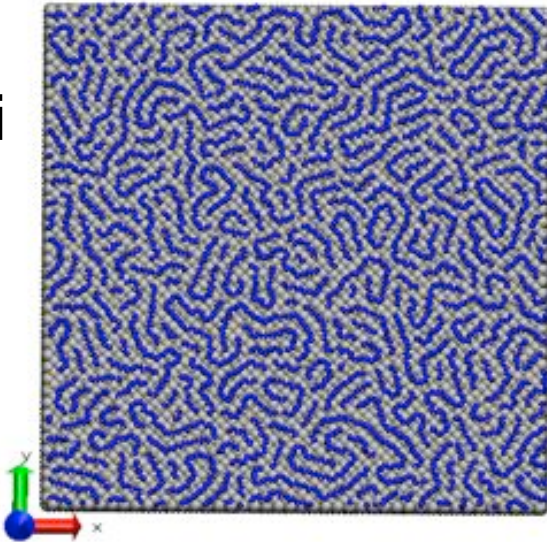
Density Profiles Across Polymer Layer



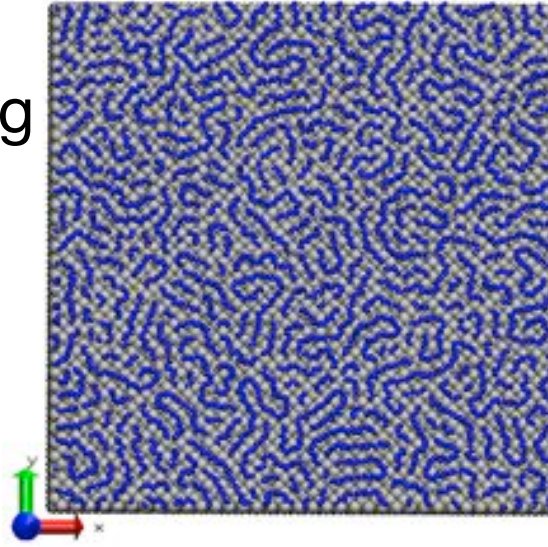
Voids present in the structures are reflected in the density profiles
Average density of bulk alkanes shown by dotted orange line

Surface Patterning – Substrate Lattice

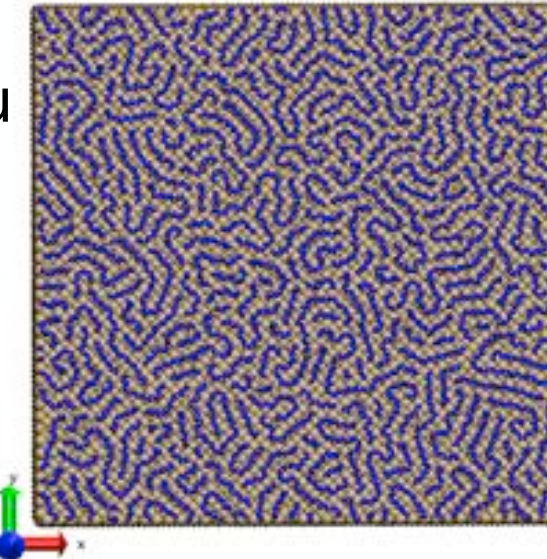
Ni



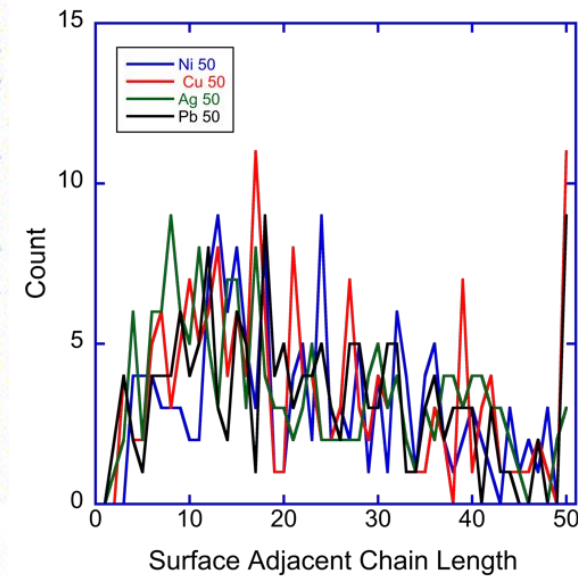
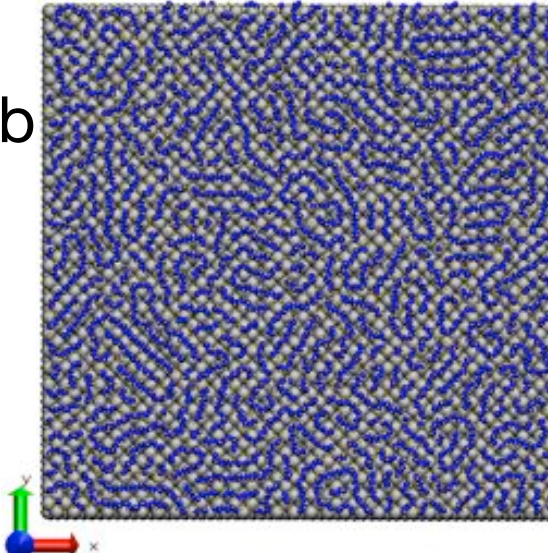
Ag



Cu



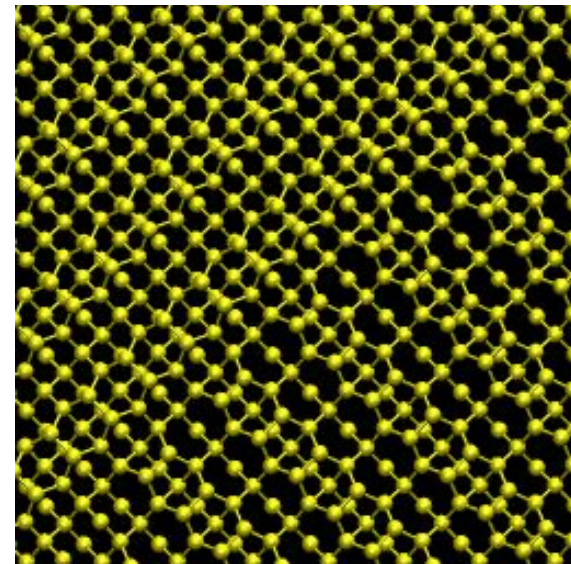
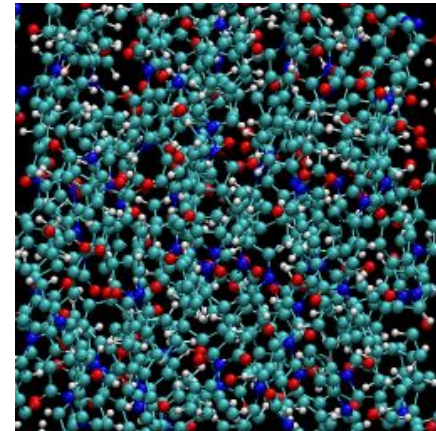
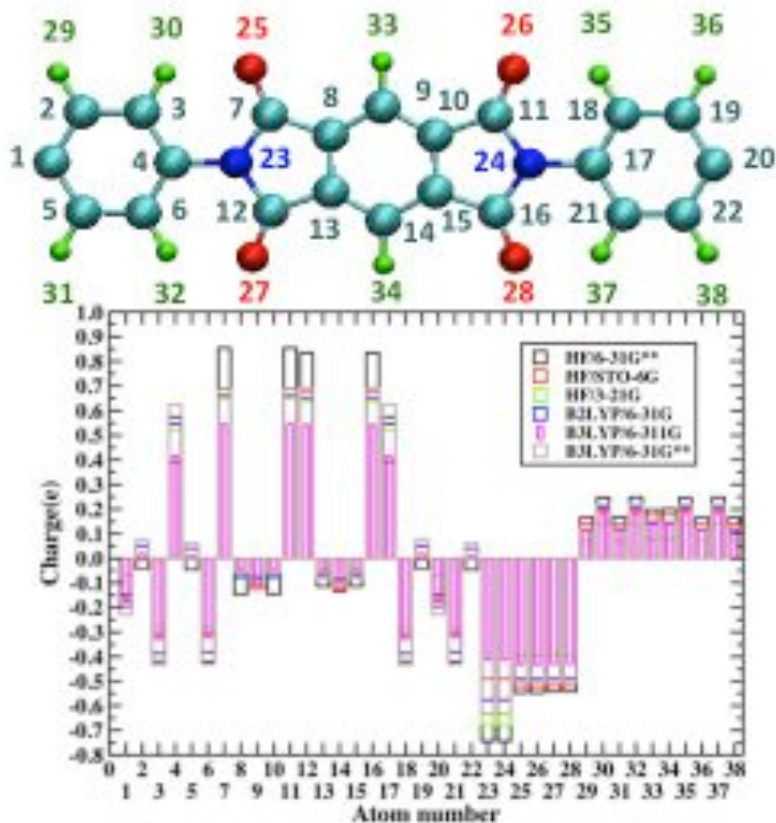
Pb



No apparent trend in surface patterns depending on substrate lattice parameters and interaction strength

Deposition of Polyimide on Si (100)

DFT optimized interaction potential for PMB molecule in bulk and with substrate

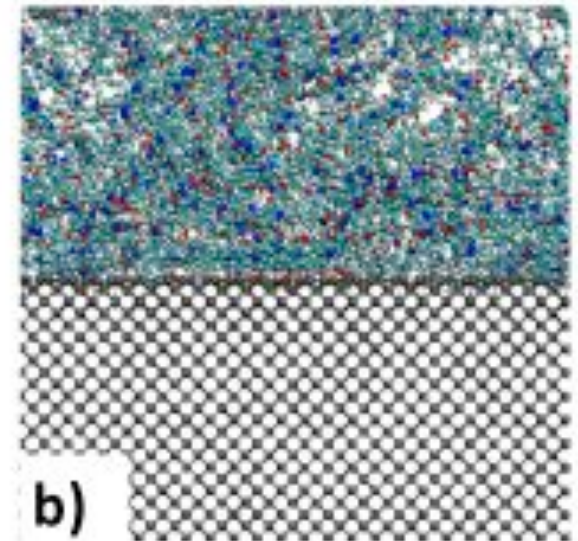
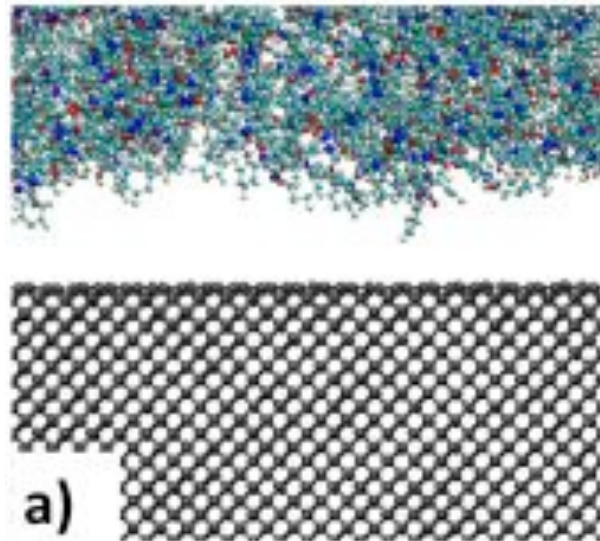
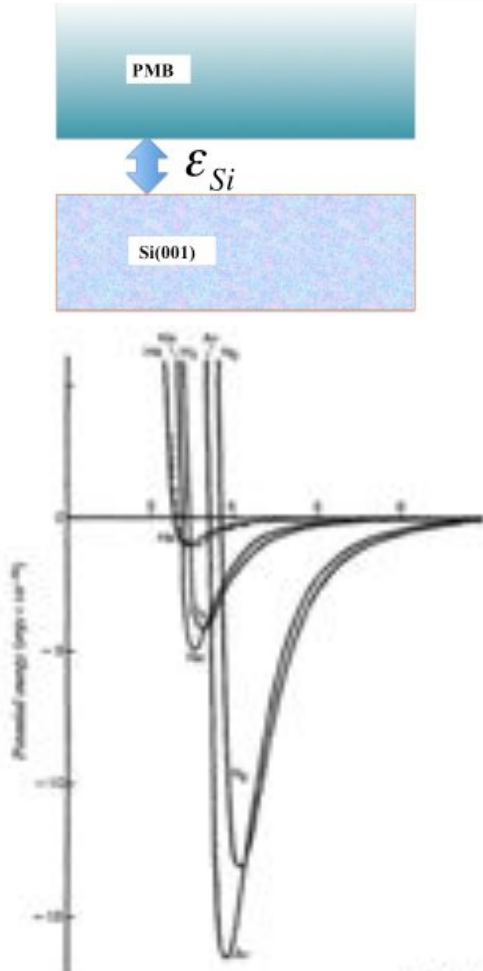


- Silicon bulk and surface
- (2x1) dimer-reconstruction of the surface
- Surface steps on reconstructed surface

Polyimide on Si (100): Contact/Non-Contact

Non-contact versus Contact Adhesion

- Relaxation from a high-temperature state to a glassy state with under-critical interface coupling
- Relaxation from a high-temperature state to a glassy state with interface coupling in excess of the critical

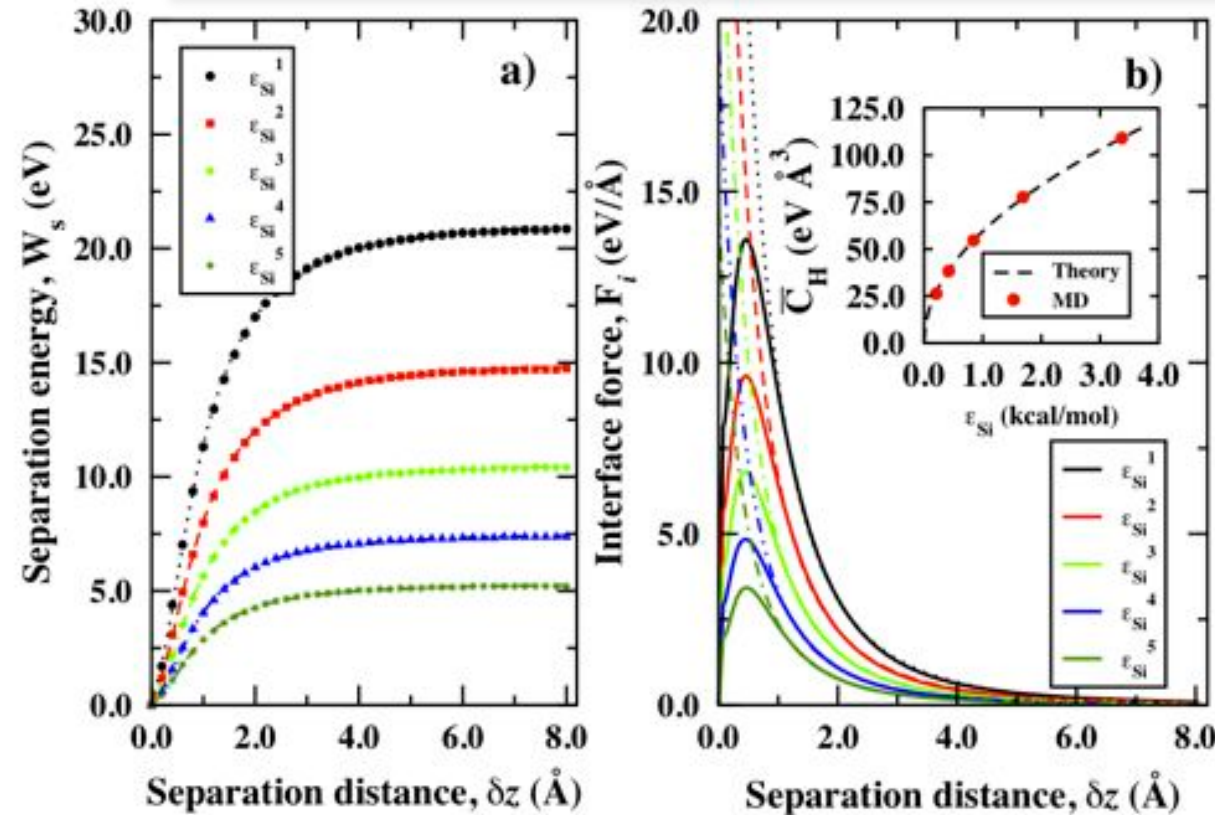


J. E. Lennard-Jones, "Cohesion",
Proc. Phys. Soc. 43, 461 (1931).

$$\epsilon_{Si} < \epsilon_{Si}^c$$

$$\epsilon_{Si} > \epsilon_{Si}^c$$

Energetics of PMB Layers on Si(001)



$$U_{Si-PI}^R(z_0) = 4\pi\epsilon\rho_{Si} \left\{ \frac{\sigma^{12}}{360} \left(\frac{1}{z_0^8} - \frac{1}{R_c^8} \right) \right\}$$

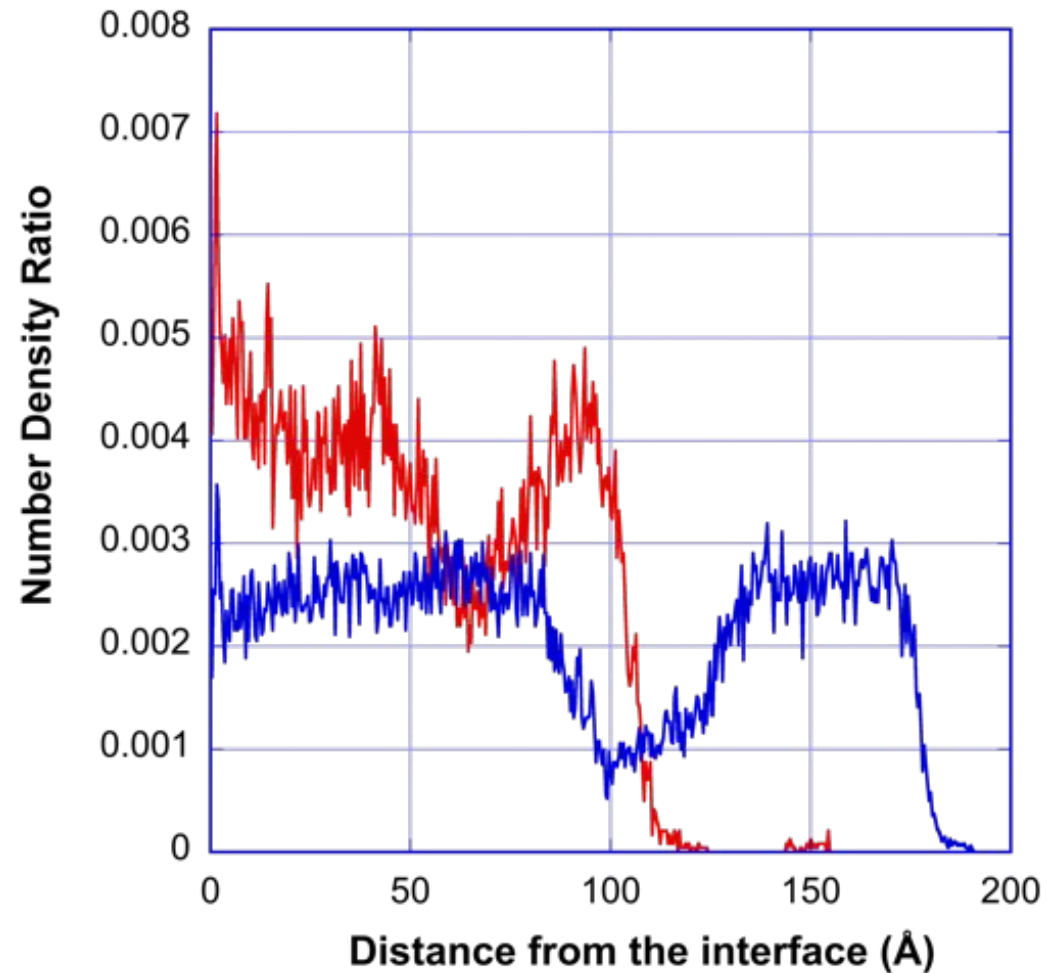
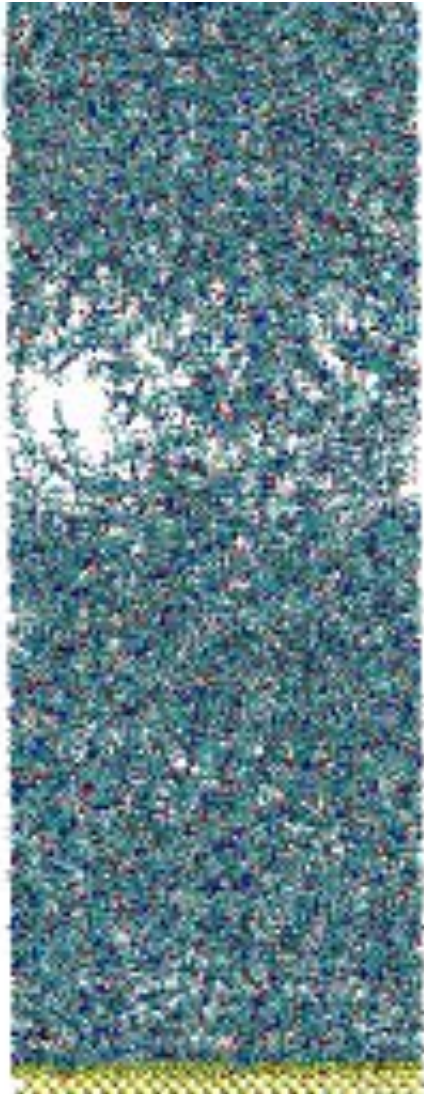
$$U_{Si-PI}^A = 4\pi\epsilon\rho_{Si} \left\{ \frac{\sigma^6}{12} \left(\frac{1}{z_0^2} - \frac{1}{R_c^2} \right) \right\}$$

Simulated behavior (within the classical model of Si-PMB interfaces) is described well by the de Boer-Hamaker model with:

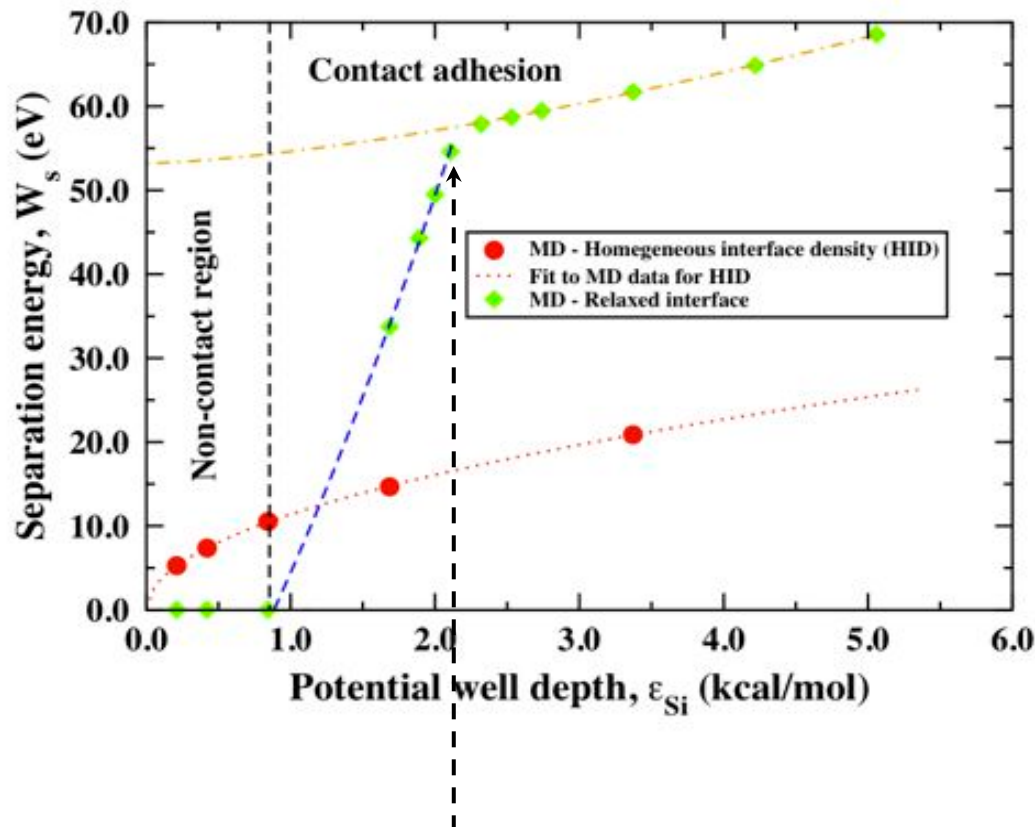
$$F_I = \frac{1}{24\pi} \left(\frac{3\pi C \rho_o \rho_{Si}}{z_0^3} \right)$$

- Homogeneous a-PMB layer on silicon
- No relaxation at the interface
- Provides reference states

Void Formation Near Free Surface

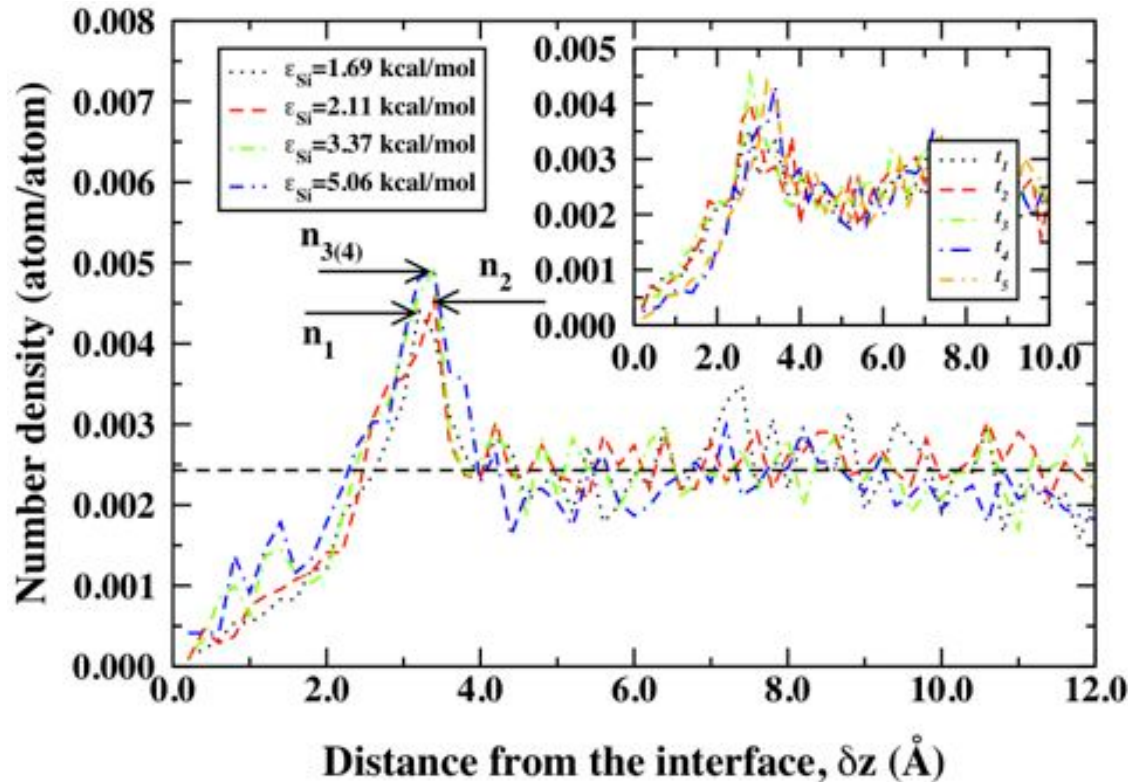


Energy Regimes of *a*-PMB-Si(001) Interfaces: Adhesive Energy Transition



- A non-contact regime holds for small coupling strength
- The transition from non-contact to contact regime is characterized by an abrupt change in W_s , with rapid increase with coupling strength
- The rapid increase is due to density and order variations
- For large values of the coupling strength, a slow increase is observed due to density saturation, with $W_s \sim \epsilon_{Si}^a$, where $a \approx 0.5$

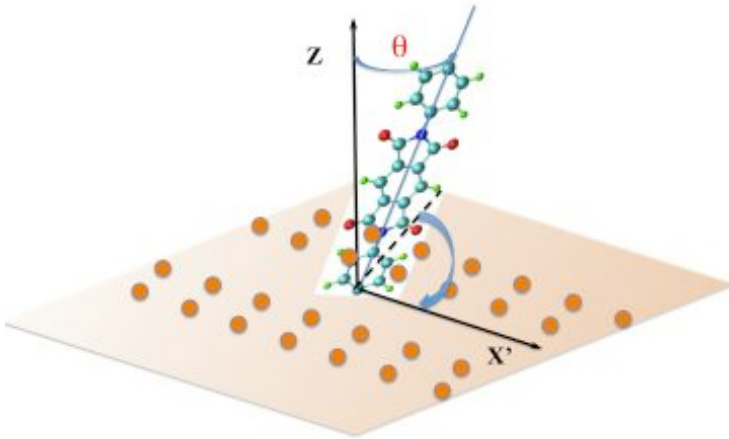
Density profiles of *a*-PMB-Si(001) Interfaces



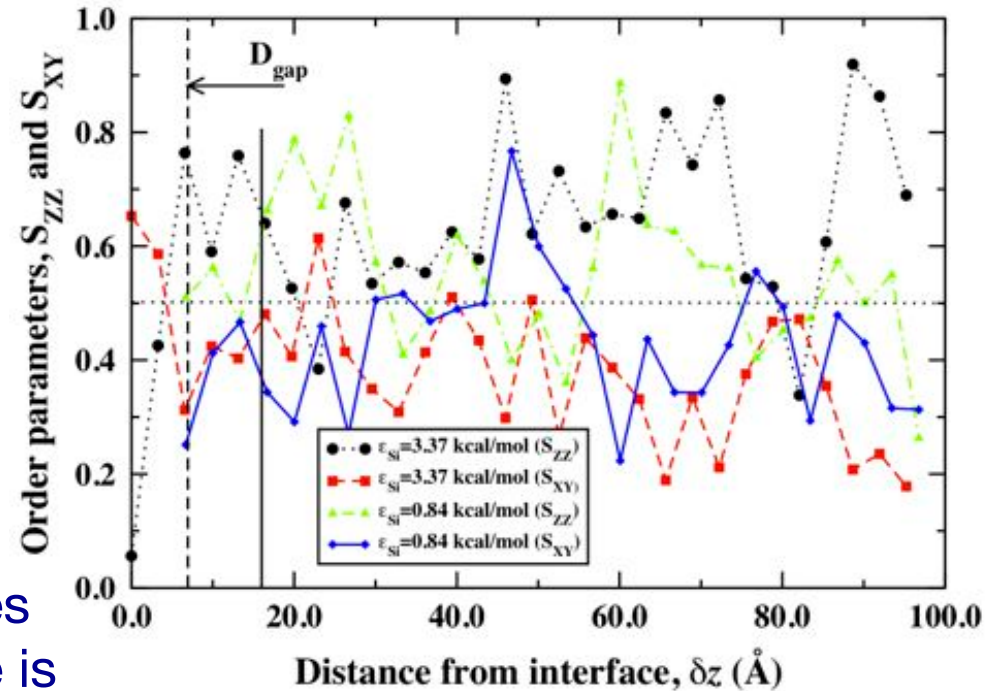
- Density profiles dynamically evolve during relaxation with non-zero coupling between adherent and substrate
- Interface relaxation (both density and ordering) largely define the adhesive behavior

Peak density grows with coupling strength (1 vs. 2) but saturates at larger couplings (3 vs. 4)

Structural Order at *a*-PMB-Si(001) Interfaces



- Parallel ordering of PMB molecules with respect to the interface plane is preferred for large coupling strengths
- At the interface, the ordering along grooves formed by 2x1 surface reconstruction is favored
- Free surface acts as a repulsive wall

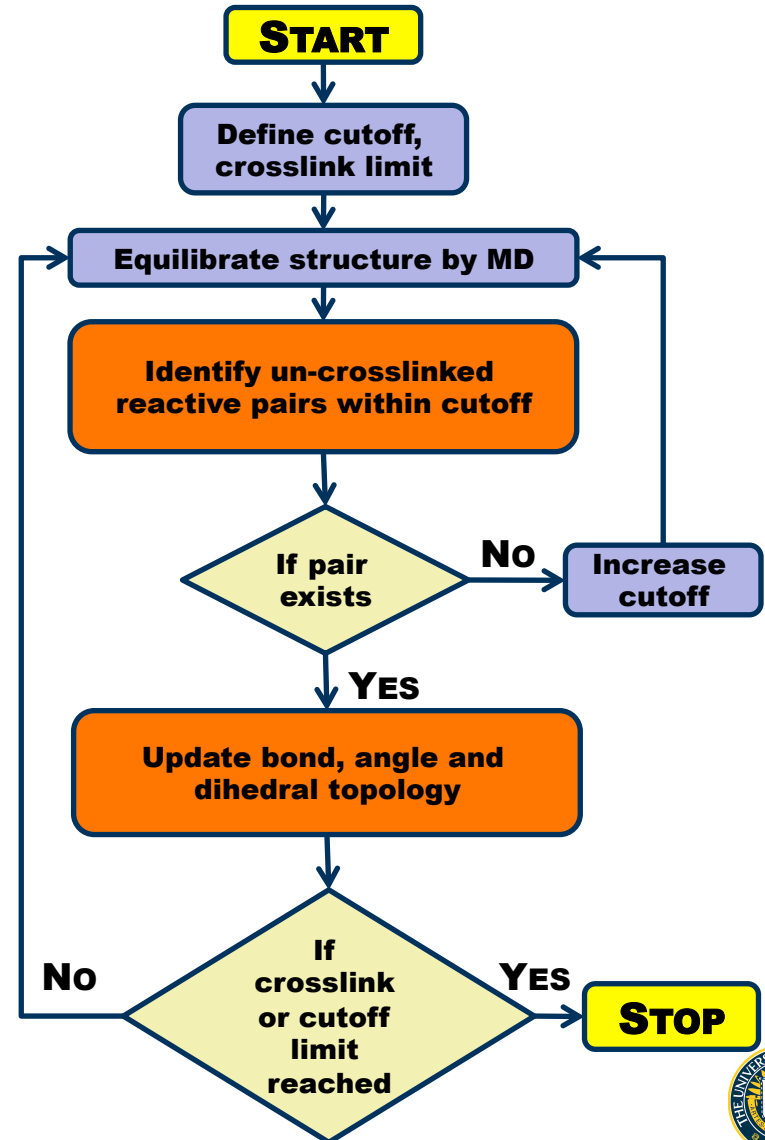


Order Parameter

$$S_{ua} = \frac{3}{2} \langle \cos(\theta)^2 \rangle - \frac{1}{2}$$

Polymerization Method

- ❑ Variation of method proposed by Varshney¹
- ❑ More efficient than one-by-one reaction²
- ❑ Less stress than static/all-at-once algorithm²
- ❑ Depending on cutoff, should not reach 100% cure, which is realistic

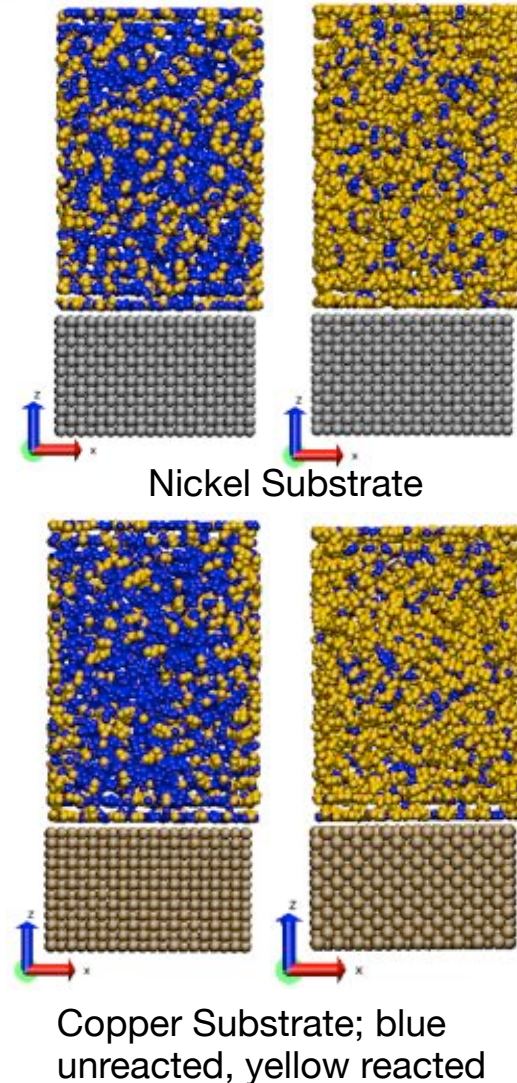
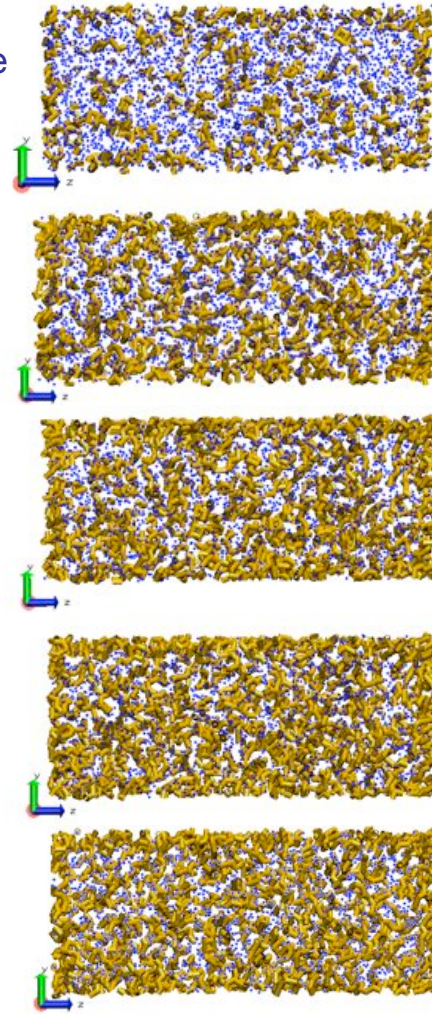
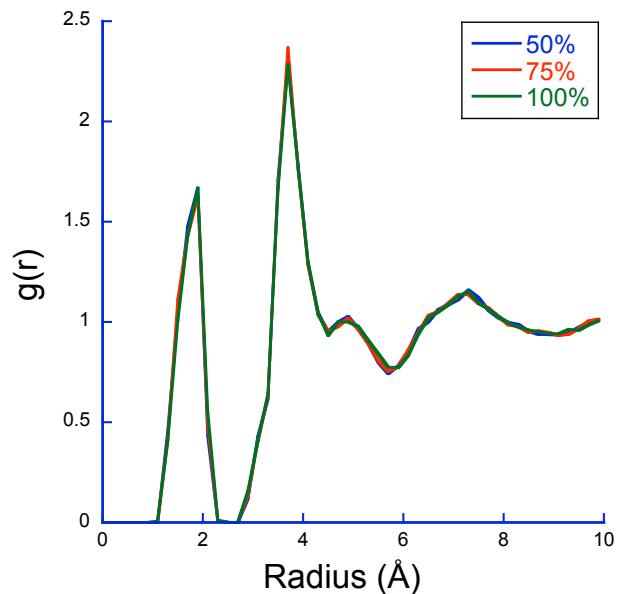


1. V. Varshney et. al., *Macromolucules*, 41 (18), 2008

2. C.K. Knox et. al, *Army Sci. Conf. Proc.* 2009

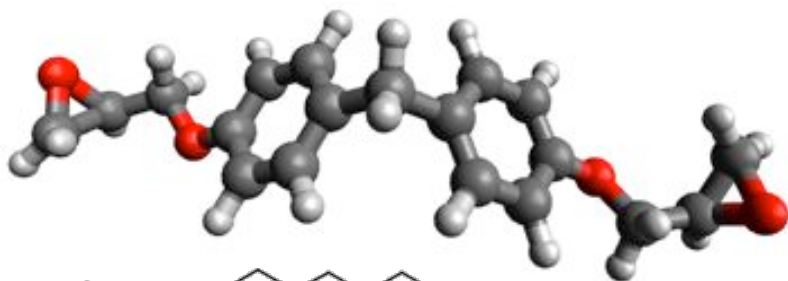
Polyethylene Bulk & Interface Structure

- ❑ Reaction probability has minimal effect on the final structure of polyethylene
 - ❖ Agrees with experimental study of chain growth polymers like PE and DCPD
- ❑ Maximum chain length uncorrelated with reaction probability:
 - ❖ 50%: 692; 75%: 811; 100%: 591

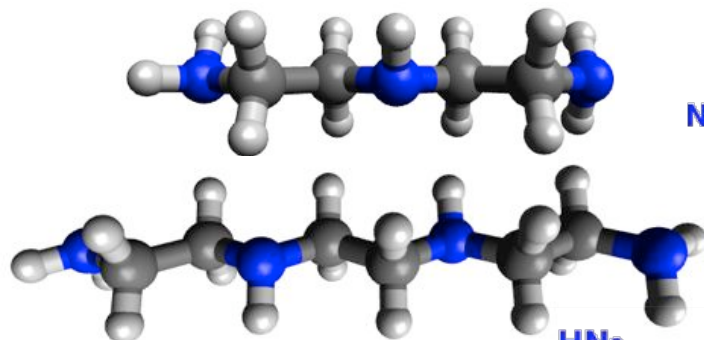


- ❑ Reaction process does not prevent layering effects

Epoxy Reaction Paths



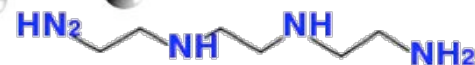
DGEBA



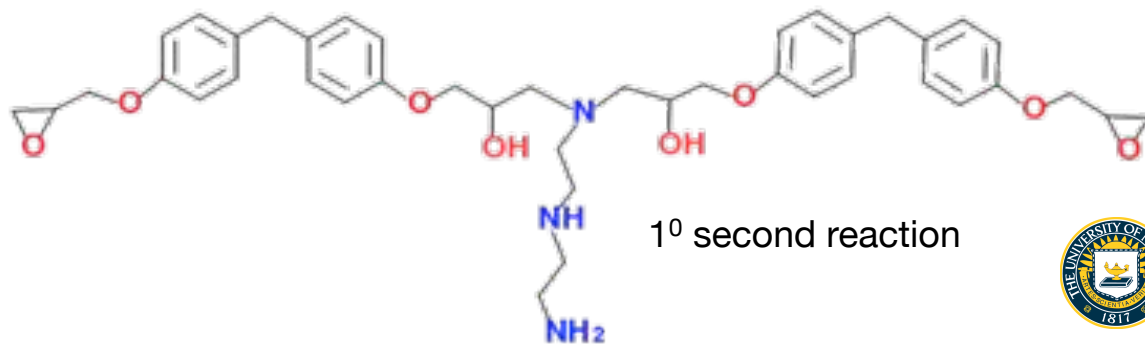
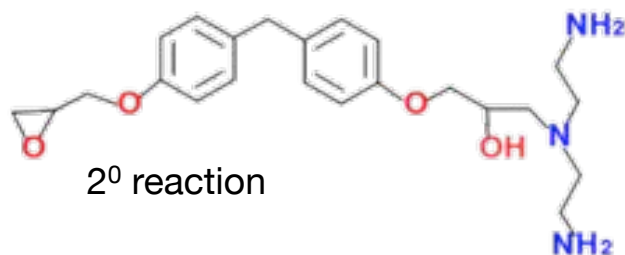
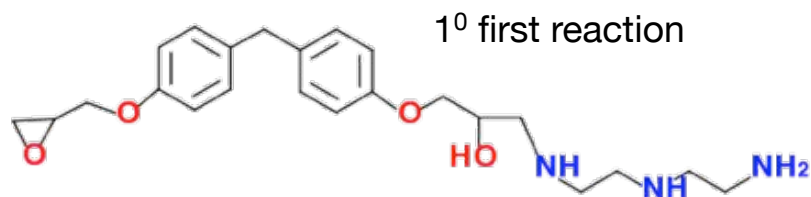
DETA



TETA

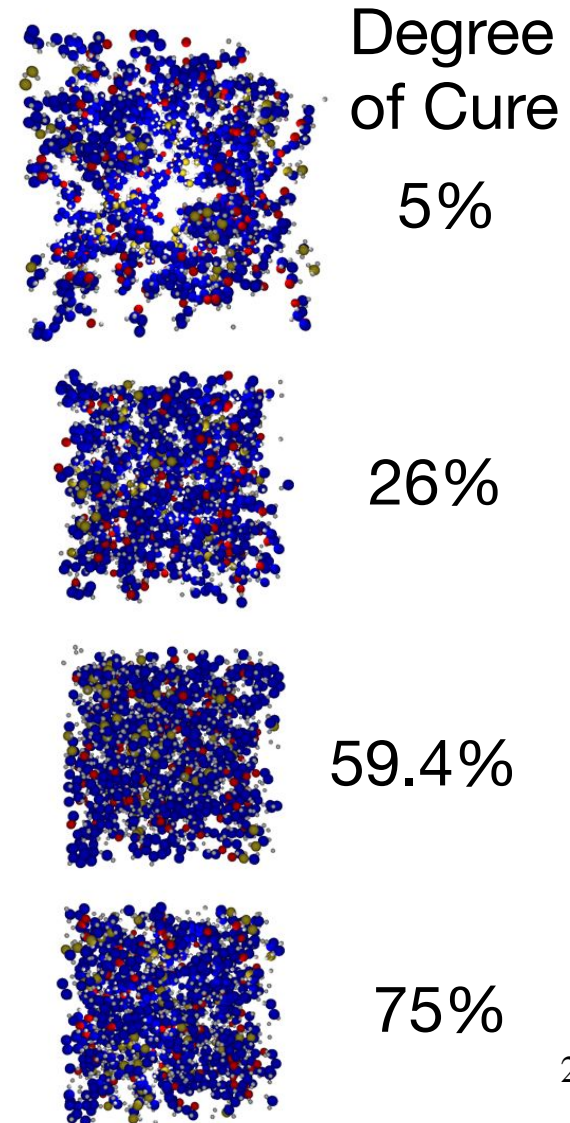
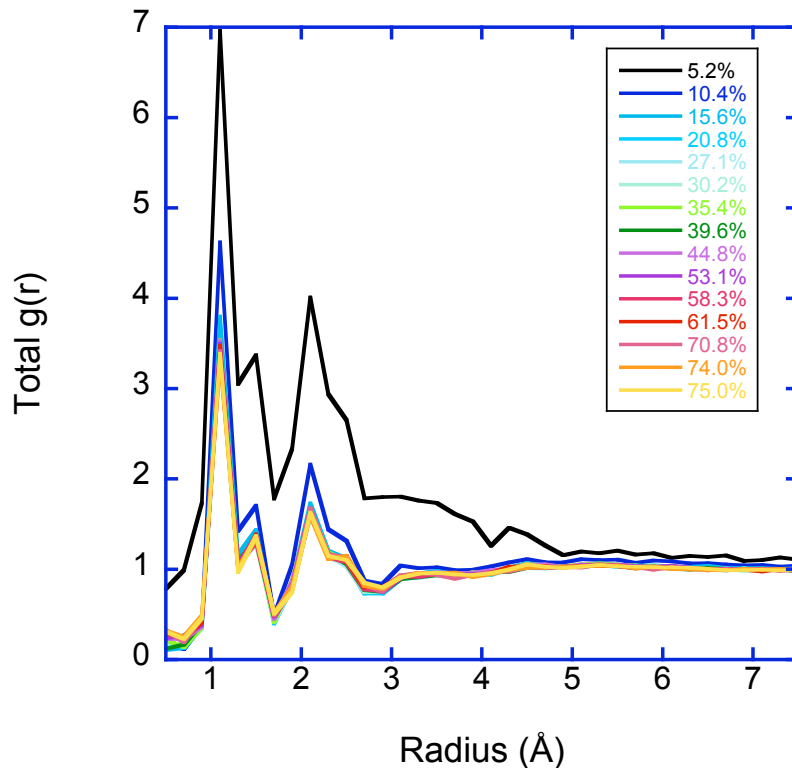


- ❑ DGEBA & DETA/TETA for hardeners
- ❑ 3 reaction pathways
 - ❖ Assumed equally reactive for a given cutoff radius
- ❑ Assumes epoxide ring activated by presence of amine group



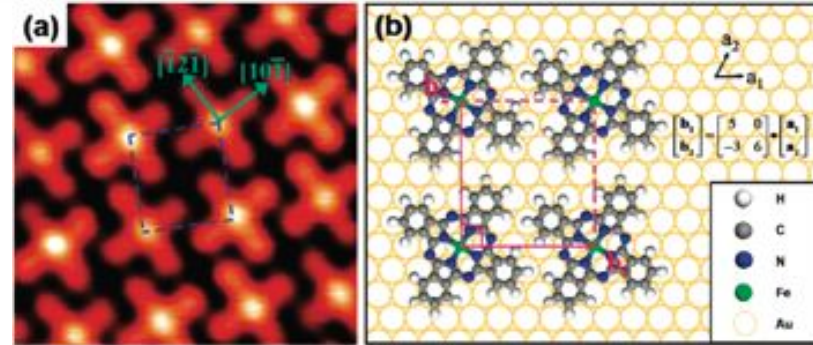
Epoxy Cure Simulations

Total RDFs as a function of the degree of cure



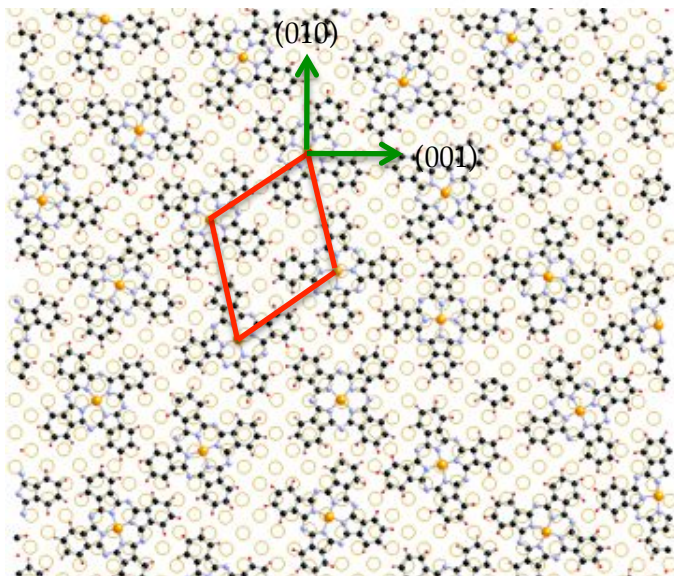
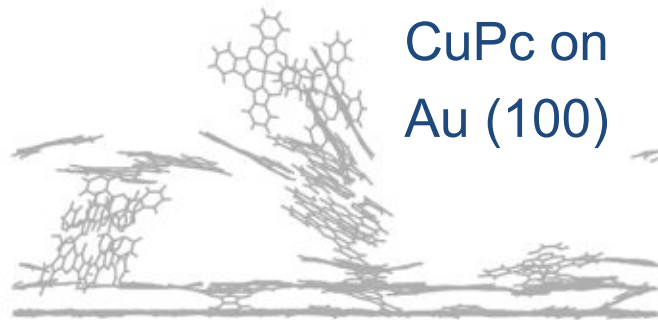
Growth Behavior of CuPc

❖ Growth behavior before force field optimization

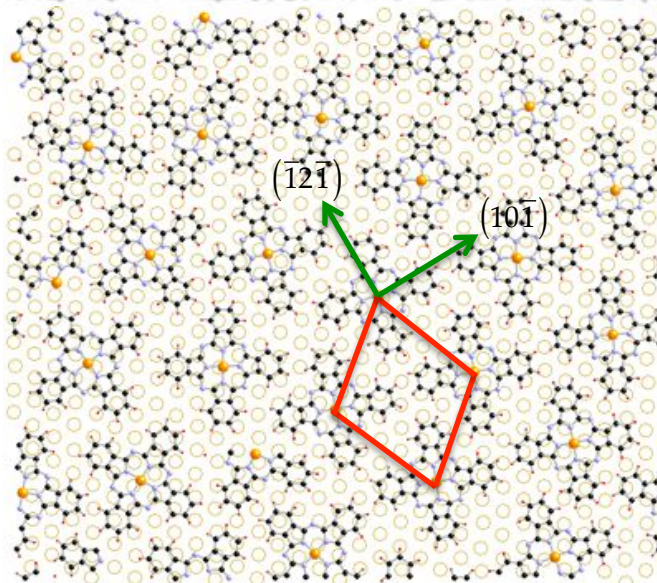
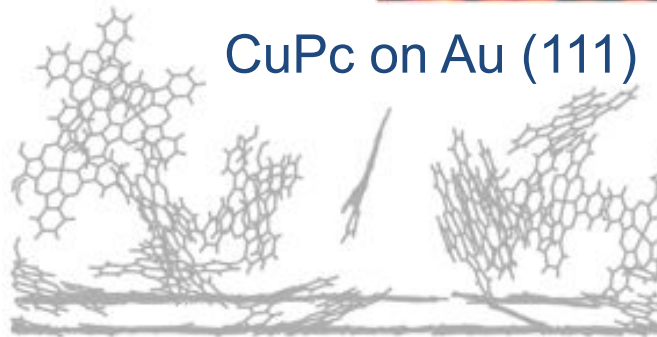


Z.H. Cheng et. al., JPC (2007)

CuPc on Au (100)



CuPc on Au (111)



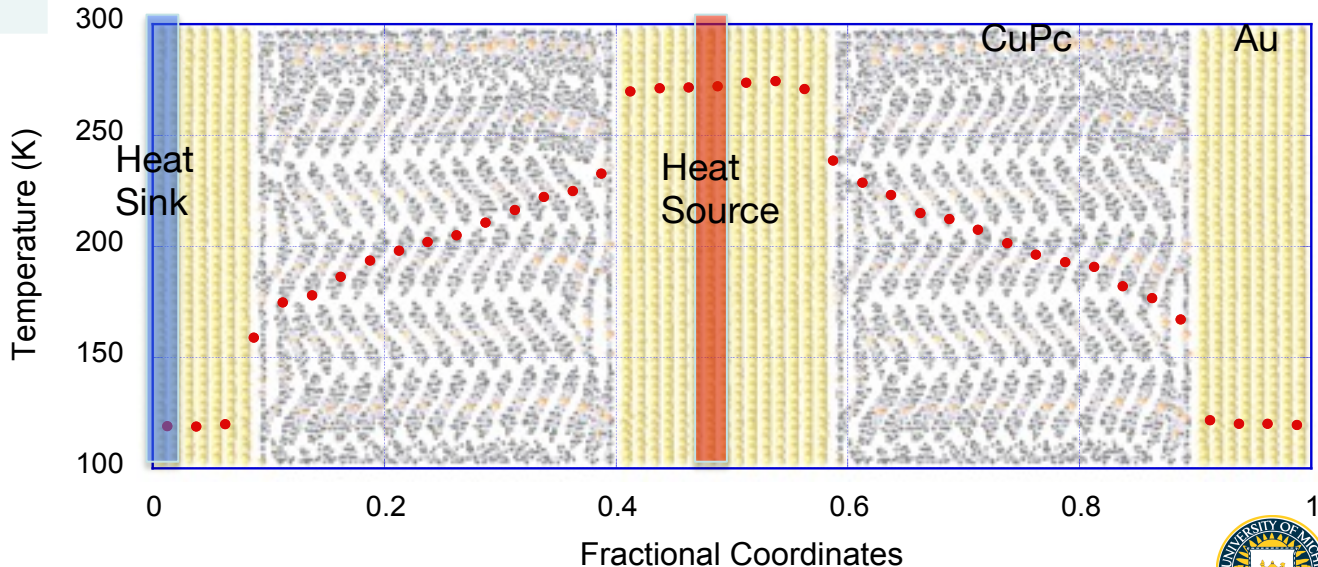
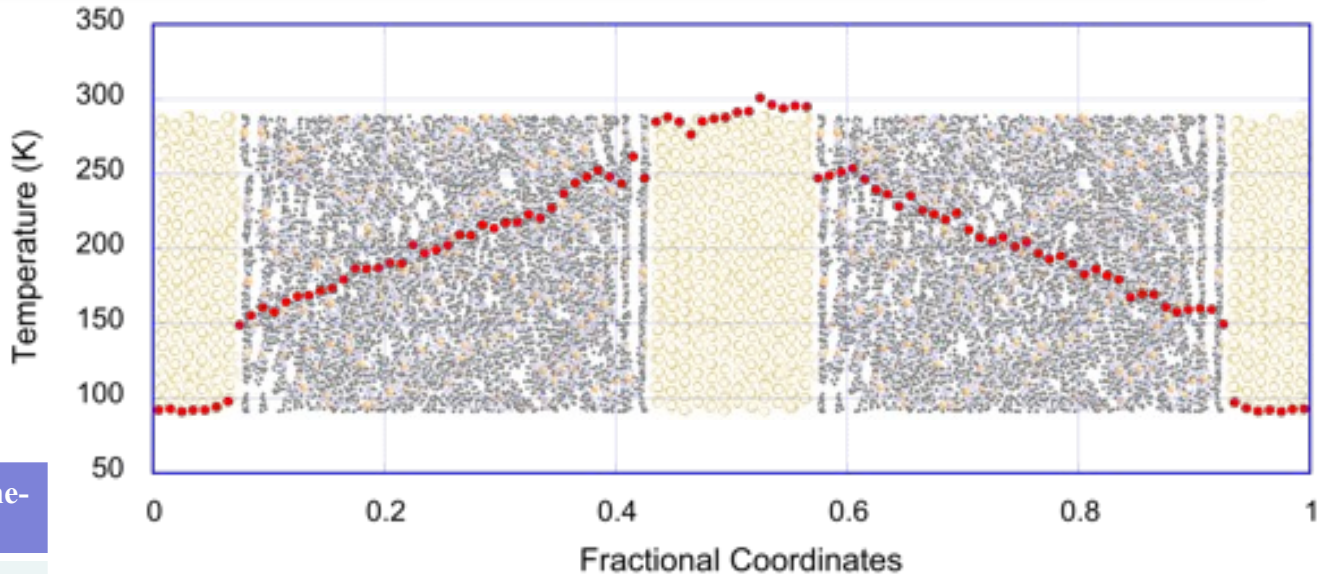
❖ Monolayer deposition of CuPc forms crystalline patterns on both (100) and (111) surfaces

❖ This growth behavior was only observed after force field optimization

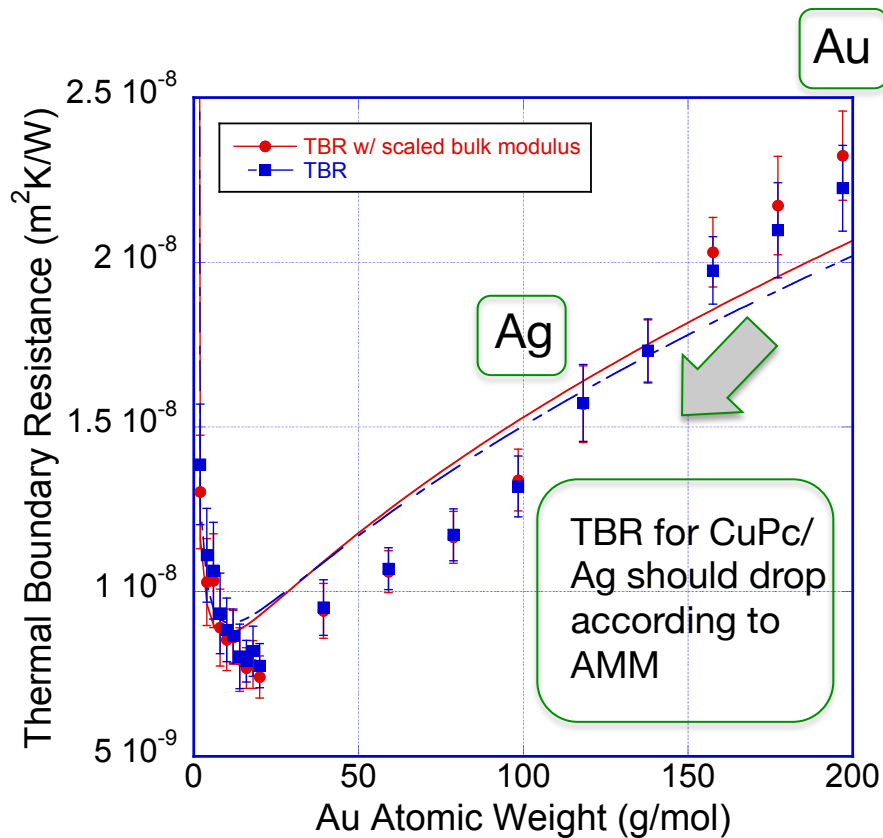
Crystalline vs. Amorphous CuPc

- ❖ CuPc molecule is deposited on Au(111)
- ❖ TBR is smaller at the amorphous-CuPc/Au than the crystalline-CuPc/Au interface

	Amorphous-CuPc/Au	Crystalline-CuPc/Au
TBR ($10^{-8} \text{ m}^2\text{K/W}$)	1.96 ± 0.24	2.36 ± 0.20



Adhesion Strength vs. Acoustic Mismatch Model



Ag has a larger TBR than Au in experiments. Adhesion strength dominates!

Acoustic Mismatch Model:

$$TBR \propto \frac{1}{\tau_b} = \frac{(Z_1 + Z_2)^2}{4Z_1Z_2}$$

$$Z = \rho \cdot u_p = \sqrt{\rho \cdot E}$$

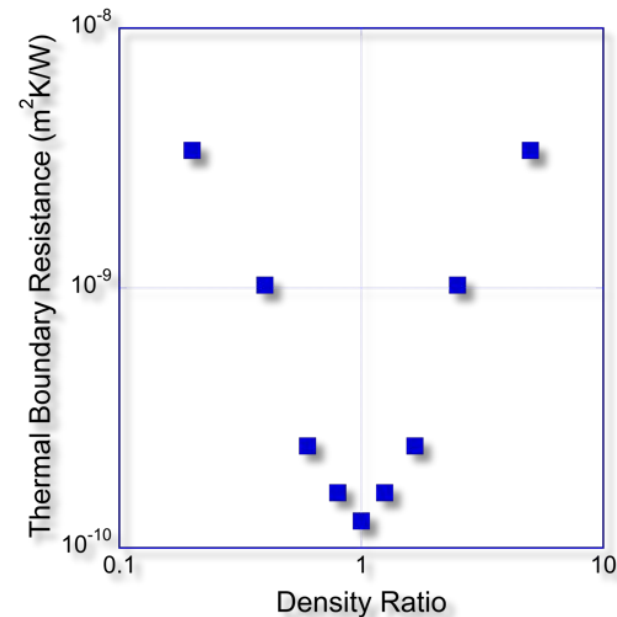
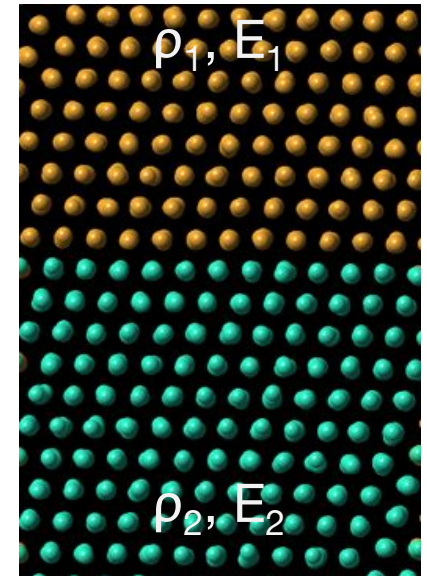
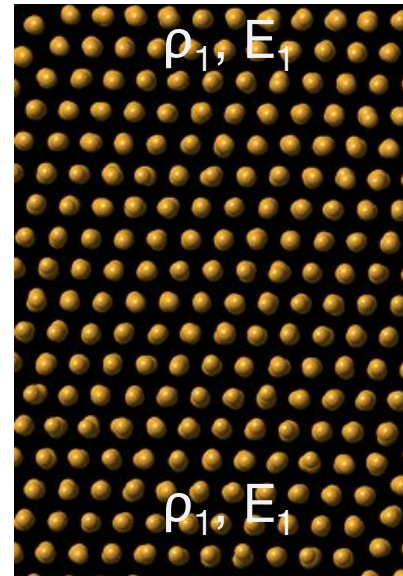
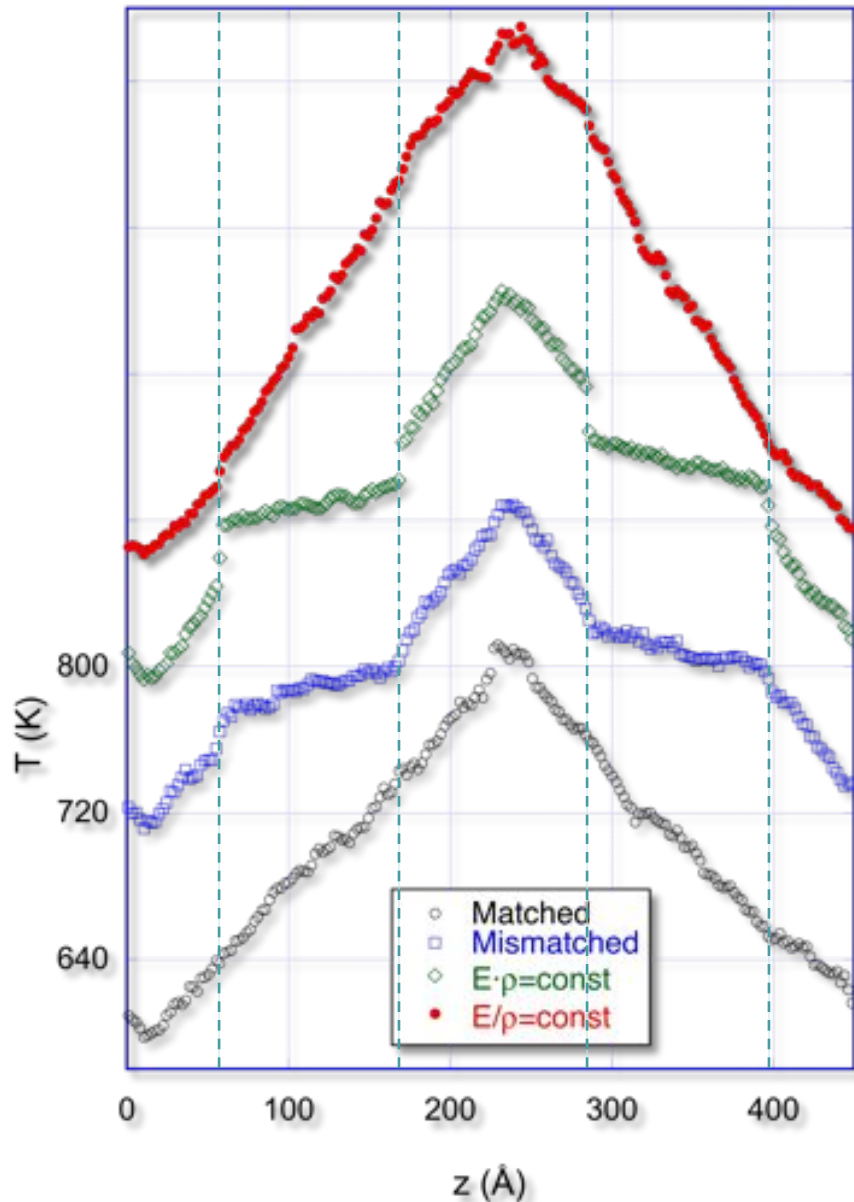
For two substrates with the bulk moduli of Ag and Au respectively, the atomic weight of the substrate is changed while keeping interactions the same.

	Ag	Au
Bulk Modulus (GPa)	100	180
Lattice Constant (Å)	4.09	4.08
Atomic Weight (g/mol)	107.8682	196.97
TBR^4 ($10^{-8} \text{ m}^2\text{K/W}$)	7.8 ± 1.6	5.4 ± 1.4

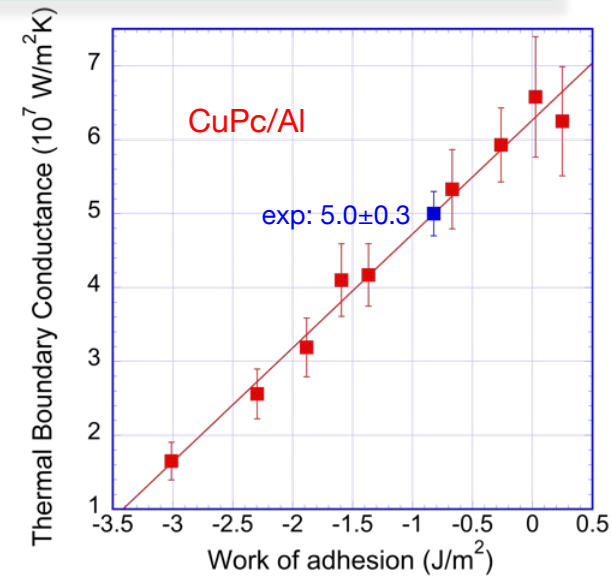
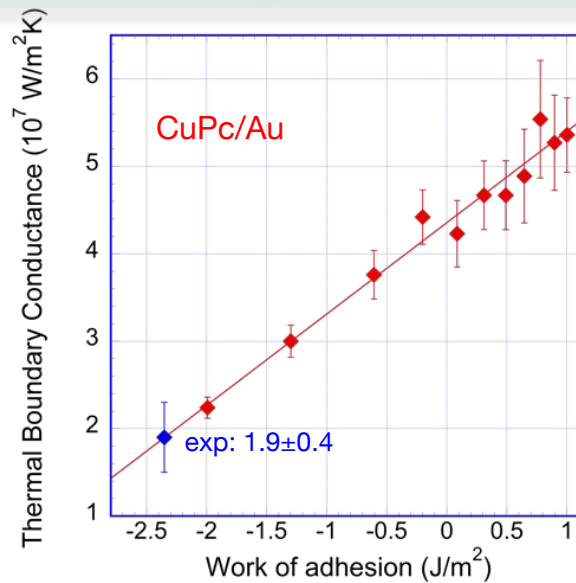
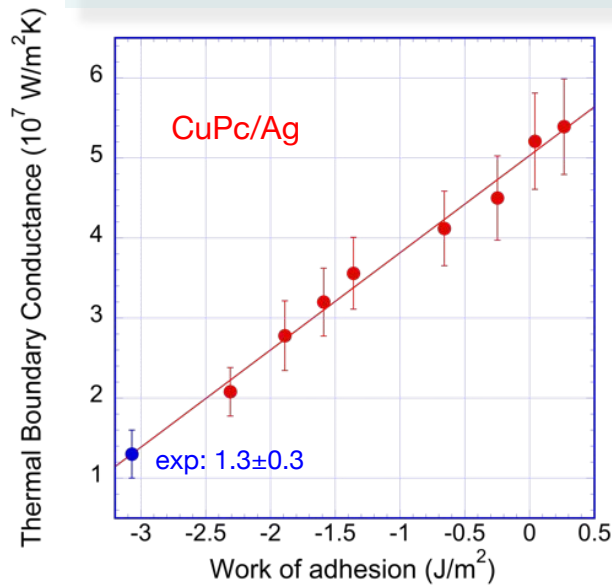
⁴ Y. Jin, et al. APL **98** 093305 2011



Interface in Properties Only



Adhesion Strength Dominates TBR



- Free surface energy for CuPc from Exp³: 0.035 J/m^2 and Work of adhesion for CuPc is 0.07 J/m^2
- Work of adhesion: CuPc/Al > CuPc/Au > CuPc/Ag
- The adhesion between CuPc/Au or CuPc/Ag is weaker than CuPc/CuPc²
- Agrees with the peel off test results from experiment²

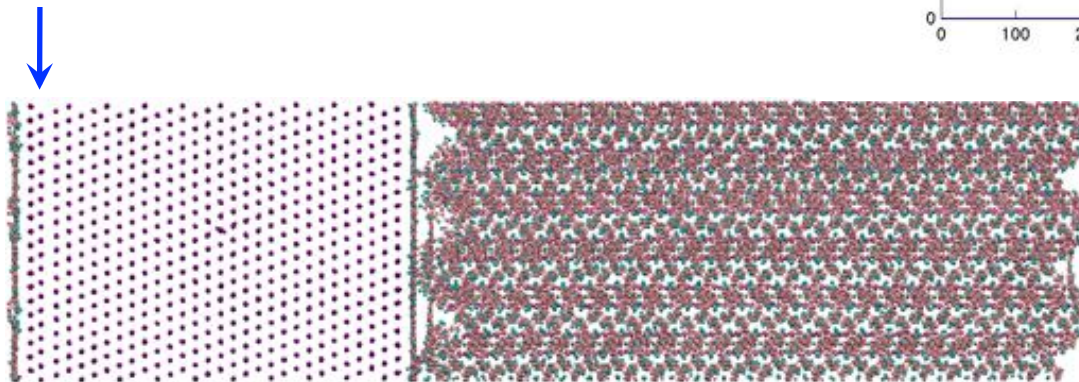
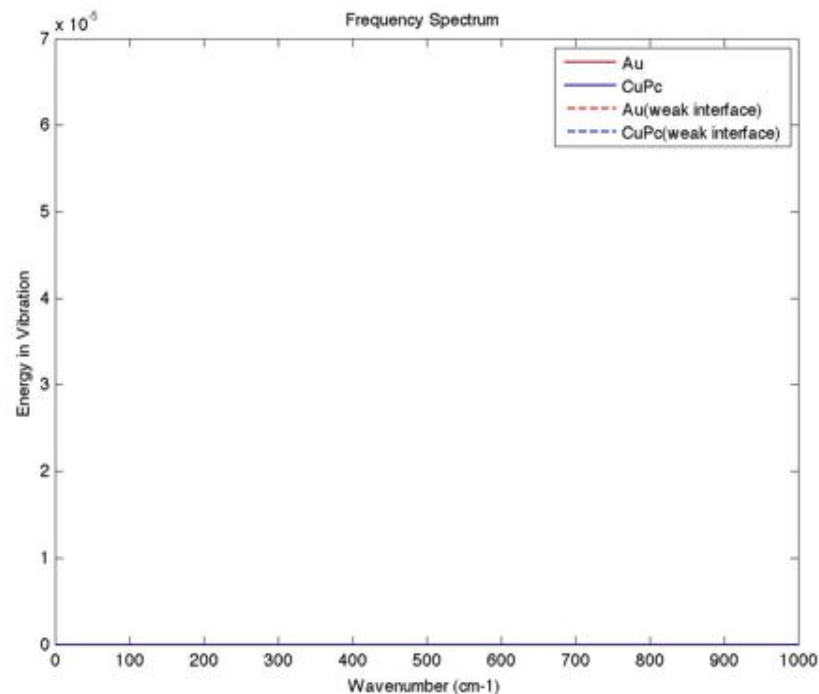
² Y. Jin, et al. MRS Spring Meeting 2011

³ H. X. Wei, et al. APL **97**, 083302 2010



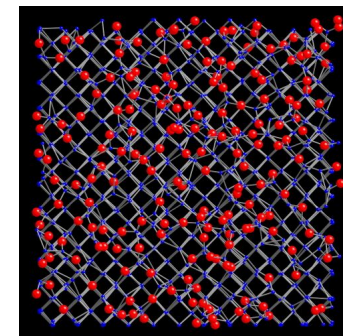
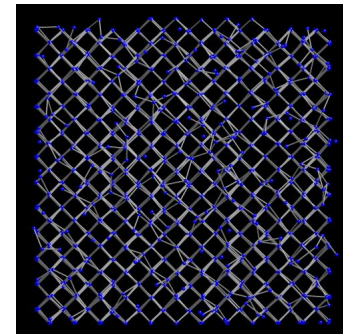
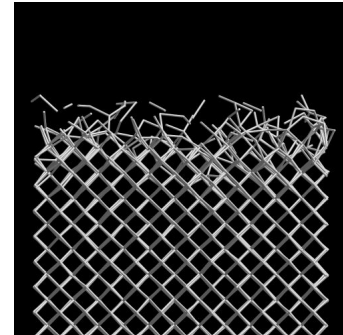
Phonon Coupling at CuPc/Au Interface

- For CuPc/Au system, 1 layer of Au atoms are perturbed
- Atomic velocity differences between perturbed and unperturbed systems are recorded to calculate phonon frequency spectrum



Summary & Outlook

- ❑ Reproduce process to generate realistic structures for property predictions and interpretation of experiments
- ❑ Findings thus far reveal:
 - ❖ Predominance of polymer layering near interfaces (staircase patterns, surface-bulk separation, surface domains, void formation)
 - ❖ Transition between contact and non-contact adhesion
 - ❖ Thermal boundary resistance (phonon velocity, mechanical impedance, structural impedance)
- ❑ Ongoing work:
 - ❖ Quantify structural signatures in materials responses
 - ❖ Thermosets
 - ❖ Interfacial modulus
 - ❖ Controlling interfacial properties



Functional molecular layers,
for monitoring, sensing, or
energy harvesting

