Examining Structure/Property Relationships in Lubricating Monolayer Films through Molecular Dynamics Screening

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MUMS Multiscale Modeling and Simulation

VANDERBILT School of Engineering

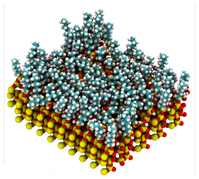
Monolayer-based Lubrication at the Nanoscale

Background

- High surface area-to-volume ratios in nanoscale devices enhance surface forces responsible for friction and wear, inhibiting traditional lubrication schemes
- Monolayer films present a promising solution
  - Typically composed of alkane backbones
  - Dense packing of chains prevents direct contact between surfaces
  - Friction coefficients reduced by >50% from values for uncoated silica
- Molecular dynamics (MD) simulations provide an atomic-level viewpoint of these systems and the ability to fine-tune system parameters

*Nanoscale devices with sliding parts are subject to friction and wear due to high surface area-to-volume ratios and inadequate lubrication. (**Above**: MEMS devices developed at Sandia National Laboratory, http://mems.sandia.gov/)*

Monolayer Chemistry and Tribology

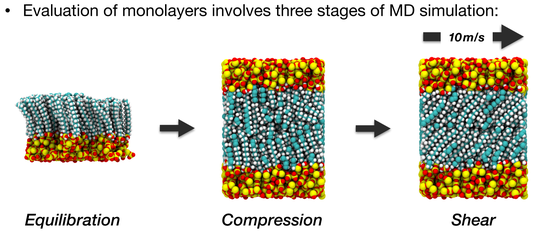


Rendering of an alkylsilane monolayer film attached to a crystalline silica surface

- Monolayers feature many structural parameters that can be tuned, e.g.
  - Chain length
  - Terminal group composition
- Monolayer chemistry has been shown to be highly linked to tribology, e.g.
  - Increased adhesion due to inter-monolayer hydrogen bonding
- ***Can MD be used to screen monolayer chemical space and yield insights into ideal monolayer characteristics for lubrication?***

Screening Monolayer Chemical Space with MoSDeF

- MoSDeF (**Mo**lecular **S**imulation and **De**sign **F**ramework) provides an architecture (as a collection of synergistic Python packages) to perform screening of soft materials (e.g. monolayers)
  - **mBuild**[1] - Model construction; provides a means for the definition of robust classes for initializing complex molecular systems
  - **Foyer**[2] - Force field application; performs automated atom typing and parameterization of molecular models
  - **Signac**[3-5] - Workflow and data management; provides an environment for simulation execution and data manipulation and storage
- Evaluation of monolayers involves three stages of MD simulation:



Equilibration → *Compression* → *Shear*

- Shear at a constant normal load (simulations at 5, 15, and 25nN) and at a constant shear velocity of 10m/s
- Simulations are performed using the GROMACS[6] simulation engine
- OPLS-aa force field parameters used for chains[7] and surfaces[8]

Acknowledgements

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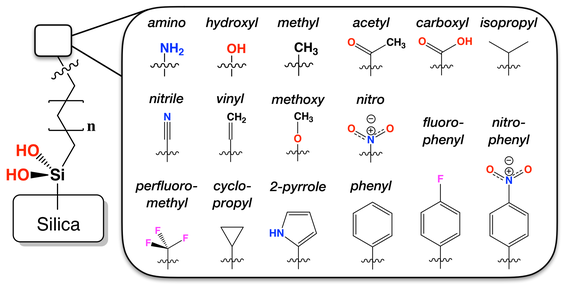
Defining a Chemical Parameter Space for Screening



*(**left**) 2D chemical structure of an alkylsilane chain with variable chain length and terminal group functionality. (**right**) The sixteen terminal groups examined in this study.*

Single-component Systems

→ 5 chain lengths (5, 8, 11, 14, 17)
→ 16 terminal group chemistries
→ 5 monolayer configurations

400 total systems → 80 unique chemical state points

Mixed Systems

→ 7 terminal group chemistries (top)
→ 16 terminal group chemistries (bottom)
→ 5 monolayer configurations

420 total systems (after removing duplicates) → 84 unique chemical state points

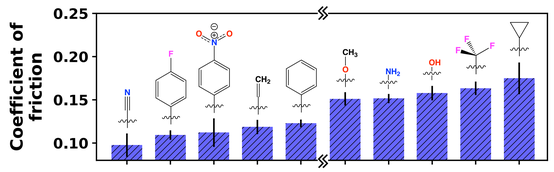
Insights from Single-component Systems

(Modified) Amontons' Law of Friction

Friction force F_f, Adhesive force F_0, Coeff. of friction μ, Normal force F_n

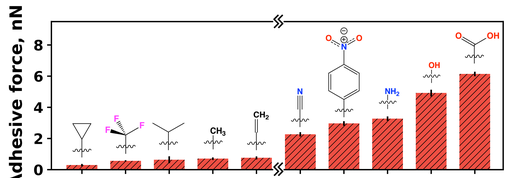
$$F_f = F_0 + \mu \cdot F_n$$

- Monolayer tribology is evaluated by calculating the coefficient of friction (COF) and adhesive force from a modified form of Amontons' Law of Friction (above)
- ↓ COF ↑ Chain length
- Terminal group chemistry appears to have a slight influence on COF
  - Small, linear groups and aromatic groups yield reduced COFs



COF as a function of terminal group chemistry for systems with a chain length of 17

Insights from Single-component Systems (cont.)



Adhesive force as a function of terminal group chemistry for systems with a chain length of 17

- Adhesion is found to be mostly independent of chain length
- Strong relationship between terminal group chemistry and adhesion
  - Hydrophobic groups (e.g. cyclopropyl, methyl) yield low adhesive forces
  - Hydrophilic groups (e.g. carboxyl, nitrile) yield high adhesive forces
  - Groups featuring the ability to form inter-monolayer hydrogen bonds have the highest adhesive forces

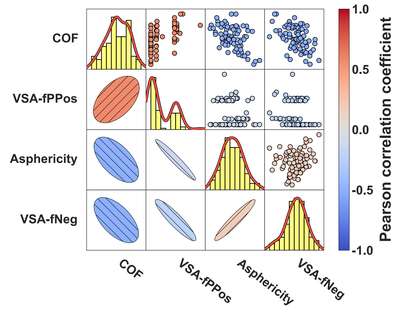
Structure-Property Relationships in Mixed Systems

Assigning Molecular Descriptors

- Correlations between terminal group chemistry and tribology are examined by assigning molecular descriptors to each system
  - Descriptors (e.g. asphericity, dipole moment) calculated for each terminal group (the dangling bond is capped by a hydrogen)
  - As each system features two different terminal groups, correlations between tribological properties and descriptor *means* are examined
- Dimensionality reduction (low variance filter, removal of highly correlated features)

Coefficient of Friction (COF)

$$F_f = F_0 + \mu F_n$$

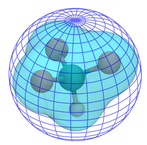


Corrgram displaying correlations between COF and the three descriptors with the highest correlations. Variable distribution is shown along the diagonal and the raw data is shown in the upper triangle.

- Correlations between terminal group descriptors and COF are fairly modest (< 0.6)
- Lowest COFs shown for chemistries where molecular volume consists primarily of negatively charged atoms
- Deviations from an ideal sphere reduce COF
  - e.g. linear and planar groups

VSA-fPPos
Fractional positive polar VDW surface area

Asphericity

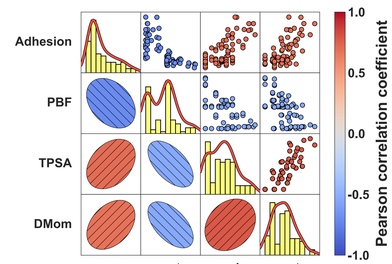


VSA-fNeg
Fractional negative VDW surface area

Structure-Property Relationships in Mixed Systems (cont.)

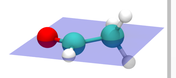
Force of Adhesion. F_0

$$F_f = F_0 + \mu F_n$$



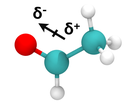
Corrgram displaying correlations between the adhesive force and the three descriptors with the highest correlations. Variable distribution is shown along the diagonal and the raw data is shown in the upper triangle.

PBF
Plane-of-best-fit



TPSA
Total polar surface area

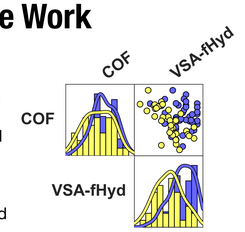
DMom
Dipole moment



- Several strong correlations are found between terminal group descriptors and adhesive force
- Groups with high dipole moments and many atoms with large absolute partial charges feature high values of adhesion
- Increased planarity yields higher adhesive forces
  - Possibly a sampling issue (multimodal distribution)
  - Currently searching for a mechanistic explanation

Conclusions and Future Work

- Terminal group chemistry influences both COF and adhesion, although stronger correlations are observed with adhesive forces
- Ideal chemistries (yielding low COF and low adhesion) should be non-spherical, non-planar, and non-polar
- Currently investigating the underlying mechanisms that describe the observed correlations
- Also examining correlations within molecular families using k-means clustering



Correlation between fractional hydrophobic VDW surface area and COF within k-means clusters describing two chemical families

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