Electronic Supplementary Material (ESI) for Soft Matter.

Supporting information for: "Tunable Transition from Hydration to Monomer-Supported Lubrication in Zwitterionic Monolayers Revealed by Molecular Dynamics Simulation"

Christoph Klein,[†,‡] Christopher R. Iacovella,[†,‡] Clare McCabe,[†,‡,¶] and Peter T. Cummings[*,†,‡]

Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States, Vanderbilt Multiscale Modeling and Simulation (MuMS) Center, Vanderbilt University, Nashville, Tennessee 37235, USA, and Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, United States

E-mail: peter.cummings@vanderbilt.edu

[*]To whom correspondence should be addressed

[†]Department of Chemical and Biomolecular Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States

[‡]Vanderbilt Multiscale Modeling and Simulation (MuMS) Center, Vanderbilt University, Nashville, Tennessee 37235, USA

[¶]Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, United States

Table S1: Summary of partial charges. Corresponding `.xyz` file for a monomer given below.

Name	q (e)
HC3	0.15
N3	0.30
CH3	-0.31
CT	-0.13
HC	0.06
CTD	0.41
HCD	-0.01
OSD	-0.61
P	1.42
O2D	-1.03
CTE	0.27
OS	-0.61
C	0.99
O	-0.69
CM3	-0.13
CM1	-0.30
HM	0.16
CH2	-0.26
OH	-0.88
HO	0.44
Si2	1.29

Listing S1: `.xyz` file for a single monomer

```
45
Silane MPC
Si2       -0.04172       -2.90982        0.22037
OH        -1.24454       -2.87736        0.00477
OH         1.10628       -3.12501       -0.13071
HO        -2.28453       -2.69327        0.34699
HO         2.19471       -3.31217       -0.36034
CH2        0.11586       -2.56520        1.31676
CM3        0.95504       -2.16260        2.51336
HC        -0.26119       -3.53452        1.71497
HC        -0.57509       -1.71410        1.52665
CM1        2.14119       -1.54573        2.37393
HM         2.55320       -1.34557        1.38814
HM         2.71388       -1.19372        3.22606
C          0.29712       -2.37195        3.84703
O         -0.83193       -2.82291        3.96183
OS         1.04002       -1.99788        4.91054
CTE        0.52719       -2.24033        6.24686
CTD        1.60798       -1.78750        7.24244
HC         0.33306       -3.31155        6.35865
HC        -0.40096       -1.68051        6.39816
OSD        1.42343       -2.42122        8.53518
HCD        1.60400       -0.69923        7.34603
HCD        2.58140       -2.10625        6.86123
P          0.69269       -1.67034        9.75920
OSD        2.24817       -1.93833       10.15396
O2D       -0.56520       -2.36912        9.40468
OSD        0.71235       -2.38080       11.20677
CTD       -0.04528       -1.85267       12.32707
CT         0.90614       -1.16063       13.33217
HCD       -0.54102       -2.69471       12.81585
HCD       -0.80235       -1.15413       11.96164
N3         0.29673       -0.57328       14.60028
HC         1.42836       -0.34232       12.82827
HC         1.64632       -1.88560       13.68450
CH3        1.39046        0.07911       15.41680
HC3        1.87522        0.86910       14.83652
HC3        2.14672       -0.65816       15.70080
HC3        0.98398        0.52350       16.33042
CH3       -0.35135       -1.65156       15.44106
HC3       -1.19803       -2.14701       14.95900
HC3       -0.71483       -1.17491       16.35686
HC3        0.38362       -2.41235       15.71859
CH3       -0.73911        0.47297       14.25681
HC3       -0.28687        1.24851       13.63252
HC3       -1.09334        0.93523       15.18306
HC3       -1.60419        0.06107       13.73049
```

Figure S1 summarizes the placement of chains on the substrate.

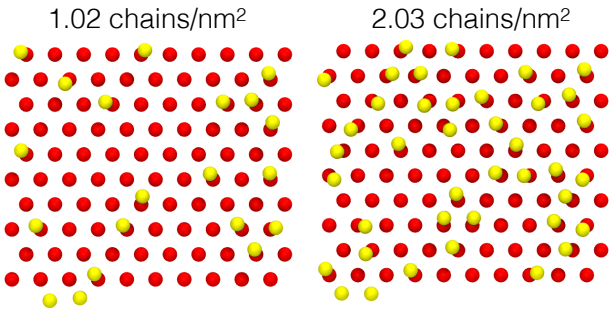

Figure S1: Binding site locations for both chain densities. Red shows available surface oxygens. Yellow shows silicon atoms at the base of bound monomers.

Figure S2 shows the hydration levels of the monolayer as a function of separation distance. These data support the trends shown in Figure 2.

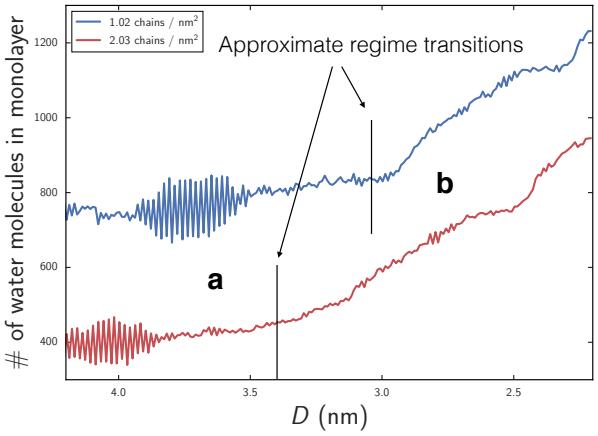

Figure S2: Amount of water trapped within the monolayers across separation distances.

Figure S3 summarizes the simulations we performed at 1 m/s shearing speeds to probe the velocity dependence of the tribology of our systems.

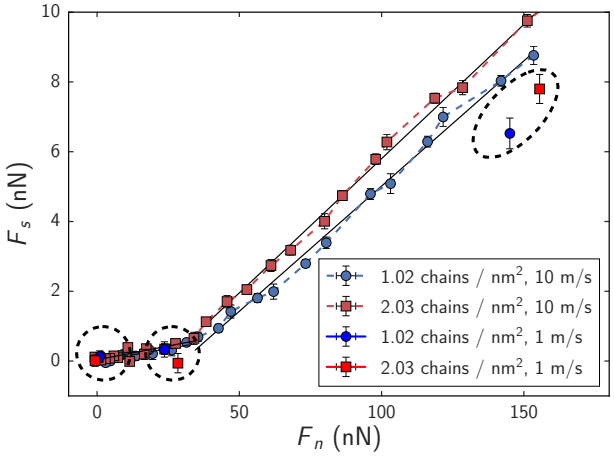

Figure S3: Velocity dependence of shear force. Data from Fig. 4 is overlaid with select runs performed at 1 m/s.

Film thickness is calculated by binning atoms in each monolayer over time according to their z-position in the system (shown in S4). The film thickness is then defined as the difference between the z-value where the cumulative distribution function reaches 0.9 and the z-value closest to the surface.

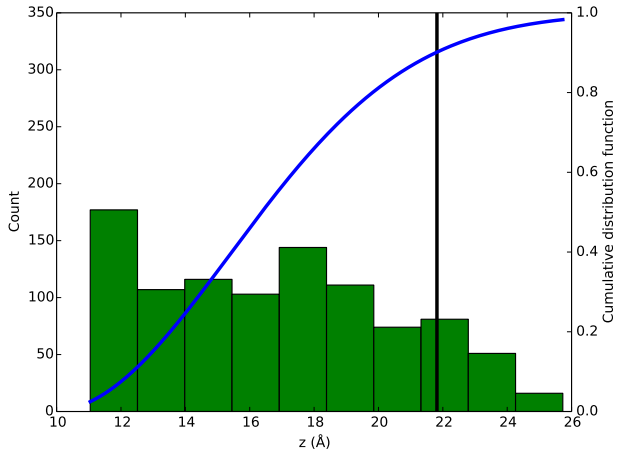

Figure S4: Example of film thickness calculation for a single frame. Green histogram shows vertical position of atoms in bottom film. Blue line denotes cumulative distribution function (CDF) of atoms in bottom film. Black vertical line denotes cutoff where CDF reaches 0.9.