1. DOE award # and institution:

DE-FG02-OGER46340 at University of California, Davis

2. Project title and PI:

"Structure-Property Relationships of Polymer Brushes in Restricted Geometries and their Utilization as Ultra-Low Lubricants"
PI Tonya L. Kuhl
Co-PI Roland Faller

3. Executive Summary:

Though polymer films are widely used to modify or tailor the physical, chemical and mechanical properties of interfaces in both solid and liquid systems, the rational design of interface- or surface-active polymer modifiers has been hampered by a lack of information about the behavior and structure-property relationships of this class of molecules. This is especially true for systems in which the role of the polymer is to modify the interaction between two solid surfaces in intimate contact and under load, to cause them to be mechanically coupled (e.g. to promote adhesion and wetting) or to minimize their interaction (e.g. lubrication, colloidal stabilization, etc.). Detailed structural information on these systems has largely been precluded by the many difficulties and challenges associated with direct experimental measurements of polymer structure in these geometries. As a result, many practitioners have been forced to employ indirect measurements or rely wholly on theoretical modeling. This has resulted in an incomplete understanding of the structure-property relationships, which are relied upon for the rational design of improved polymer modifiers.
Over the course of this current research program, we made direct measurements of the structure of polymers at the interface between two solid surfaces under confinement and elucidated the fundamental physics behind these phenomena using atomistic and coarse grained simulations. The research has potential to lead to new lubricants and wear reducing agents to improve efficiency.

4. Accomplishments:

The specific aims or our proposal were: (1) In situ characterization of the density profile, lateral friction, and normal interaction forces of polymer brushes at high and ultra-high grafting density as a function of confinement, solvent quality, and shear; and (2) Investigate the structure, dynamics, thermodynamics and shear response of a variety of different polymer brushes dependent on polymer identity, environmental conditions, confinement and applied shear using multiscale computer simulations. Under (1) measurements were carried out that characterized the density profile, lateral friction, and normal interaction forces of polymer brushes at high and ultra-high grafting density as a function of confinement. Under (2) we performed simulations of polymer brushes at various length scales and under a large variety of models and conditions. Several models were for the first time applied to brushes and we extended the simulation methodology of Iterative Boltzmann Inversion to confined systems. Also a novel technique to perform simulations under constant chemical potential was developed.

5. Summarize Project Activities:

In this project, physical experiments that characterized the density profile, lateral friction, and normal interaction forces of polymer brushes at high and ultra-high grafting density as a function of confinement, and shear were carried out. Complementary multiscale computer simulations investigated the structure, dynamics, thermodynamics and compression response of a variety of different polymer brushes dependent on polymer identity, environmental conditions, confinement and applied compression. Experimental neutron reflectivity measurements of polymer brushes in non-good solvent conditions were difficult to carry out and insufficient to reach conclusions. Ultra-high density brushes in good solvent conditions were found to have excellent lubricity and wear protective properties. Simulations elucidated polymer brush properties under a large variety of models and conditions.

6. Papers:

Published papers that at some point during the period of the DOE award were partially supported through supply purchases, facility use, student support, etc. and that acknowledged DOE support, but were not solely funded by DOE are:

Elliott, I.G., Mulder, D.E., Träskelin, P.T., Ell, J.R., Patten, T.E., Kuhl, T. L., Faller, R." Simulations and Neutron Scattering in Confined Polymer Systems" DOI:10.1039/b910693f Soft Matter 5:4612-4622 (2009).

Traskelin, P, Kuhl, T. L., and Faller, R. "Molecular dynamics simulations of polystyrene brushes in toluene solution" Physical Chemistry Chemical Physics 11:11324-11332 (2009).

Ell, J.R., Mulder, D.E., Faller, R., Patten, T.E., Kuhl, T.L. "Structural Determination of High Density, ATRP Grown Polystyrene Brushes by Neutron Reflectivity" Macromolecules 42:9523-9527 (2009).

Elliott, I.G., Kuhl, T.L., and Faller, R. "Molecular Simulation Study of the Structure of High Density Polymer Brushes in Good Solvent" Macromolecules 43(21):9131–9138 (2010).

Jayeeta Ghosh, Masaomi Hatakeyama, Petra Träskelin, Chenyue Xing and Roland Faller "Molecular Modeling in confined polymer and biomembrane systems" Songklanakarin J. Sci. Technol. 31 (2), 167-173, Mar. - Apr. 2009.

Mulder, D.J. and Kuhl, T.L. "Polymer Brushes in Restricted Geometries" Soft Matter 6:5401-5407 (2010).

Watkins, E.B., Miller, C.E., Majewski, J., and Kuhl T.L. "Membrane texture induced by specific protein binding and receptor clustering: active roles for lipids in cellular function" Proceedings of the National Academy of Science, 108 (17) 6975-6980 (2011).

Beste Bayramoglu and Roland Faller "Structural properties of polystyrene oligomers in different environments: a molecular dynamics study" Phys. Chem. Chem. Phys., 13, 18107-18114 (2011).

El-khouri, R., Bricarello, D., Watkins, E.B., Miller, C.E., Patten, T.E., Parikh, A., Kuhl, T.L. "pH Responsive Polymer Cushions for Probing Membrane Environment Interactions" Nano Letters 11(5); 2169-2172 (2011).

Giulia Rossi, Ian G. Elliott, Tapio Ala-Nissila, Roland Faller: Molecular Dynamics study of a MARTINI coarse-grained polystyrene brush in good solvent: Structure and dynamics Macromolecules 45(1) 563–571 (2012)

Liao, W.-P. and Kuhl, T.L., "Steric Forces of Tethered Polymer Chains as a Function of Grafting Density: Studies with a Single Diblock Molecular Weight" Macromolecules 45, 5766−5772 (2012).

Elliott, I.G., Kuhl, T.L., Faller, R. "A Molecular Dynamics Technique to Extract Forces in Soft Matter Systems Under Compression With Constant Solvent Chemical Potential" Journal of Chemical Theory and Computation 8(3)1072-1077 (2012).

Elliott, I.G., Kuhl, T.L., and Faller, R. "Compression of High Grafting Density Opposing Polymer Brushes Using Molecular Dynamics Simulations in Explicit Solvent" Journal of Physical Chemistry 117(15)4134-4141 (2013).

Balko, S.M., Kreer, T., Costanzo, P.J., Patten, T.E., Johner, A., Kuhl, T.L., and Marques, C.M. "Polymer brushes under high load" PLos ONE 8(3): e58392. doi:10.1371/journal.pone.0058392 (2013).

Liao, W.-P., Elliott, I.G., Faller, R. and Kuhl, T.L., "Normal and Shear Interactions between High Grafting Density Polymer Brushes Grown by Atom Transfer Radical Polymerization" Soft Matter DOI: 10.1039/c3sm50261a (2013).

Elliott, I.G., Kuhl, T.L., and Faller, R. "Compression of High Grafting Density Opposing Polymer Brushes Using Molecular Dynamics Simulations in Explicit Solvent" Journal of Physical Chemistry 117(15)4134-4141 (2013).

Beste Bayramoglu, Roland Faller: Modeling of Polystyrene under Confinement: Exploring the Limits of Iterative Boltzmann Inversion Macromolecules 46(19) 7957–7976 (2013)

Balko, S.M., Kreer, T., Mulder, D.J. Costanzo, P.J., Patten, T.E., Kuhl, T.L.,"Using thiol-gold bond formation to bridge surfaces with a polymer brush: SFA experiments and MD simulations", Macromolecules DOI: 10.1021/ma4015356 (2014).

7. Computer Modeling:

For projects involving computer modeling, provide the following information with the final report:

a. Model description, key assumptions, version, source and intended use; Largely existing codes were used (Gromacs V 3.2-4.5, www.gromacs.org, all purpose MD code) novel models were partially developed:
    1. atomistic simulations (e.g. Traskelin 2009) were performed with existing literature models (here: the Gromos forcefield http://www.gromacs.org/Documentation/Terminology/Force_Fields/GROMOS)
    2. Martini simulations: The Martini model (http://cgmartini.nl/cgmartini/) which contains one interaction for every 3-5 heavy atoms was extended for the use with polymer brushes. PEG and PS models were tested and validated. The models are published in the literature. The PS simulation (Rossi 2012) bases on a model from our collaborator Giulia Rossi. The PEG model (e.g. Elliott 2010) was self developed and tested.
    3. IBI simulations: Here the models are fully numerical models which are intended only for the specific state, The test and development of such models was published (e.g. Bayramogly 2013)
b. Performance criteria for the model related to the intended use; validation of models against each other and against literature data, Coarse-grained simulations several order of magnitude faster than atomistic simulations allowing larger length scales.
c. Test results to demonstrate the model performance criteria were met (e.g., code verification/validation, sensitivity analyses, history matching with lab or field data, as appropriate); all simulations were validated against existing models in the literature and experiments where available, largely models were developed rather than codes.
d. Theory behind the model, expressed in non-mathematical terms: Newtons equations, statistical mechanics (semi grand-canonical ensemble), equivalence of potentials if radial distribution functions are equal basing on the uniqueness of pair potentials.
e. Mathematics to be used, including formulas and calculation methods; no special mathematics needed, standard Molecular Dynamics with Verlet integrators.
f. Whether or not the theory and mathematical algorithms were peer reviewed, and, if so, include a summary of theoretical strengths and weaknesses;: all methodologies are either standard simulation software which is based on many peer reviewed articles or new methodologies were peer reviewed in this project. Relevant papers are: Elliott 2009, Elliott 2012, Bayramoglu 2013. All IBI models have the fundamental problem that they are heavily state dependent, whereas they are much faster and structurally equivalent to high resolution models. The Martini model (e.g. used in Elliott 2010, Rossi 2012) is thermodynamically coarse grained and therefore has a strong performance in free energies and is structurally not as strong. So cross checking the two strongly different models allows to combine their strengths. The new compression technique (Elliott 2012) is a combination of the well-established Widom insertion and standard MD.
g. Hardware requirements: Linux cluster
h. Documentation (e.g., users guide, model code): no users guides were developed, most codes are existing open source codes which were partially adapted for the research here.