AFOSR-TR-97-0373

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
		FINAL 01 Jul 94 To 30 Jun 97

4. TITLE AND SUBTITLE
MOLECULAR SIMULATIONS OF ULTRATHIN PERFLUOROPOLYETHER FILMS UNDER SHEAR

5. FUNDING NUMBERS
F49620-94-1-0319
3484/XS
61103D

6. AUTHOR(S)
Dr Steve Granick

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Illinois
Dept of Materials Science & Engineering
105 S. Goodwin Ave.
Urbana IL 61801

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NL
110 Duncan Ave Room b115
Bolling AFB DC 20332-8050

Maj Hugh C. De Long

10. SPONSORING MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release;
distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

In this project dealing with aqueous films confined between solid surfaces at spacings comparable to the molecules themselves, we succeeded, for the first time, to investigate the effect of deformation frequency and amplitude on the shear dynamics of these films. We also succeeded, for the first time, to observe molecular ordering of aqueous ions at the solid-liquid interface. These unique experiments not only open new directions in research on liquids in confined geometries, but also have important implications for the field of tribology.

14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT (U)	18. SECURITY CLASSIFICATION OF THIS PAGE (U)	19. SECURITY CLASSIFICATION OF ABSTRACT (U)	20. LIMITATION OF ABSTRACT (UL)

AFOSR-TR-97-0372

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
		FINAL 01 Jul 94 To 30 Jun 97

4. TITLE AND SUBTITLE
MOLECULAR SIMULATIONS OF ULTRATHIN PERFLUOROPOLYETHER FILMS UNDER SHEAR

5. FUNDING NUMBERS
F49620-94-1-0319
3484/XS
61103D

6. AUTHOR(S)
Dr Steve Granick

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Illinois
Dept of Materials Science & Engineering
105 S. Goodwin Ave.
Urbana IL 61801

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NL
110 Duncan Ave Room b115
Bolling AFB DC 20332-8050

Maj Hugh C. De Long

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release;
distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

In this project dealing with aqueous films confined between solid surfaces at spacings comparable to the molecules themselves, we succeeded, for the first time, to investigate the effect of deformation frequency and amplitude on the shear dynamics of these films. We also succeeded, for the first time, to observe molecular ordering of aqueous ions at the solid-liquid interface. These unique experiments not only open new directions in research on liquids in confined geometries, but also have important implications for the field of tribology.

19971003 048

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
(U)	(U)	(U)	(UL)

FINAL TECHNICAL REPORT ON AASERT GRANT

F49620-94-1-0319

Period Covered: July 1, 1994 - June 30, 1997

Steve Granick
University of Illinois
Department of Materials Science and Engineering
105 S. Goodwin Ave.
Urbana, IL 61801

Steve Granick 8/18/97
Signature Date

PII Redacted [redacted]: [redacted]

1. Objectives

This AASERT project was originally conceived to provide molecular dynamics simulations of ultrathin perfluoro-polyether films under shear. In 1994, after the grant was awarded, it proved not to be feasible to continue the research as planned because a key collaborator, Professor Van Swol at the University of Illinois, did not receive tenure and left the university. Captain T. Erstfeld (Program Manager at the time) gave provisional approval to change the project objectives to "Nanorheology of Molecularly-Thin Films of Polyelectrolytes and Simple Electrolytes." Major H. DeLong (current Program Manager) also approved this shift of emphasis. The objective of the grant became to characterize the mechanical properties of molecularly-thin aqueous films and to understand why their rheology differs from that of thicker films.

2. Summary of Research Progress

In this project dealing with aqueous films confined between solid surfaces at spacings comparable to the molecules themselves, we succeeded, for the first time, to investigate the effect of deformation frequency and amplitude on the shear dynamics of these films. We also succeeded, for the first time, to observe molecular ordering of aqueous ions at the solid-liquid interface. These unique experiments not only open new directions in research on liquids in confined geometries, but also have important implications for the field of tribology.

3. Specific Research Accomplishments under Grant F49620-94-1-0319

We have contrasted the flow, under infinitesimally-small and large deformations, of aqueous $MgCl_2$ films ($\approx$0.6 nm thick) and KCl confined between atomically smooth single crystal sheets. The experimental procedures were the same as those employed in our parent grant (URI Grant to the University of Illinois). The main idea was modification of a surface forces apparatus to measure dynamic oscillatory shear forces by use of piezoelectric elements. To apply controlled shear motion, with amplitudes 0.1 - 10 nm, sinusoidal shear forces were applied to one piezoelectric bimorph and the resulting displacement was monitored by a second piezoelectric bimorph.

In the case of small deformations (linear response). The significance of linear response, obtained by deflection amplitudes less than 0.1 - 0.2 nm, was to probe the unperturbed film structure, as it was a rest. In this case the films slid smoothly in the manner of viscous liquids. But though large-deformation motion was smooth when the forcing frequency was less than the inverse linear relaxation time, it occurred by intermittent stick-slip events when the forcing frequency was

larger. An example of this intriguing difference is shown in Fig. 1.

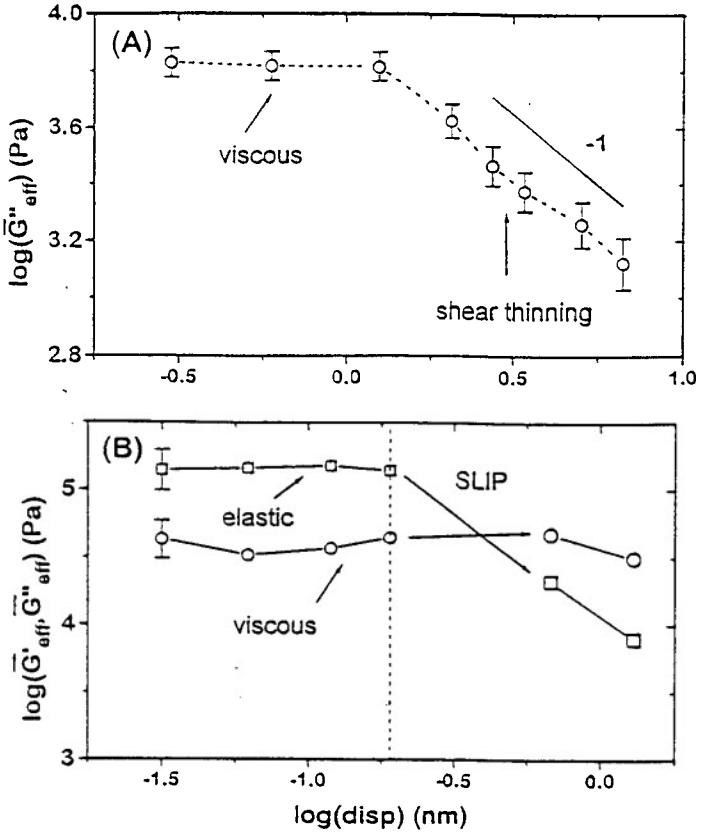

Fig. 1. Transition to large-amplitude sliding. **(A)** *Log-log plot of effective loss modulus at 1 Hz against deflection amplitude for aqueous magnesium chloride (100 mM) confined between mica surfaces at thickness 0.6±0.2 nm. Deflection was monotonic in the force amplitude.* **(B)** *Log-log plot of effective loss and elastic shear moduli (circles and squares, respectively) at 100 Hz, plotted against deflection amplitude for the same films as in Panel A. The deflection shows discontinuous "stick-slip" character.*

It is interesting to evaluate this observation in the light of various proposed models of stick-slip. Traditionally, stick-slip has often been interpreted to signify that friction force decreases with increasing distance traversed or velocity. But this approach cannot predict the point at which the effect will be observed. A more recent model, that confinement induces crystallization, cannot apply to this system because the system was demonstrably in a liquid state to start with. Stick-slip in this system is thus a matter of time scale: it occurred only when the films were deformed faster than a natural relaxation time. The practical implication for tribology is that stick-slip

response should be expected for any lubricant film at appropriately high frequency.

An additional important observation, arising out of this work, was that "granularity" of the confined fluid came into play. To test the possibility that the film thickness might increase in the course of motion, a new device was built. The bottom mica surface was mounted on a double cantilever spring of piezoelectric bimorphs in a manner analogous to the design of our shear cell -- but in this case, it was employed to measure forces and displacements in the normal direction. Changes of film thickness could thus be monitored.

Fig. 2 shows that the film thickness was constant for linear deformations but that abrupt thickness increase accompanied shear-induced slip. The amount of increase (≈0.5 nm) was not noticed in any laboratory's previous experiments because it is below the resolution of the multiple-beam interferometry commonly used to measure film thickness in a surface forces apparatus. In fact, the amount of increase was less than the size of a water molecule. Nonetheless, it amounted to 10% of the film thickness. An intriguing implication of possible tribological significance is that such events, during lubrication, could generate wear.

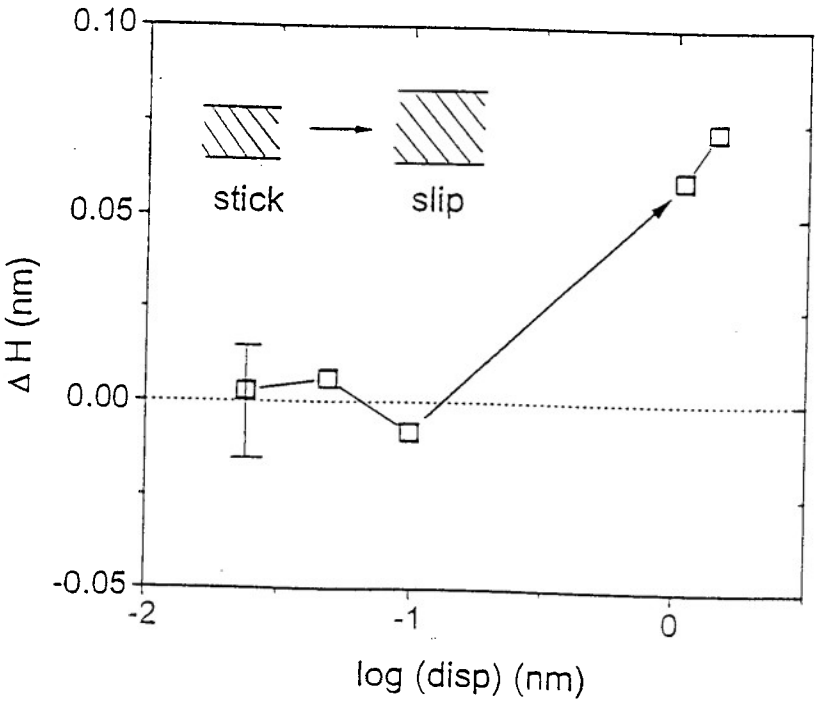

Fig. 2. Shear-induced increase of thickness during stick-slip plotted against logarithmic displacement amplitude. Frequency was 256 Hz. Inset shows a schematic diagram of shear-induced dilation.

Another thrust of research has consisted of developing methods to obtain molecular information on surface orientation of organic species at the solid-liquid interface. The method here is infrared dichroism measured in the geometry of attenuated total reflection. This allows one to measure the infrared absorptivity of a surface layer in two orthogonal polarization directions of molecularly-thin layers adsorbed at an aqueous or organic interface.

An apparatus has been constructed for this purpose; a unique feature of the apparatus is that flow-induced deformations can be measured at controlled rates of flow past the surface, thus emulating conditions of hydrodynamic lubrication:

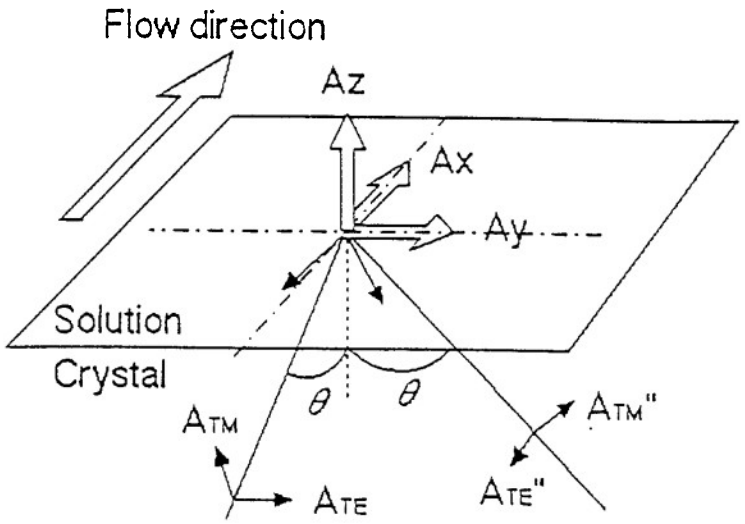

Fig. 3. Schematic illustration of the flow cell. A hemispherical silicon crystal is employed for Fourier transform infrared spectroscopy in attenuated total reflection (FTIR-ATR). Here x indicates the direction of shear flow, y is also in the plane of the surface but perpendicular to the flow, and z is the direction normal to the surface. Infrared light travels from the crystal side (lower portion of the figure) and it totally reflected at the solid-liquid interface. Polarized ATR intensities of the evanescent wave are measured both perpendicular (A_{TM}", A_{TE}") and parallel ((A_{TM}, A_{TE}) to the flow direction. Electric field of the evanescent wave is parallel to the incident beam in the TM mode and is normal to the incident plane in the TE mode. These four absorbances can be related to the absorptivity of the adsorbed lubricant additives in x, y, and z directions at the solid-liquid interface.

The purpose of this new flow cell is to study flow-induced deformations of lubricant additives. We anticipate that the apparatus will be useful during the course of a new AASERT Award, Control Number 97NL055, "Molecular Tribology of Lubrication Additives with Emphasis on Perfluoroalkylpolyethers."

4. Personnel Supported

Paul J. R. Reese
Annette Ostling

6. Publications

none to date

7. Interactions/Transitions

a. presentations at meetings:

Univ. of Chicago, Physics Dept., 10/3/94
Exxon Corp., Annandale, NJ, 11/8/94
PPG Corp., Pittsburgh, PA, 11/10/94
Medtronic Corp., Minneapolis, 11/14/94
MRS Symp., Liquids in Confined Geometries, Boston, 12/1/95
Les Houches, Slow Relaxations in Soft Matter, France, 1/30/95
Carnegie-Mellon Univ., Dept. Chem. Eng., 2/28/95
ACS Symp., Physical Chemistry of Polymers, Anaheim, CA, 4/3/95
ACS Symp., Molecular Tribology, Anaheim, CA, 4/3/95
AFOSR Tribology Workshop, Washington, DC, 9/21/95
Exxon Research & Engineering, Annandale, NJ, 10/5/95
Columbia Univ., Chem. Eng. Dept., New York, NY, 10/6/95
Yale Univ., Chem. Eng. Dept., New Haven, CT, 11/6/95
Harvard Univ., Chem. Dept., Cambridge, MA, 11/8/95
IBM Rüschlikon Lab., Zürich, Switzerland, 12/13/95
ETH, Inst. für Polymere, Zürich, Switzerland, 12/15/95
Max-Planck-Institut für Polymerforschung, Mainz, Germany, 12/18/95
Institut für Mikromaschine, Mainz, Germany, 12/19/95
Northeastern Univ., Physics Dept., 2/29/96
Kansas State Univ., Physics Dept., 3/7/96
APS Symp., Confined Polymers, St. Louis, 3/21/96
Univ. Mass., Polym. Sci. Eng. Dept., 4/5/96
Am. Cer. Soc. Symp., Basics of Processing, Indianapolis, IN, 4/15/96
NSF Tribology Workshop, Richmond, VA, 4/16/96
Cornell Univ., Chem. Eng. Dept., 4/18/96
Inst. of Tribology, Tsinghua Univ., Beijing, China, 5/13-15/96
Dept. Mech. Eng., Zhe Zhiang University, Hanghou, China, 5/20/96

Dept. Precision Instruments, Jiatong Univ., Shanghai, China, 5/21/96
NATO Conf. on Friction, Lisbon, Portugal, 6/20/96
Gordon Conference on Tribology, New Hampshire, 7/1/96
Argonne National Laboratory, Chicago, IL, 8/6/96
ACS Symp., Polymer Interfaces, Orlando, FLA, 8/25/96
Boston College, Chem. Dept., Boston, MA, 9/19/96
Exxon Corporate Research, Annandale, NJ, 9/23/96
Univ. of Wisconsin, Chem. Eng. Dept., Madison, WI, 10/3/96
Northwestern Univ., Materials Dept., Chicago, IL, 10/15/96
MRS Symp., Dynamics in Confining Systems, 12/2/96.
Gordon Conference on Polymers, Ventura, CA, 1/5/97
Swiss. Fed. Inst. Technology, Lausanne, Switzerland, 1/23/97.
3M Research, St. Paul, MN, 2/3/97.
Univ. North Carolina, Chem. Dept., Chapel Hill, NC, 2/27/97.
Harvard Univ., Applied Physics Dept., Cambridge, MA, 3/7/97.
Distinguished Visitors Program, NIST, Gaithersburg, MD, 4/14/97.
NSF Center for Polymer Interfaces, Brooklyn, NY, 5/8/97.
Hitachi Corporate Research, Hitachi City, Japan, 6/9/97
Japan/US Polymer Conference, NIST, Gaithersburg, MD, 6/18/97.

b. Consultative and advisory functions to other laboratories

Consultation visit to Wright-Patt AFB, 10/30/94.
primary individuals involved: S. Granick, H. Paige, K. Eisentraut, S. Sharma, L. Gschwender.

Consultation visit to Wright-Patt AFB, 5/9/95.
primary individuals involved: S. Granick, H. Paige, S. Sharma, L. Gschwender.

Consultation visit to Wright Patterson AFB, 8/20/96.
primary individuals involved: S. Granick, **H. Paige, Sharma, L. Gschwender.**

c. Transitions

none

8. New discoveries, inventions, patent disclosures

none

9. Honors/Awards

In 1995, Granick was listed in Who's Who in Science and Engineering.

In May, 1996, Granick was honored with the International Nanotribology Award by Tsinghua University, China.