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FINAL REPORT

PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

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R&T Code: 413V003

Investigation of Compact Layers at a Liquid/Liquid Interface

Jiri Janata

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April 27, 1993

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**ONR Final Report
PART I
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT**

R&T number: 413V003

Grant Number: N00014-91-J-1926

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- a. Number of papers submitted to refereed journals, but not yet published: 0
- b. Number of papers published in refereed journals: 1
- c. Number of books or chapters submitted, but not yet published (at press): 1
- d. Number of books or chapters published: 0
- e. Number of printed technical reports/non-refereed papers: 0
- f. Number of patents filed: 0
- g. Number of patents granted: 0
- h. Number of invited presentations: 4
- i. Number of submitted presentations: 2
- j. Honors/Awards/Prizes for grant employees: 1
- k. Total number of **full-time equivalent** Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:
 Graduate Students: 1
- l. Other related funding: none

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Citation List (PART I)

b. Papers published in refereed journals:

Bruckner-Lea, C.; Janata, J.; Conroy, J.; Pungor, A. and Caldwell, K. "Scanning Tunneling Microscopy on a Mercury Sessile Drop", *Langmuir*, 9, 3612-3617, 1993.

c. Chapter accepted, but not yet published:

Janata, J.; Bruckner-Lea, C.; Conroy, J.; Pungor, A.; and Caldwell, K. "Scanning Tuneling Microscopy on a Compressible Mercury Sessile Drop", in ACS Series: Chemically Sensitive Interfaces, 1994.

h. Invited presentation:

Janata, J.; Bruckner-Lea, C.; Conroy, J.; Pungor, A. and Caldwell, K. "Molecular Vise", Washington, D.C. Section of the Electrochemical Society, Washington D.C., November 4, 1994.

Janata, J.; Bruckner-Lea, C.; Conroy, J.; Pungor, A. and Caldwell, K. "Molecular Vise", Brookhaven Natl. Laboratory, March 28, 1994.

Janata, J.; Bruckner-Lea, C.; Conroy, J.; Pungor, A. and Caldwell, K., "Molecular Vise and Scanning Microscopy at a Liquid/Liquid Interface", *Heyrovsky Discussions*, Trest, Czech Republic, June 5-9, 1994.

Bruckner-Lea, C.; Janata, J. "Molecular Vise", *Gordon Conference on Electrochemistry*, Ventura, CA, Jan 15-19, 1995.

i. submitted presentations:

Bruckner-Lea, C.; Janata, J., Conroy, J.; Pungor, A. and Caldwell, K. "Compact Layers at a Liquid Interface: A Molecular Vise System", *Gordon Conference on Organic Thin Films*, Ventura, CA, February 21-25, 1994.

Bruckner-Lea, C.; Janata, J., Conroy, J.; Pungor, A. and Caldwell, K. "Scanning Probe Microscopy on a Mercury Sessile Drop", *Electrochemical Society Meeting*, San Francisco, CA, May 22-27, 1994.

j. Honors/Awards/Prizes for contract/grant employees:

Project highlighted in *Science* Article:

Amato, I. "Scanning Probe Microscopes Look Into New Territories", *Science*, 262, 178, 1993.

ONR Final Report

PART II

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Project Description

The two objectives of this project are: (1) to utilize the atomic resolution provided by the scanning tunneling microscope (STM) to obtain molecular information about molecules adsorbed on a liquid surface; and (2) to provide a compression/expansion micro-Langmuir-Blodgett system. Standard techniques for studying liquid surfaces only describe the average behavior of large numbers of molecules. The STM may supply molecular-scale information about the electronic structure of a liquid surface if the molecules of interest are immobilized into a two-dimensional crystal.

We have studied the mercury/air interface as a function of adsorbate surface pressure using a mercury sessile drop that can be expanded and contracted using a digitally controlled microliter syringe (Molecular Vise system). The added feature of this arrangement is the ability to control precisely the volume and, thus, the surface area of the sessile mercury drop. The drop then represents a micro-Langmuir-Blodgett experiment in which thin films of adsorbates can be examined in various stages of compression. The macroscopic phase transitions of an octanethiol surface film during the compression/expansion regime are observed visually, and STM images of the mercury/air interface are obtained before and after thiol deposition. We have used thin film mercury electrodes for investigating the origin of the waving of the mercury surface, and we are currently using atomic force microscopy (AFM) and electrochemical techniques to complement the STM measurements.

Significant Results

We have constructed a Molecular Vise system for use as a micro-Langmuir-Blodgett system, and published two papers that describe STM and visual observations obtained using this system. We believe these to be the first STM images obtained on a liquid interface. These experiments were conducted at the mercury/air interface and with the addition of vapor deposited octanethiol. One problem encountered during STM imaging of the mercury sessile drop was low frequency waving of the liquid surface. This difficulty was circumvented by operation in constant height mode while providing

enough feedback to follow the low frequency waves. STM and visual observations showed that the micro-structure of the octanethiol adsorbate depends on the compression of the surface film. We found that when a mercury drop is vapor deposited with octanethiol, the expanded drop is spherical in shape and contains "island-like" STM features. And, the compressed drop becomes flattened in shape and often contains "parallel ridge" STM features. Uncoated mercury drops remain spherical when compressed, and contain no STM surface features.

While these STM images on mercury show 10 nm resolution and provide information about the liquid surface micro-structure, one of our goals is to obtain molecular-scale image resolution. In order to reach this goal, we are working to minimize the surface waves, which cause problems when attempting high resolution STM imaging of the liquid interface. To understand the origin of the surface waves, we are analyzing the power spectra of the height of an STM tip that is held at constant current over a single location on a thin film mercury electrode. Initial results show that waving in these systems primarily occurs at frequencies less than 4 Hz, and the magnitude of the waving can be decreased by replacing the air above the mercury with a fluid such as glycerol.

We are also using atomic force microscopy and electrochemical measurements as additional methods for characterizing the liquid interface. These experiments are being conducted at Pacific Northwest Laboratories using a new Molecular Vise sessile drop system which was designed and built at the University of Utah. This system is modular and compact in order to minimize vibrations; and it includes an x-y sample translation mechanism for tip positioning of the scanning probe microscope. Initial AFM results indicate that constant height AFM imaging on a mercury drop is possible. Electrochemical results show that the octanethiol vapor deposited mercury drops are electrochemically passivated and thus coated with a compact surface layer. This agrees with the interpretation of the "island-like" STM features described above to be multilayer regions or multiple compact phases on the mercury drop.

Future Work

The ability to perform STM experiments on liquid surfaces opens a new area of tunneling microscopy using a disordered, electronically conducting substrate. And, the ability to compress or expand the liquid interface is particularly important in view of the fact that the interfacial ad-layer can be examined in a compressed (i.e., ordered two-dimensional solid) or an expanded (i.e., disordered two-dimensional solid) state. The

Molecular Vise sessile drop system allows these compression studies to be conducted in a controlled manner, and using very small sample volumes (microliter-size drops).

Future work should include continued efforts to obtain molecular information from STM images on a mercury surface. In addition, theoretical models describing tunneling into a liquid substrate should be developed to explain the STM images; and multiple techniques (e.g., atomic force microscopy, electrochemistry, drop shape, ellipsometry, brewster angle microscopy) should be used to characterize the liquid interface, and thus aid in interpretation of the STM images. The next major step will be replacing mercury with other electronically conducting liquids.

Students, Research Associates and Post-Doctoral Associates:

Cindy Bruckner-Lea	Research Scientist, Pacific Northwest Laboratories (PNL supported)
Andras Pungor	Research Associate, U of Utah
John Conroy	Graduate Student, U of Utah

Part III Project Summary

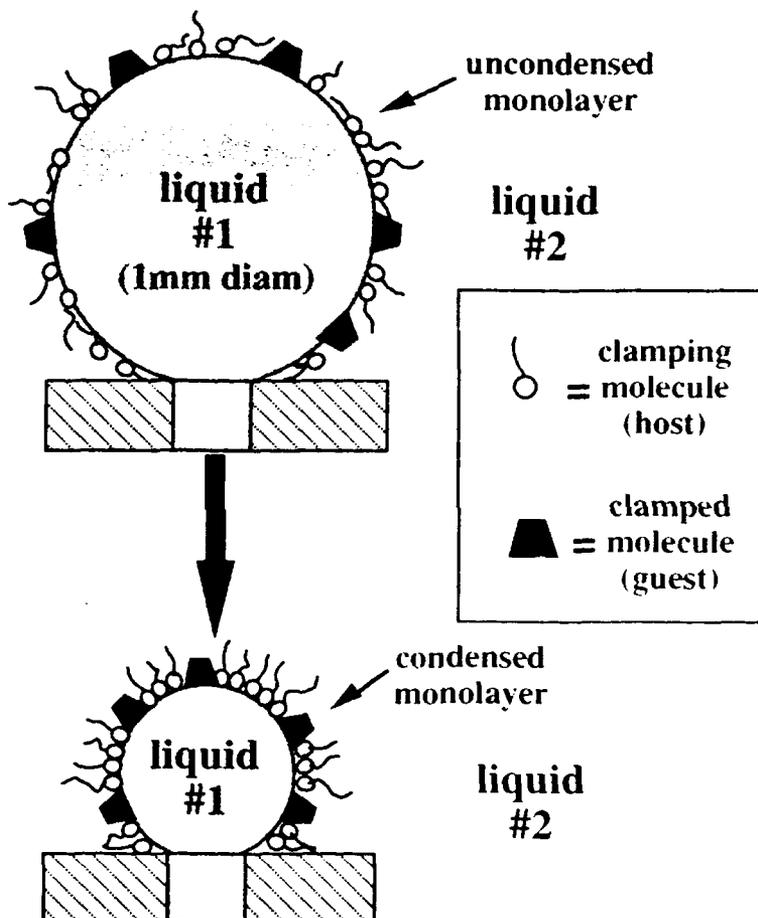
We have studied the mercury/air interface as a function of adsorbate surface pressure using a mercury sessile drop that can be expanded and contracted using a digitally controlled microliter syringe. This "Molecular Vise system" is shown schematically in Figure 1. The unique feature of this arrangement is the ability to control precisely the volume and, thus, the surface area of the sessile mercury drop. The drop then represents a micro-Langmuir-Blodgett experiment in which thin films of adsorbates can be examined in various stages of compression. The macroscopic phase transitions of an octanethiol surface film during the compression/expansion regime are observed visually as changes in drop shape, and STM images of the mercury/air interface are obtained before and after thiol deposition (Figure 2). We believe these to be the first STM images obtained on a liquid interface. We have used thin film mercury electrodes for investigating the origin of the waving of the mercury surface, and we are currently using atomic force microscopy (AFM) and electrochemical techniques to complement the STM measurements. Electrochemical measurements have shown that octanethiol forms compact films on the mercury drop, and initial AFM results show that constant height imaging is possible.

Future work should include continued efforts to obtain molecular information from STM images on a mercury surface. In addition, theoretical models describing tunneling into a liquid substrate should be developed to explain the STM images; and multiple techniques (e.g., AFM, electrochemistry, drop shape, ellipsometry, brewster angle microscopy) should be used to characterize the liquid interface, and thus aid in interpretation of the STM images. The next major step will be replacing mercury with other electronically conducting liquids.

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**Investigation of Compact Layers
at a Liquid/Liquid Interface**

Principle Investigator: Jiri Janata
Scientific Officer: Robert Nowak

Molecular Vise Concept...

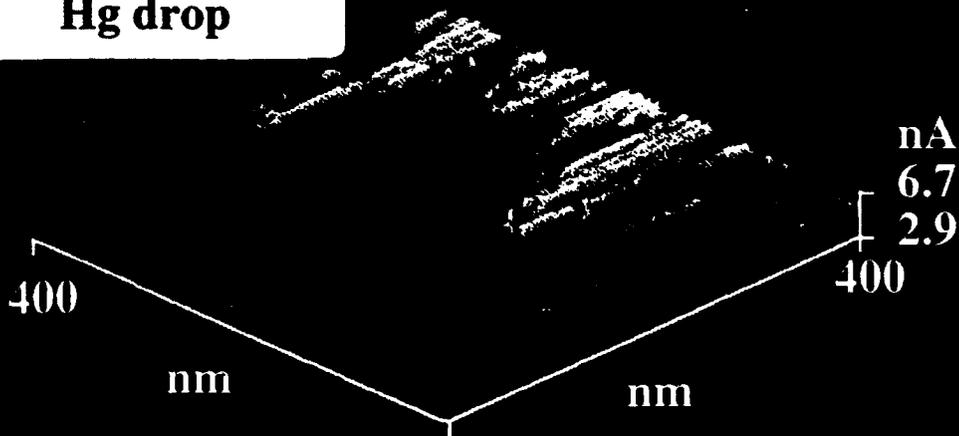


- * *In Situ* Control of Surface Area
- * Only small amounts of chemicals

- molecular-scale information about the interphase (STM, AFM)
- average properties of the interface (drop shape, electrochemical techniques, etc.)

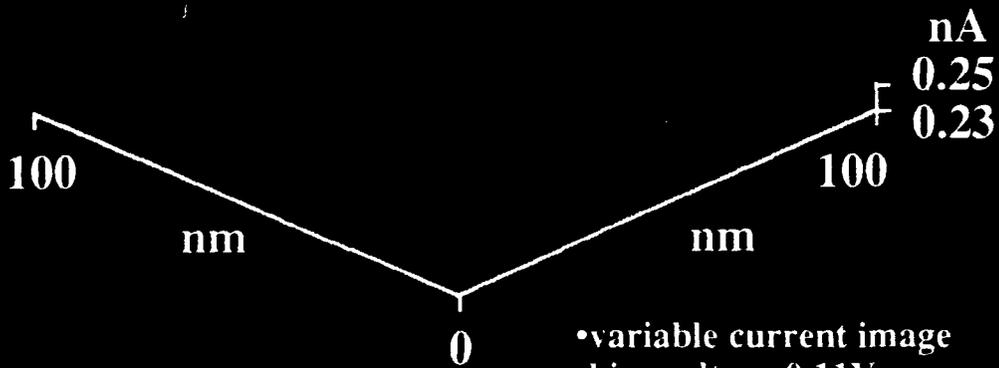
STM images of Hg sessile drops...

Octanethiol coated Hg drop



- 50 sec vapor deposition
- variable current image
- bias voltage 2.92 V
- setpoint current 0.95 nA
- scan frequency 39 Hz

Uncoated Hg drop

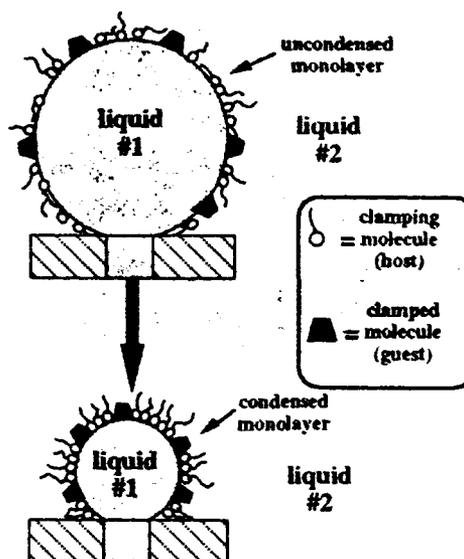


- variable current image
- bias voltage 0.11V
- setpoint current 0.7 nA
- scan frequency 11.6 Hz

STM imaging on a liquid!!

••• Molecular Vise Summary...

- **Controlled system for studying liquid-gas or liquid-liquid interfaces.**



- **Nanoscale measurements: STM, AFM**
Macroscopic: visual, electrochemical
- **Future directions?**
 - **STM/AFM technology** for imaging soft samples: minimize force, maximize sampling rate, maximize resolution.
 - **use multiple techniques** (optical, electrochemical, AFM/STM) to understand molecular and macroscopic properties of liquid/liquid interfaces
 - **theoretical modelling:**
 - STM/AFM theory
 - liquid/liquid interfaces
 - **liquid/liquid interfaces:**
 - other electronically conducting liquids and liquid/liquid interfaces.

Scanning Tunneling Microscopy on a Mercury Sessile Drop

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Received May 27, 1993. In Final Form: September 21, 1993[•]

An apparatus for obtaining scanning tunneling microscopy (STM) images at the mercury/air interface is described. The mercury/air interface is studied as a function of adsorbate surface pressure using a mercury sessile drop that can be expanded and contracted using a digitally controlled microliter syringe. The added feature of this arrangement is the ability to control precisely the volume and, the surface area of the sessile mercury drop. The drop then represents a micro-Langmuir-Blodgett experiment in which thin films of adsorbates can be examined in various stages of compression. The macroscopic phase transitions of an octanethiol surface film during the compression/expansion regime are observed visually, and STM images of the mercury/air interface are obtained before and after thiol deposition.

Introduction

The Langmuir-Blodgett technique is one of the main tools for preparation and study of controlled packing of molecules under defined surface pressures at the air/liquid interface. In this manner, it has been possible to observe the assembly of membrane-like structures and to demonstrate that interfacially accumulated molecules undergo two-dimensional phase transitions from a highly disordered gas-like state at low surface pressure to a more condensed liquid-like state at intermediate pressure and then to a highly compressed solid-like state under high pressure.^{1,2} Since surface pressure is an average property of the monolayer, the actual arrangement of molecules at the interface can only be inferred from surface pressure measurements. The same lack of localized molecular information exists when using other standard techniques for studying adsorbed layers at liquid/liquid or liquid/air interfaces. Fluorescence microscopy has shown the existence of two or more existing phases when molecular mixtures are deposited at the air/water interface;³ however, the molecular arrangement (and mobility) within each phase and at the phase boundary is unknown. The effect of adsorbate packing (surface pressure) on ion transport has been investigated using electrochemical studies of the mercury/solution interface.⁴⁻⁷ Such electrochemical observations can, by necessity, only indicate the average behavior of a large number of molecules. And, recent X-ray diffraction studies have measured the average orientation of molecules at the air/water interface as a function of surface pressure, but these measurements are also limited to the average behavior of large numbers of molecules. As a result, a strong interest has developed in the surface

science community to actually observe specific molecules or groups of molecules on a liquid surface. The advent of the scanning tunneling microscope (STM)⁸ has provided a tool with the potential for such observations if the molecules of interest are immobilized in a two-dimensional crystal.

Scanning tunneling microscopy is an imaging method that in some cases provides images of surfaces with resolution at the atomic level. The images are obtained with a voltage-biased microelectrode tip that is rastered across the sample surface, producing a tunneling current that varies as a function of position. Thus, a mapping of the tunneling current yields an image of the surface electronic and geometric structure. As the tip probe is brought sufficiently close to the sample, the magnitude of the electric field increases until there is enough energy for electrons to escape from the negatively biased electrode to cross the intervening barrier. This flow of electrons is the tunneling current, which is dependent on the distance between the sample and the probe tip and on the electronic structures of both electrodes. Although there are a number of papers that show STM images of biological and organic molecules, this imaging process is not routine.⁹⁻¹² The major problems with these applications have included immobilizing biological samples for imaging, identifying substrate artifacts, and obtaining STM images at molecular- or atomic-level resolutions of samples with low conductivity.

The major motivation for this work has been to clamp and study single organic molecules on a liquid substrate by STM. The control over packing of molecules at a liquid/air and liquid/liquid surface, as offered by the Langmuir-Blodgett (LB) technique, can be translated into a "molecular vise" for clamping molecules within a two-dimensional crystalline array. In such an arrangement, single molecules of the minority component can be

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[•] Abstract published in *Advance ACS Abstracts*, November 1, 1993.

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effectively immobilized by the surrounding molecules of the majority component in a compressed state of a two-dimensional binary mixture. This concept defines two experimental requirements: (1) the liquid phase (substrate) must be electronically conducting and (2) the surface area of the interface must be controllably compressible and expandable. A mercury/air or mercury/water sessile drop system satisfies both requirements and allows the use of a combination of STM and LB techniques.

The first step in this coupling involves tunneling into a liquid (i.e., stochastic) substrate. Since STM involves extremely small scan areas and signal currents, the instrument and the sample must be extremely electrically and mechanically stable and well insulated from noise. The vibrational problem is compounded by the fact that the substrate is a liquid, which is inherently less mechanically stable than a solid. A high-density/inertia liquid such as a mercury is beneficial because it migrates the vibration per given energy input. Viscosity is a frequency-dependent property, which means that higher frequency vibrations will be more strongly attenuated.

The second step in this union involves the ability to tunnel through an adsorbed film at varying degrees of compression. There are some obvious difficulties in tunneling through compact, insulating organic layers atop a conducting substrate. While molecular-resolution STM images of *n*-octadecanethiol have recently been reported,¹³ these images have been difficult to reproduce.¹⁴⁻¹⁶ From the variability in STM images of similar organic molecules, it is evident that tunneling parameters, tip-sample and sample-substrate interactions, film preparation, and the substrate material are all important factors in interpreting and obtaining STM images. McCarley et al.¹⁵ have obtained images of gold coated with *n*-octadecanethiol that are consistent with reconstructed Au(111) after removal of the thiol by the STM tip. Ross et al.¹⁷ used STM to purposely etch 18-carbon *n*-alkanethiol from gold, and Edinger et al.¹⁴ report STM tip induced defects in thiol monolayers on gold when imaging a 22-carbon *n*-alkanethiol, but not when imaging an 8-carbon *n*-alkanethiol monolayer on gold. Since it has been shown electrochemically that electron transfer along an 8-carbon chain is possible,¹⁸ and thiols have high affinity for mercury,¹⁹ *n*-octanethiol (rather than the 18- or 22-carbon thiols discussed above) was chosen to adsorb at the interface. Octanethiol-coated gold surfaces have been extensively studied using other surface analysis techniques and are known to form compact monolayers on gold.²⁰

It is known from scanning probe microscopy that one problem specific to imaging individual molecules on surfaces is the tip-substrate interaction.²¹⁻²⁴ If the tip comes into contact with a molecule, the molecule may transfer from the substrate to the tip. Thus, in effect, the tip becomes enlarged, resulting in decreased resolution.

This effect is accentuated by a liquid substrate. Since the substrate surface is not fixed, interfacial molecules adsorbed to both electrodes can follow the tip microelectrode as it travels across the surface. By restraining the guest within a compressed host lattice, high-resolution images on a liquid substrate may be possible.

Experimental Section

The imaging system used is a Digital Instruments Nanoscope II with a 12- μm STM head. The range of this head is $12 \times 12 \times 4.4 \mu\text{m}$ in the *x*, *y*, and *z* directions, respectively. This large head allows us to follow waving of the mercury surface. The mercury is triply distilled and filtered. In the course of our experiments, we have used both platinum/iridium (80%/20%) and tungsten tips prepared by electrochemical etching.²⁵ Although STM images have been obtained using both, the best results were obtained with tungsten tips.

There have been two different systems used in this work for presenting the mercury sample to the STM head. The first system involved placing a single mercury drop in a conical dimple on a metal sample stage. Such drops are less susceptible to vibration when they are small and well supported by the sample stage. Obviously, the stability of the drop is traded for the ability to manipulate the surface area. Best results were obtained with drop diameters less than 0.5 mm, positioned in a steel cradling cone with an end radius of almost 1 mm. Electrical contact with the mercury was made through the sample plate. The large contact area ensured a good connection. In order to guarantee good contact, the dimple was scraped using a wire brush before each use. The head was then arranged over the sample on the Digital Instruments three-screw sample stage. The head and sample were both enclosed in a Faraday cage and then placed inside a plexiglass and acoustical foam "deaf box" built upon an optical breadboard. This setup was then suspended from bungee cords. The first and most stable images of mercury were obtained using this system. These images showed surface waving with an amplitude of 600 nm.

The second system involved a mechanism for expanding and contacting the mercury surface (Figure 1). A 25- μL syringe (Gilmont Instruments, Barrington, IL), operated by a stepper motor, was used to regulate the size of the mercury sessile drop, which was extruded through a disposable 0.2-mm-i.d. stainless steel capillary with a conical dipole on the end to support the drop. Also connected to the mercury flow system was a 2.5-mL syringe (Gilmont) designed to provide a practically inexhaustible supply of mercury, while reducing the amount of handling required. Electrical contact to the drop was made through the metal capillary. If needed, a glass tray (2.8 mL) was placed around the capillary end to allow liquid phase depositions. The piezoelectric tube scanner holding the STM tip was positioned over the drop using a three-screw, stand-alone support. This support was fixed to a stage using five parallel springs. The stage was connected to a plexiglass cube that encased the glass T-valve holding the capillary. To ensure mechanical contact between the STM and the glass T-valve, the glass valve was permanently fixed into the plexiglass cube using epoxy (Master Bond No. EP21CLV-2SP, Hackensack, NJ). The glass conduit begins with the vertical capillary sample support, which is held by a ground-glass joint on top of a 2-mm glass tube. The tube descends vertically to the plexiglass/epoxy until it reaches a T-joint with a stopcock in the middle of the plexiglass cube. One branch from the T-joint was left open, while the other extended horizontally through a glass ball and socket joint to a second plexiglass support containing another glass T-joint and stopcock, with the two branches leading to each of the syringes. Both plexiglass encasements were fixed to a supporting optical bench, through a stiff steel tray designed to catch any inadvertent mercury spills. One problem encountered with this design was the trapping of air bubbles within the flow system, especially at the stopcocks, during the filling with mercury. Since the presence of air bubbles increases the sensitivity of the sessile drop to

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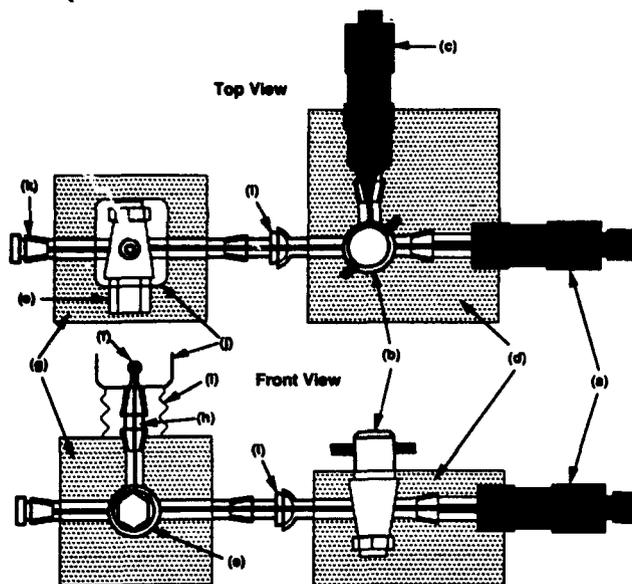


Figure 1. Schematic of the mercury sessile drop flow system (not drawn to scale). The sessile drop size is controlled by a small syringe (25 μ L, Gilmont) (a). A glass T-valve (b) connects the small syringe to a large syringe (2.5 mL, Gilmont) (c) which serves as a reservoir for refilling the small syringe. Both syringes and the T-valve rest in a plexiglass mold (d) and are held by screws to the optical breadboard. Another glass T-valve (e) leads to the sessile drop (f). This valve is permanently epoxied into a transparent plexiglass holder (g) which is mounted to the optical breadboard. The mercury sessile drop (about 1-mm diameter) sits on a stainless steel capillary (0.1-mm inner diameter) at the top of a male/male joint (h). Springs (i) are used to hold a glass reservoir (j) onto the male/male joint leading to the mercury drop. The third outlet of this T-valve is closed (k), but may be used for an additional mercury reservoir. It was necessary to add a glass ball joint (l) to allow fine positional adjustments between the two rigidly mounted valves.

mechanical vibrations and adds capacitance to the drop volume control system, great care was taken to remove the trapped air bubbles by using a syringe to apply a slight vacuum after filling each section of the flow system. The flow system was also electrically shielded and placed on an optical breadboard, which was suspended by bungee cords. The surface waving of the mercury substrate (~ 900 nm), while larger than that of the first system (~ 600 nm), was still within a range that can be compensated for by the STM head.

The drop area was optically imaged using a remote, color CCD camera and a single lens microscope with a magnification of $200\times$. This optical system has proven indispensable when positioning the STM tip over the surface, and for monitoring the sessile drop during compression experiments.

Octanethiol was deposited from the vapor phase onto the mercury surface. A piece of cotton wrapped around a wooden stick was soaked in the liquid thiol, and then held approximately 1 cm away from the mercury drop, under an inverted beaker. Vapor deposition times ranged from 30 s to 5 min. After venting the mercury drop for several minutes in a fume hood, the STM was placed over the mercury drop and positioned for imaging. STM imaging was performed on a clean mercury drop, on mercury drops after thiol deposition of varying time lengths, and on thiol-deposited mercury drops after compression.

Results

Optical Observations. Simple optical inspection of the mercury surface after octanethiol vapor deposition shows evidence of the extent of surface coverage. The most dramatic effects can be seen after a long (>30 min) deposition period, at which time highly refractive crystallites form on the mercury, creating a nonuniform surface that can be seen with the naked eye. These crystallites

appear stationary on the liquid mercury drop. With short deposition times (<5 min) the presence of octanethiol cannot be seen with the naked eye, but its presence is evident when monitoring the mercury drop during contraction. Withdrawal of mercury (compression) causes the mercury drop to change in shape from spherical (Figure 2a), to "flattened" (Figure 2b), to a torroid as the drop surface area-to-volume ratio increases to allow the drop to maintain its original large surface area. When the drop remains spherical as its volume is decreased, we are operating in the gas- or liquid-like regions of the LB pressure-area curve. However, flattening of the drop with a decrease in drop volume suggests a solid-like surface layer. When octanethiol-coated drops are compressed and then rapidly expanded, the drop surface appears to have smooth cracks showing between larger textured regions. If the STM tip is allowed to penetrate into the thiol film, the tip adheres to the surface film and can be used to lift the surface film from the mercury drop (Figure 2c). We believe that some mercury is still bound to the underside of this lifted film as its optical properties (i.e., reflectivity) remain the same as before removal.

A freshly extruded, uncoated mercury drop remains spherical as the drop size is decreased, and STM tips do not stick to the uncoated mercury surface. However, after exposure to air for 10 min, the presence of contamination on the drop surface is indicated by a flattening of the drop shape when the drop size is decreased to about 1/100 of its original volume. Also, small particles can sometimes be seen moving across the surface of drops exposed to air for more than 10 min. This is not surprising since the surface tension of mercury is about 485 dyn/cm, making surface contamination an important consideration.²⁶ Consequently, we minimized the time between extruding a clean drop and beginning the thiol deposition and STM imaging procedure. Thiol deposition of 5 min or less proceeded immediately after extruding a fresh mercury drop, and STM imaging began several minutes after thiol deposition.

Scanning Tunneling Microscope Results. One consequence of the mechanically unstable mercury substrate is the difficulty in obtaining several consecutive STM images of the same area without collisions between the tip and the waving surface. Figure 3 is a height measurement mode image in which the waving of the mercury surface is traced by the STM scanning head (constant current). While these waves are large in amplitude compared to the surface features we were examining, they are low in frequency (3-5 Hz) and, thus, are easily eliminated by signal processing. The reason the surface waves are observed only along one axis is that this is the slow-scan (y) axis. The waving is too slow to significantly affect the image as the tip scans along the fast-scan (x) axis.

Our first attempts at STM imaging of octanethiol-coated mercury drops involved long (>5 min) vapor deposition times, resulting in octanethiol layers that could not be imaged. In these cases, the STM tip would pierce the surface layer and contact the mercury drop. In contrast, after shorter (<2 min) vapor deposition times, stable STM images were obtained. For direct comparison of thiol-coated and uncoated mercury sessile drops, Figure 4 shows STM images of a mercury drop that was vapor deposited for 50 s with octanethiol (a) and an uncoated mercury drop (b). Both are current mode images that are produced by resetting the height baseline for every x scan in order to remove the y -direction surface waving shown in Figure

(26) Smith, T. *Adv. Colloid Interface Sci.* 1972, 3, 161.



Figure 2. A series of photographs of a mercury sessile drop after 40 s of octanethiol vapor deposition. Initially, the drop is a 1-mm-diameter sphere (a, top left). When the drop volume is decreased, the sphere flattens to maintain constant surface area (b, top right). The surface film sticks to an STM tungsten tip when the tip penetrates the drop surface (c, bottom).



Figure 3. Height mode STM image with feedback to obtain a constant current image of the surface of a 1-mm-diameter mercury sessile drop (no thiol coating). The bias voltage is 272 mV, the setpoint current is 0.75 nA, and the scan frequency is 39 Hz. The scanning range is 20×20 nm, with the fast-scanning x direction shown into the paper and the slow-scanning y direction across the paper. The z range in the photograph is 0–1000 nm. Surface waves of approximately 600-nm amplitude are evident in the slow-scanning (y) direction.

3. Since we are imaging in current mode (constant tip height), the vertical scales in Figures 4–6 are shown in nanoamperes.

While the thiol-coated drop shows large surface features (Figure 4a), the uncoated mercury appears smooth within the resolution of the system (Figure 4b). Due to the heterogeneous nature of the thiol-coated drop, the 2-nA step seen in Figure 4a cannot be converted to nanometer thickness. The current step results from a combination

of two factors: a change in tunneling distance due to the deposited layer(s), and a change in the electronic nature (i.e., work function) of the surface due to the deposited layer(s).

Visual observations of a change in drop shape with a decrease in drop volume supply information about the general properties of the surface film in Figure 4a. Octanethiol layers formed with 50 s of vapor deposition remain spherical with small decreases in volume and then flatten with large volume decreases. This initial spherical drop compression indicates that image a of Figure 4 was obtained in the liquid-like region of the surface pressure–area curve. This type of drop behavior would result if the drop surface contained regions of submonolayer thiol coverage, as either a patchy or uniform film. The STM image of the thiol-coated surface (Figure 4a) indicates that the surface layer is patchy rather than uniform. However, one must not overlook the possibility that the surface patchiness is induced by the STM imaging process.

To our knowledge, the set of consecutive scans over an octanethiol-contaminated surface, shown in Figure 5, represent the first stable images ever recorded on mercury. The octanethiol vapor deposition time was 45 s, and these images were taken in current measurement mode, 20 s apart. Figure 5 shows reproducible islands of similar tunneling current on a background of lower tunneling current. These images may be interpreted as being due to nonuniform deposition of the thiol. The interpretation is consistent with a recent report of *n*-alkanethiol island formation on gold under conditions for submonolayer coverage²⁰ and the results of an atomic force microscope study showing octadecyltrichlorosilane island formation on mica.²⁷ The blurring of the images of Figure 5 in the

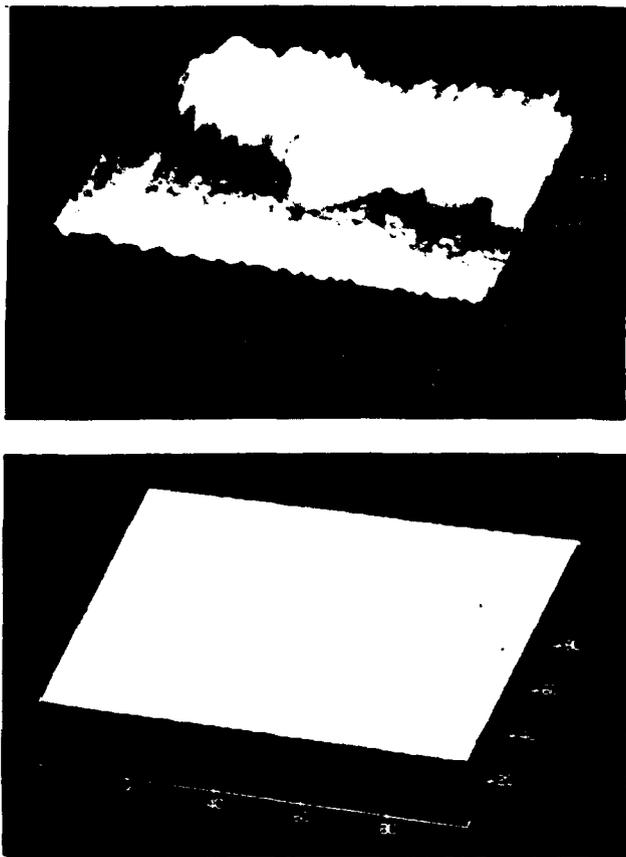


Figure 4. STM images of an octanethiol-coated mercury drop (a, top) and an uncoated mercury drop (b, bottom). While the thiol-coated drop shows large surface features, the uncoated drop appears smooth within the sensitivity of the system. Both are current mode images, with the tip-sample distance reset at the beginning of each x -scan line to remove the y -direction surface waving shown in Figure 3. The imaging conditions for the thiol-coated drop shown in (a) are vapor deposition time, 50 s; bias voltage, 2.92 V; setpoint current, 0.95 nA; scan frequency, 39 Hz; scanning range, 500 \times 500 nm; and vertical scale, 10 nA. And, the imaging conditions for the uncoated mercury drop in (b) are bias voltage, 0.11 V; setpoint current, 0.70 nA; scan frequency, 11.6 Hz; scanning range, 100 \times 100 nm; and vertical range, 8 nA.

fast-scan (x) direction is probably due to tip-sample interactions and the movement of material on the surface. Since initial spherical drop compression suggests that the STM images shown in Figure 5 were obtained in the liquid-like region of the pressure-area curve, it is surprising that the islands show little motion on the liquid mercury substrate during the 2 min that elapsed between the start of the first image and the completion of the last image. The image stability suggests that the island features are not formed by the STM scanning process, but are stable surface features present prior to scanning. At this point we can only speculate about the nature of the islands; they may represent different thiol phases on the drop surface, incomplete thiol coverage, or regions of multilayer formation.

After compression of the mercury drop to a flattened shape, it was easier to obtain STM images of the drop without contacting the mercury when engaging the STM tip, and we sometimes obtained island images as shown in Figure 5. However, we often obtained images as shown in Figure 6, which appear to contain small octanethiol ridges (1–10 nA high). This STM image was obtained after an approximately 50% reduction in drop volume,

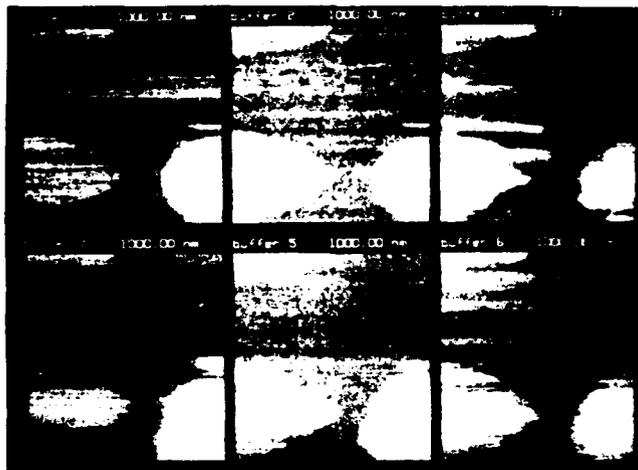


Figure 5. Six consecutive current mode STM images of the same location on an octanethiol-coated mercury drop. The octanethiol vapor deposition time is 45 s, and the time between the beginning of each image is 20 s. The scanning range is 1000 \times 1000 nm, with the fast- and slow-scanning directions shown horizontally and vertically. The z range is 10 nA. Other imaging conditions are bias voltage, 2.9 V; setpoint current, 0.95 nA; and scan frequency, 39 Hz.

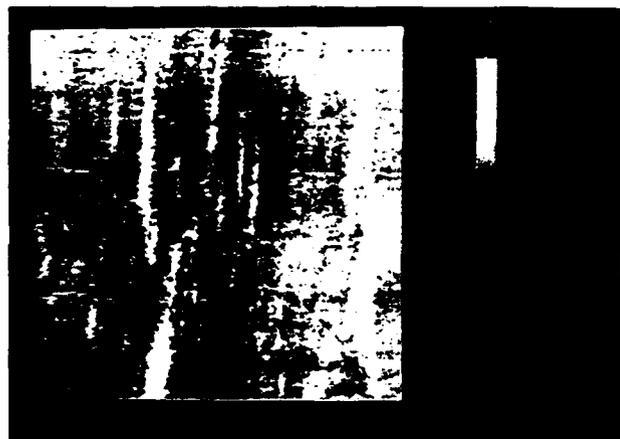


Figure 6. Current mode STM image of an octanethiol-coated mercury drop after a 50% drop volume reduction beyond the close-packed surface (assume close packed at minimum drop volume to maintain a spherical drop). The scanning range is 500 \times 500 nm, and the z range is 4 nA. The imaging conditions are bias voltage, 1.64 V; setpoint current, 0.95 nA; and scan frequency, 39 Hz.

relative to the volume at the compaction point. The image shows a series of parallel regions of higher current density on the surface. The direction of the ridges is independent of the scan direction, indicating that the ridges are not strongly influenced by the STM scanning process. These ridge images were never seen on the uncompressed (spherical) drops, and thus must be produced by the compaction of the thiol surface film.

Summary

The series of self-consistent visual and STM observations described in this paper confirm the possibility of performing tunneling microscopy on a mercury surface. Both STM images and visual observations of drop shape and the STM tip-drop surface interaction indicated the presence and absence of octanethiol on the mercury drop. In addition, STM images and sessile drop shape are both affected by the compression of an octanethiol-coated drop. Expanded drops are spherical in shape and contain island-

like STM features. And, compressed drops become flattened in shape and often contain parallel ridge STM features. These island and ridge STM features seen on octanethiol-deposited mercury drops were never seen on uncoated mercury drops. The apparatus performed adequately; however, some modifications will be incorporated in the next generation, which is presently under construction. Although images of single molecules clamped in a Langmuir-Blodgett-like experiment have not yet been obtained, we believe that with some modifications this goal will be achievable.

The absence of periodicity of the bulk substrate on the time scale of our experiment opens a new area of tunneling

microscopy investigation. This use of a liquid substrate is particularly important in view of the fact that the interfacial adlayer can be examined in a compressed (i.e., ordered two-dimensional solid) or an expanded (i.e., disordered two-dimensional liquid) state.

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