FORCE MICROSCOPY OF SELF ASSEMBLED AMPHIPHILIC FILMS

by

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A Dissertation Submitted to the Faculty of the

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

2003
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ACKNOWLEDGEMENTS

I would like to thank my advisor, Prof. Srin Manne, whose support, guidance and encouragement have made this work possible. I would also like to thank Prof. Donald Huffman, and his former students Dr. Lowell Lamb and Dr. Frank Tinker for patiently teaching me careful experimental techniques when I was an undergraduate. Thanks also to Dr. Dong Chen, Dr. Todd Ruskell and Dr. Mark Gallagher, who taught me a lot during my time at Optical Sciences. Thanks also to Dr. Bruce P. Jacobsen who first taught me AFM.

Thanks to my parents for recognizing my interest in science and buying my first (and second, and third...) electronics and chemistry kits starting when I was 5 years old.

Thanks also go to my wife Marcia for many useful discussions and her love and support. This work is dedicated to my son Alexander.

The work in this dissertation was funded by National Science Foundation Grant 0094385 and a Career Award, Procter and Gamble Corporation UERP Award, and the University of Arizona Department of Physics; this financial support is gratefully acknowledged.
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ABSTRACT

Scanning force microscopy is a powerful technique to study surfaces in vacuum, air or liquids because of its nanometer spatial resolution and piconewton force resolution. The work presented here uses colloidal (steric and double layer) forces to investigate the shape of surfactant micelles on an isotropic hydrophobic surface (Chapter 3). Frictional forces are used in this work as a useful contrast mechanism in the study of monolayer water films (Chapter 4), self-assembled monolayers (Chapter 6), and to detect the presence and concentration of a 2D gas phase of molecules on a surface (Chapter 5).

The invention of “soft contact” mode Atomic Force Microscopy imaging¹ allows the direct imaging of surfactant micelles at the solid-liquid interface. One of the results in this work was the determination of the structure of surface micelles on an isotropic hydrophobic surface. This model system is useful for comparison to crystalline surfaces to determine the relative importance of simple hard-wall confinement versus the influence of the underlying substrate lattice.

Lateral (friction) forces have also proven to be a useful contrast mechanism in imaging surfaces. The results presented here demonstrate the use of lateral force (friction) microscopy as a highly sensitive method to detect a 2D gas of amphiphiles on a mica surface, making this technique useful in studying the early stages of monolayer formation. This sensitivity also makes friction a useful contrast mechanism when imaging patterned self-assembled monolayers and ultra-thin water films.
A simple and inexpensive method of creating micrometer to sub-micrometer structures was reported by Kumar and Whitesides in 1993. This technique, called microcontact printing, uses an elastomeric replica of a master to pattern a surface, typically with self-assembled, covalently bonded molecules.

Microcontact printing of non-covalently bonding molecules has not been as extensively studied, with the exceptions of lipid bilayers of phosphatidylcholine and proteins. Chapters 5 and 6 will show results of stamping several types of alkyl derivatives on a model surface (mica). These non-covalently bonding molecules show much greater diffusion and spreading during stamping, which reveal details of the mechanisms of microcontact printing that are obscured with the strongly interacting, covalently bonding systems.
CHAPTER 1: BACKGROUND

1.1 Atomic Force Microscopy (AFM)

1.1.1 History

High resolution measurement of the vertical relief of surfaces was first made possible by the stylus profiler, invented by Gustav Schmaltz\(^{11}\) in 1929. This device moved a surface under a sharp stylus mounted on a cantilever. The movements of the stylus were monitored by recording the motion of light reflected off a small mirror at the end of the cantilever onto a piece of photographic film. An intermittent contact version of this device was developed by Becker\(^{12}\) in 1950, and later by Lee\(^{13}\) in 1978, to address problems of stylus damage by tall surface features. The first such system using feedback to keep the stylus a constant distance from the surface was developed in 1972 by Young.\(^{14}\) This non-contact method maintained the field emission current between a sharp metal stylus and the surface constant by moving the probe with a piezoelectric ceramic. The modern Atomic Force Microscope (AFM) took shape in 1986 when Binnig, Quate, and Gerber used a miniaturized cantilever and atomically sharp stylus to measure topography. They used the tunneling current between the cantilever and the tip of a scanning tunneling microscope to sense the motion of the stylus, but this was soon replaced by the optical lever method of Schmaltz. Binnig \textit{et al.} realized that if the cantilever could be made softer than the interatomic spring constant of atoms in a solid, atomic scale features could be imaged. Binnig’s small (handmade) cantilever had a
spring constant of order 1 N/m, lower than a typical interatomic spring constant of ~10 N/m. The very low forces exerted by the AFM tip on the sample ($10^{-7}$ to $10^{11}$ N) set it apart from the much higher forces used in stylus profilers ($10^{-4}$ N).

Figure 1.1 shows a schematic of an atomic force microscope. A sharp tip mounted on a cantilever is scanned in the X-Y plane of the sample using a piezoelectric scanner. A laser is reflected off the cantilever into a position sensitive detector. This detector is a photodiode split into an upper and lower half. The motion of the cantilever is measured as a difference between the upper and lower half signals of the photodiode. The difference signal is normalized by dividing by the sum of the upper and lower signals to remove any effect of laser intensity variations. This arrangement is sensitive enough to detect sub-Angstrom deflections of the cantilever.

Chapter 2 of this dissertation discusses the development of a temperature controlled sample stage for AFM that allows molecular resolution in fluids or air from -5 to 130 °C. This covers the entire aqueous temperature range, allowing the study of surface phase transitions at the solid/liquid interface such as the micellar Krafft point. This range has also proven useful for varying the surface diffusion rate, and solid/liquid phase transition for long chain amphiphiles (Chapter 6)
Figure 1.1 Schematic drawing of an Atomic force microscope. A laser reflects off the cantilever into a photodetector split into two halves, A and B. The deflection of the cantilever is measured as the difference signal A-B. It is then normalized by dividing by A+B, eliminating errors due to intensity fluctuations.
1.1.2 Contact Mode

The simplest mode of AFM operation simply scans the tip and cantilever over the surface and the deflections of the cantilever are recorded as a function of position. This method has the disadvantage of applying a varying force to the sample, depending on the deflection of the cantilever. The varying force can lead to incorrect height measurements, as high features are pressed harder than lower features. This drawback is overcome by operating the microscope in constant deflection (and therefore, constant force) mode. In this mode, a feedback loop moves the cantilever up or down to keep the deflection of the cantilever constant. A 2-dimensional plot of the z-piezo motion vs. the xy position gives the topography of the surface. AFM operated in contact mode has Ångstrom resolution in the xy plane of the sample and sub-Ångstrom resolution in the z direction (see Figure 1.1) allowing it to resolve crystal lattices and single atomic steps on conductors or insulators, in air, liquids, or vacuum. No other technique can match this resolution and flexibility.

1.1.3 LFM

Scanning the tip over a surface with varying composition, such as an organic film on an inorganic substrate, can result in varying frictional forces acting on the tip. Frictional forces cause a twist in the cantilever (a rotation around the cantilever axes), which causes a lateral movement of the reflected laser spot on the detector. The cantilever twist motion can be detected if the upper and lower photodiode is further split
4 quadrant position sensitive detector

Figure 1.2 Lateral force microscope. Twisting of the cantilever from lateral forces causes the reflected laser spot to move laterally on the detector.
into left and right quadrants (see Figure 1.2). The lateral-force-induced motion of the cantilever can be acquired simultaneously with the contact mode image. This mode of operation is called Lateral Force Microscopy (LFM).

Like contact mode AFM, Lateral Force Microscopy is also able to resolve atomic lattices and atomic steps, in fact it is often easier to resolve atomic lattices in LFM mode. LFM has the additional capability of detecting varying surface composition at nanometer length scales. For example, LFM has been used to detect the sorption of metal ions on calcite in aqueous solutions. LFM has been used to detect the sorption of metal ions on calcite in aqueous solutions. Figure 1.3 shows the growth of a chemically distinct phase on the surface of calcite (CaCO₃) in a solution containing strontium.* Figure 1.3a and b are height and deflection images, respectively, (at different times) of a calcite surface in a strontium solution undersaturated with respect to SrCO₃. Some dissolution is evident from the slight expansion of etch pits 1 and 2 and from the retreat of the irregular step at top left in the 10 minutes between Figure 1.3a and b. Figure 1.3c and d show the same area after exchanging with a supersaturated solution of Sr²⁺. The dotted lines in Figure 1.3c and d indicate the step positions from Figure 1.3b. The height image (Figure 1.3c) shows that the monomolecular steps have moved from their previous positions, etch pit 1 has filled in completely, and etch pit 2 partially. The friction scan (Figure 1.3d) shows

* This work has been published as Hay, M.; Workman, R. K.; Manne, S. "Mechanisms of Metal Ion Sorption on Calcite: Composition Mapping by Lateral Force Microscopy", Langmuir 2003.
Figure 1.3 Effect of high-pH Sr$^{2+}$ solutions on the calcite surface. (All images show the same 13.1 $\times$ 13.1 $\mu$m area). a) and b) Height and deflection images taken $\sim$30 minutes apart in a slightly undersaturated solution. Some dissolution is evident. c) and d) Height and friction images $\sim$10 minutes after exchanging with supersaturated solution. The friction scan (d) shows that these changes are due to the growth of a new phase, topographically indistinguishable from calcite. z-ranges 4.0 nm for (a), 5.0 nm for (c), and 50 mV for (d). From Hey et al.$^{15}$
that these changes are due to the growth of a new phase, topographically indistinguishable from calcite, originating at the calcite steps and growing along the bottom terraces.

The utility of LFM is shown further in Chapter 5 of this dissertation which discusses the detection of a 2D gas phase of molecules by lateral force microscopy. The results demonstrate that friction measurement and mapping can detect amphiphile densities down to 1% of a monolayer, making this technique useful in studying the early stages of monolayer formation.

1.1.4 Non-contact imaging

Contact mode scanning of very soft samples, such as living cells, DNA or surfactants (see section 1.2), can be very difficult if even the softest available cantilevers are too stiff. Additionally, lateral forces can cause imaging artifacts, or even damage, to soft or weakly adhered layers. To overcome both of these problems, non-contact (tapping) or electrostatic double layer (EDL) mode can be used. In tapping mode, the cantilever is oscillated at or near its resonance frequency, and the amplitude of vibration is used for the feedback loop. As the vibrating tip approaches the sample, the gradient in the attractive van der Waals force reduces the spring constant of the lever, decreasing its resonance frequency, and causing the amplitude of vibration to decrease. The feedback loop moves the cantilever up or down to keep the vibration amplitude constant.

Figure 1.4 illustrates the effect of lateral forces on soft samples. A soft polymer grating (compression modulus of ~20MPa) imaged with contact mode (Figure 1.4a)
Figure 1.4  a) Contact mode image of poly-(dimethylsiloxane) (PDMS) grating replica (see section 2.3). Large lateral forces create a distorted topography. b) Tapping mode image of same PDMS replica showing the true topography.
shows significant distortion from the lateral (and normal) forces exerted by the scanning tip. The same grating imaged in tapping mode (Figure 1.4b) reveals the true topography.

1.1.4.1 "Soft Contact" mode AFM imaging of surfactants

While contact mode AFM relies on the Born repulsion between the tip and surface, other types of repulsive forces can be used for imaging. If the AFM tip and sample are immersed in an aqueous surfactant solution, surfactants adsorbed on both the tip and sample can create a steric or electrostatic repulsive force. This force can be used to image surface micelles in "soft contact" mode. Figure 1.5 illustrates this technique for a cationic surfactant adsorbed on an anionic surface, such as mica, or a hydrophobic surface, such as graphite. The AFM tip is typically made of either silicon dioxide or silicon nitride, so it acts as an anionic surface at neutral pH. As the tip approaches the surface micelles, the repulsive electrostatic (for ionic surfactants) or steric (for non-ionic surfactants) force causes a deflection of the cantilever. Setting the imaging force to this pre-contact deflection allows the adsorbate topography to be imaged.

The shape of interfacial micelles was unknown before this soft contact method was discovered. Some evidence for lateral structure in interfacial aggregates came from neutron reflection and fluorescence quenching, however no other technique is able to identify the size, shape and lateral organization.
Figure 1.5 Schematic of AFM imaging mechanism for surfactant aggregates on surfaces. (From reference Manne et al.15)
AFM images show half-cylindrical aggregates on graphite for any surfactant capable of cylindrical curvature. This is due to the strong hydrophobic interaction between the crystalline graphite surface and the hydrocarbon tails of the surfactant.\(^{19}\) The hydrocarbon tails orient along a graphite symmetry axis, resulting in half-cylindrical micelles oriented perpendicular to the underlying graphite lattice. Surfactants that form only lamellar or bicontinuous solution phases, and surfactants with 10 or fewer carbon atoms, typically form monolayers on graphite. In chapter 3, results are shown for ionic, zwitterionic, and non-ionic surfactants on an amorphous hydrophobic surface. Hydrophilic surfaces like mica have shown spherical, cylindrical and bilayer aggregates, corresponding to the bulk packing shapes shown in Figure 1.7. Amorphous hydrophilic surfaces like silica show spherical or very short cylindrical aggregates for surfactants that form spherical or cylindrical micelles in solution, and bilayers for surfactants that form bilayers or vesicles in solution.

1.1.5 Temperature control

AFM has been used to study critical phenomena and image chemical kinetics such as step motion in crystal growth,\(^{20-22}\) potential induced surface changes in electrochemistry,\(^{23}\) enzymatic action and polymerization reactions in biochemical systems,\(^{24,25}\) and surface melting of polymers and refractory materials.\(^{26,27}\)

The variation of temperature allows us to probe structural changes associated with critical phenomena and to measure activation energies associated with interfacial reactions. Since critical phenomena and surface reactions often take place in a liquid
environment, a temperature controlled liquid environment for atomic force microscopy (AFM) is desirable. In particular, such an environment allows us to study phase transitions in "soft condensed matter" such as proteins, surfactant micelles, model membranes, and adsorbed polymers.

Chapter 2 presents the design and first results of a stable, temperature controlled stage, capable of atomic resolution in liquids over the entire aqueous temperature range.

1.1.6 Corroborating technique: RBS

While AFM is a useful tool for characterizing the morphology of a surface, and LFM can identify chemical differences across a surface, they are unable to perform surface elemental identification. In many of our AFM experiments, the key to understanding the results was to find out what elements were present on a sample surface. This question can be answered by Rutherford Backscattering Spectroscopy (RBS). When a beam of high energy ions (~MeV, typically He\(^+\)) strikes a target, a small fraction of the incident ions are backscattered. The energy of the backscattered ion is dependent on the mass of the target atom, with larger atomic masses producing larger backscattered energies. Additionally, the fraction of incident ions backscattered is proportional to the square of the atomic number of the target atom. These two properties give RBS higher sensitivity to heavy elements due to the larger backscattering cross-section, but low mass discrimination for heavy elements due to the small difference in backscattered energy (for example it is not possible to discriminate between Fe and Ni). RBS is able to
discriminate between atoms of lower atomic mass (for example C from N), but with lower sensitivity.

In chapter 4 RBS data is presented showing small amounts of potassium on a polydimethylsiloxane stamp, which allowed us to determine the mechanism of patterned water film formation on mica.

1.2 Self assembly at interfaces

Amphiphiles are a class of molecules with two regions: an oil-soluble (hydrophobic) “tail” and water-soluble (hydrophilic) “head”\(^{28}\). In aqueous solutions at low concentrations, these molecules exist as monomers, and tend to adsorb at the air-liquid and solid-liquid interfaces. As the concentration is increased, the air-water interface becomes packed with the molecules, with the hydrophilic heads in the water, and hydrophobic tails extending into the air. Near this same concentration, the interactions among these molecules give rise to spontaneous self-assembly in solution. These self-assembled aggregates are called *micelles*, and the concentration at which self-assembly begins is called the critical micelle concentration, or CMC. Micelles form into one of three basic structures in aqueous solutions -- spheres, cylinders or bilayers, with the hydrophobic tails pointing towards the interior of the micelle, and the polar head group towards the water (see Figure 1.6). The type of structure formed depends on the volume.
Figure 1.6  Solution and surface behavior of surfactants.  a) Below the critical micelle concentration surfactants exist as isolated monomers in solution and on surfaces.  b) Above the CMC, micelles form in solution, the air-liquid interface is packed with surfactants and surface micelles form at the solid-liquid interface.  Hydrophobic surfaces are shown, resulting in hemi-micelles.  All interfacial structures were hypothetical prior to "soft contact' AFM.
of the hydrophilic part of the molecule, the length of the hydrophobic part (generally a hydrocarbon chain), and the effective occupational area of the headgroup.

The self-assembly morphology results from a balance of two types of interactions: attractive hydrophobic forces between tailgroups and repulsive (ionic or steric) forces between the headgroups. The structure which forms due to this balance of forces can be found from geometric considerations. It has been shown that for surfactants with optimal head area $a_0$, chain length $l$, and tail volume $v$, the so-called "dimensionless packing parameter", $v/(a_0 l)$ predicts the shape of the micelle.\textsuperscript{29} For $v/(a_0 l) < 1/3$, the surfactant will form spherical micelles, $1/3 < v/(a_0 l) < 1/2$ yields cylindrical micelles, $1/2 < v/(a_0 l) < 1$ forms bilayers or vesicles, and $v/(a_0 l) > 1$ forms inverted structures. Figure 1.7 shows a schematic of these basic micelle structures.

At still higher concentrations, the micelles themselves aggregate into higher-order structures called lyotropic liquid crystalline phases. The phase behavior is dependent on surfactant geometry, concentration and temperature. The phase diagram for dodecylmethylammonium chloride-water shown in Figure 1.8 shows a typical phase progression with increasing concentration from micellar solution to hexagonal liquid crystal to lamellar liquid crystal. At concentrations not far above the CMC, there is an isotropic micellar solution above the Krafft boundary (explained below); at $\sim 25$ wt % surfactant a hexagonal phase forms, composed of cylindrical micelles in a hexagonally close packed structure; at $\sim 60$ wt. % surfactant begins a lamellar phase, composed of regularly packed bilayers with water intercalating between each bilayer. This surfactant shows a relatively simple phase progression, but other surfactants can also form so-called
<table>
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<th>Critical packing shape</th>
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<td>Truncated cone</td>
<td>Flexible bilayers, vesicles</td>
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Figure 1.7 Packing shapes of surfactants and the structures they form. From Israelachvili.²⁹
Figure 1.8 Dodecylmethylammonium chloride-water phase diagram. Illustrated are common liquid crystal phases and the Krafft boundary.
"cubic" phases. There are two types of cubic phase that can occur. The first of these, the discontinuous cubic phase, occurs on the more dilute side of the hexagonal phase. Although its structure is still controversial, the discontinuous cubic phase is thought to be composed of two interlocking arrays of discrete short cylindrical micelles. A better characterized cubic phase, the bicontinuous, occurs between the hexagonal and lamellar phase. This is composed of bilayers interconnected along a periodic minimal surface. The hexagonal, lamellar, bicontinuous cubic and discontinuous cubic phase structures are illustrated in Figure 1.1.

There are many surfactant phase transitions that occur due to a change in temperature. For example, many surfactants separate from solution as a crystal phase below a certain temperature. This crystal solubility boundary is called the Krafft boundary. As can be seen in Error! Reference source not found., above the Krafft boundary, at concentrations below ~25 wt %, the surfactant is in the isotropic micellar phase. Below the Krafft boundary, the hydrocarbon chains freeze and surfactants cannot form micelles; instead, surfactant crystals exist in equilibrium with surfactant monomers (not micelles) in solution. The Krafft "eutectic" indicated in Error! Reference source not found. is a three-phase discontinuity with liquid, surfactant liquid crystal, and surfactant crystal phases coexisting. The Krafft boundary knee on the left side of the phase diagram, where the slope of the boundary changes from roughly horizontal to nearly vertical, constitutes the low temperature arm of the Krafft boundary.
Figure 1.1 Liquid crystal phases. a) hexagonal phase comprised of regularly packed cylindrical micelles b) lamellar phase comprised of regularly packed bilayers with water intercalating between each bilayer c) bicontinuous cubic phase comprised of lamellae curved along a periodic minimal surface (adapted from Laughlin\textsuperscript{15}) d) discontinuous cubic phase comprised of short cylindrical micelles (from Fontel\textsuperscript{66}).
Nonionic surfactant solutions can also have an unusual miscibility gap above a temperature called the cloud point. This gap is interesting because the coexisting phases are composed of similar structures, one being a surfactant-rich phase and the other a surfactant-poor phase. This boundary is caused by the dehydration of the headgroups with increasing temperature, causing the solubility to decrease.

At surfaces, a similar progression occurs if either the hydrophilic or hydrophobic part of the molecule is attracted to the surface. At low solution concentrations, monomers adsorb to the surface randomly, as a 2D gas. As the solution concentration is increased, the molecules aggregate into surface micelles. For surfaces in air, deposited amphiphiles, such as from microcontact printing (see section below), can form a 2D gas on the surface or a self-assembled solid phase. Chapter 3 shows results of non-ionic surfactants adsorbing to amorphous hydrophobic surfaces from solution and chapter 6 details the formation of a self-assembled solid and 2D gas of amphiphiles deposited on mica in air.

1.3 Microcontact printing

While self-assembly is useful for simple surface-wide patterning, it cannot create individual structures of complex shape. For this, a new method is needed. A simple and inexpensive method of creating micrometer to sub-micrometer structures was reported by Kumar and Whitesides in 1993. In this method, dubbed microcontact printing, an elastomeric pre-polymer such as Dow Corning Sylgard 184 is cast onto a hard template. The polymer is cured and peeled off the master, creating a replica of the master with
fidelity better than ~10 nm (Figure 1.10a). This replica is then inked, typically by immersion in a dilute (~1mM) solution of the desired molecules (Figure 1.10b), then placed ("stamped") onto a surface for several seconds (Figure 1.10c). When the replica is removed, the surface is decorated with the desired pattern of the ink molecules (Figure 1.10d). The thin (1-2 nm), high definition patterns can be created over ~1 cm² areas.

The first such system studied, and the most thoroughly studied system in the literature since 1993, is that of alkanethiol inks on gold substrates. Alkanethiols on gold serves as a model system for microcontact printing because the thiol ink forms a covalently bonded, self-assembled monolayer (SAM) on gold with stamp contact times of just several seconds. This alkanethiol SAM can be used, for example, as an etch resist,²,³,₂² or to modify the wettability of the surface.³³-³⁶

Microcontact printing of non-covalently bonding molecules has not been as extensively studied. The exceptions are lipid bilayers of phosphatidylcholine³-⁶ and proteins.⁴,⁷-¹⁰ Chapters 5 and 6 will show results of stamping several alkanes, long-chain fatty acids, long-chain alcohols, lipids, cationic surfactants and a fat on a model surface (mica).

While the stamping mechanism in Figure 1.10 is appealing in its simplicity, the actual inking and transfer processes are poorly understood. Even for the strongly interacting system of alkanethiols on gold, lateral diffusion of the ink across the sample surface and vapor phase transport of ink from the stamp channels to the surface can limit the resolution.
Figure 1.10 Schematic of microcontact printing.
Chapter 5 details the surface diffusion and spreading during microcontact printing of two non-covalently bonding molecules and Chapter 6 has a more general discussion of how non-covalently bonding molecules behave during microcontact printing.
CHAPTER 2: VARIABLE TEMPERATURE FLUID STAGE FOR AFM

The design of a simple, variable temperature fluid cell for an atomic force microscope is presented. The stage is based on a thermoelectric heating/cooling element, which allows control of sample and fluid temperature from -5 to 130 °C. The stage is stable enough to image at molecular resolution almost throughout the range of accessible temperature and can be used for imaging in either gas or liquids. This allows the molecular scale investigation of surface phase transitions and chemical kinetics at solid/liquid interfaces by varying the temperature. As an example, we present results of temperature-induced phase transitions in self-assembled surfactant aggregates at solid/liquid interfaces.

2.1 Introduction

Atomic force microscopy provides the promise of imaging critical phenomena and chemical kinetics in real space, in real time, and at molecular resolution. This potential has been realized in diverse applications; examples include the imaging of step motion in crystal growth, potential induced surface changes in electrochemistry, enzymatic action and polymerization reactions in biochemical systems, and surface melting of polymers and refractory materials.

The variation of temperature allows us to probe structural changes associated with critical phenomena and to measure activation energies associated with interfacial reactions. Since critical phenomena and surface reactions often take place in a liquid (and often aqueous) environment, a temperature controlled liquid environment for atomic force microscopy (AFM) is desirable. In particular, such an environment allows us to study phase transitions in “soft condensed matter” such as proteins, surfactant micelles, model membranes, and adsorbed polymers. Variable temperature AFM measurements have been made at low temperatures, and at elevated temperatures. All of the low temperature designs have used a custom-built AFM. These designs typically used a cryogenic liquid for cooling either the entire AFM, or just the sample, which allowed the temperature to be continuously varied between 100 K and room temperature. Most of the elevated temperature designs were for commercial AFM’s and were used primarily in air. Resistive heating of the sample mount was the most commonly used method, however, laser heating has also been used. Only two previous designs have used the combination of a heat stage with a fluid cell; a custom-built AFM has been used to image mineral surfaces under hydrothermal conditions, and a heated sample stage has been used in a commercial fluid cell to measure polymeric forces at up to 53 °C. There have been no published reports of atomic resolution AFM in temperature-controlled fluids.

Here we present design details and first results for a stable, temperature controlled stage, which is capable of operating over the entire temperature range of aqueous
solutions. This stage uses a thermoelectric cooler for both cooling and heating, depending on the direction of current flow through the device.

2.2 Instrumentation

The stage was constructed for a commercial AFM (Digital Instruments Dimension 3100), which is based on a standalone design. Here the cantilever is mounted on the piezoelectric translator and the sample is fixed on a stationary stage. This allows greater accessibility to the sample area and greater flexibility for instrumentation design to modify the sample environment. In addition, the piezo is naturally thermally isolated from the heating or cooling of the sample.

In designing this temperature-controlled cell, our primary goal was to achieve sufficient mechanical stability to permit molecular resolution over the entire temperature range of aqueous solutions. In addition, thermal stability was also a consideration. This is because stable imaging at low force is a requirement of soft materials and the thermally induced bending of a cantilever can increase imaging forces. For a typical cantilever, the thermally induced bend has been estimated to be of order of 100 nm/K.\textsuperscript{47} To take a particular example, a force stability of order 0.1 nN is typically required for imaging interfacial surfactant micelles.\textsuperscript{1} This translates to a thermal stability requirement of order 10 mK over imaging time scales (~1 min). This level of temperature control can be attempted by two different design routes;(i) a high gain feedback loop with a system capable of fast thermal response (low thermal mass), or (ii) open-loop operation using a system with comparatively slow thermal response(moderate thermal mass). Since route
(i) involves highly conductive materials with large thermal expansivities (e.g., aluminum, copper), and since the imaging fluid in any case compromises the fast response of such materials, we opted for route (ii). This also allowed us to build a much simpler cell without the need for closed-loop temperature control. The moderate thermal mass prevents fast temperature drift once the target temperature is reached (usually in less than 5 min).

A schematic drawing of the prototype stage is shown in Figure 2.1. A thermoelectric cooler was sandwiched between an aluminum heat sink and a type 303 stainless steel fluid cell. Stainless steel was chosen for its corrosion resistance; type 303 was due to its easy machineability. The pieces were mechanically held together by three stainless steel screws which screwed into the Macor legs. The legs incorporate small SmCo magnets at the ends to attach the stage to the sample chuck. The Macor legs were made to extend slightly beyond the bottom of the heat sink, which minimized the sample z drift due to thermal expansion of the heat sink. A stainless steel spring clip was used to hold the sample in place and a platinum resistive temperature device (Pt-RTD) was attached to the top of the cell to measure temperature. The temperature of the cell was determined by a four-wire resistance measurement of the Pt-RTD.

The thermoelectric (TE) cooler (Melcor HT4-12-30L) was chosen to cover the entire surface beneath the fluid cell for even heating/cooling and for its heat pumping capacity sufficient to reach 0 °C. This model is also able to withstand operation up to 200 °C compared to typical TE cooler ratings of 130 °C.
Figure 2.1 Schematic drawing of variable temperature stage and AFM scanner. The inside diameter of the stainless steel cell is 20.6 mm and the depth is 4.8 mm. It holds ~0.5 ml of fluid with the tip engaged.
Removing heat from the heat sink was found to be the limiting factor in the lowest temperature achievable by the fluid cell. With passive air cooling of the heat sink, the filled liquid cell reached a minimum temperature of only 19 °C. To improve heat removal, a "wading pool" was constructed around the heat sink from a 1.5 cm high section of 4 1/2 in. outer diameter PVC plastic pipe and Saran wrap (Figure 2.2). This was filled with antifreeze to a level just below the top of the heat sink. In this configuration, the lowest achievable temperature was found to be 7 °C. To achieve lower temperature operation, a heat exchanger was constructed by immersing three loops of 1/8 in. OD Tygon® tubing into the pool and water was recirculated through the tubing at the rate of 50 ml/min using a centrifugal pump. With recirculating water at room temperature, the temperature of the cell reached 2 °C; with recirculating ice water, the temperature reached -5 °C. Heating of the cell did not require the bath around the heat sink.

The temperature of the cell was set by adjusting the voltage (and therefore the power) applied to the thermoelectric cooler. The minimum temperature of -5 °C was achieved with a voltage of 7.9 V applied to the thermoelectric cooler, at the current limit of our power supply of 1.55 A (12.2 W). Presumably a lower temperature could be achieved with a higher current power supply. The primary problem with low temperature operation was water vapor condensing on the cold cell. Keeping the inside of the Dimension 3100 enclosure dry, with desiccant and flowing dry nitrogen, diminished this problem. Eliminating excess water vapor in the local environment was the primary reason for using antifreeze in the heat sink bath instead of water.
Figure 2.2 Photograph of the experimental setup. The flexible tubing near the piezo directed a nitrogen gas stream at the optics in the piezotube. This reduced condensation of vapors on the optics when imaging fluids at high temperature.
2.3 Results and Discussion

One concern with low temperature operation was that water flow through the heat exchanger would introduce too much mechanical or acoustic noise to permit stable imaging at molecular resolution. However, this proved not to be the case, as long as the heat exchange tubing was flexible.\textsuperscript{52} Figure 2.3a shows atomically resolved mica (unfiltered image) in water at 5 °C.

The maximum temperature we recorded was 130 °C, which was also at the current limit of our power supply (10.1V, 1.55 A). The thermoelectric cooler is rated to 33 W and 200 °C. Based on its measured performance of about 0.15 W/(°C above room temperature), the cell should be able to reach the rated temperature limit (~ 200 °C) of the thermoelectric cooler. The most troublesome aspect of high temperature operation with fluids was fast evaporation of the liquid in the cell. The ~1 ml of water in the cell allowed imaging for a few hours below ~60 °C, but at higher temperatures, rapid evaporation made stable imaging increasingly difficult. However, lower vapor pressure liquids such as formamide, ethylene glycol and silicone oil proved more successful.

Figure 2.3b shows the mica lattice resolved at 113 °C in Dow Corning DC 200 silicone oil (unfiltered image). This fluid was chosen for its low vapor pressure at elevated temperatures. Operation of the cell with fluids at high temperatures often caused imaging problems due to vapors condensing on the optics in the piezo tube. This condensation caused scattering of the AFM laser, which led to poor imaging. For
Figure 2.3 Unfiltered image showing lattice resolution on mica in water at 5 °C. Contact mode friction image size 20 nm x 20 nm. The heat sink cooling bath had 3 loops of 1/8 in. tubing with 50 ml/min of room-temperature water circulating through it. This recirculation had no visible effect on the image. The fast Fourier transform (inset) shows the expected hexagonal symmetry. b) Unfiltered image showing lattice resolution on mica in silicone oil (Dow Corning DC 200 10 mPa·s at 25 °C) at 113 °C. Contact mode friction image size 20 nm x 20 nm. The fast Fourier transform (inset) shows the expected hexagonal symmetry.
relatively high vapor pressure liquids such as water and ethylene glycol, blowing a stream of nitrogen on the optics (see Figure 2.2) eliminated this condensation.

Since our primary interest in building this stage was the investigation of soft materials, we studied phase transitions in interfacial surfactant micelles as a model system. Ionic surfactants in solution exhibit a phase transition at the so-called Krafft temperature. Above this temperature the hydrocarbon tails are labile, allowing surfactants to self-assemble into curved micelles.\(^{29}\) Below the Krafft point, the hydrocarbon chains are in a frozen state, preventing the formation of micelles and causing surfactant in excess of the critical micelle concentration (CMC) to precipitate out as crystals. Recent results\(^{1,53}\) have shown that surfactants also self assemble into well-defined aggregates at solid/liquid interfaces. These aggregate morphologies often differ from those in the bulk, and they generally reflect a balance between intermolecular interactions (spontaneous curvature) and molecule-surface interactions (the "boundary condition").\(^{53}\) Recent studies have investigated the effects of counterions,\(^{54,55}\) added alcohol,\(^{56}\) and variable surface potential\(^{23}\) on the interfacial aggregate phase. However, the effects of temperature were unknown.

We investigated phase changes in interfacial micelles of cetyl trimethylammonium bromide (CTAB) on graphite.\(^{57}\) Previous results have shown that CTAB makes roughly half-cylindrical micelles on graphite above the CMC. This result is reproduced in Figure 2.4a, which was obtained in 3 mM CTAB solution at 29 °C. This image shows bright stripes, characteristic of parallel half-cylindrical micelles.\(^{53}\) Although contact mode imaging with electric double layer forces was possible, better results were obtained with
phase contrast imaging in tapping mode.\textsuperscript{58} (All CTAB images were obtained with V-shaped silicon nitride levers at their resonance frequency of ~7.3 KHz, with scan rates of ~2 Hz.)

Figure 2.4b shows a nearby area imaged at 19 °C, below the Krafft point of CTAB (which is 24 °C in dilute micellar solutions).\textsuperscript{59} In this image, half-cylindrical micelles are still visible, but in addition, isolated disordered structures are also present. These structures are often attached to steps on the graphite surface and are often elongated along step directions or along micelle directions. (These two directions are distinct, since graphite steps tend to follow the surface symmetry axes, whereas half-cylindrical micelles are oriented at 30°, 90°, and 150° relative to these axes.)\textsuperscript{1} The shape and size of these structures were reproducible between successive scans, although small changes could be observed over ~30 min.

Larger scans at low temperature also showed evidence for particulate structures that were easily moved by the AFM tip. Figure 2.5a and Figure 2.5b show identical 10 μm x 10 μm areas of the graphite surface in CTAB solution at 17 and 8 °C, respectively. The substrate symmetry axes are revealed by the predominant step orientation. Although the scans are too large to resolve individual micelles, the expected micellar orientations based on previous work\textsuperscript{1} are shown on Figure 2.5a top left. Both scans reveal bright streaks that occur along specific orientations. The streaks are not images of static features on the surface, as evidenced by the fact that they do not reproduce between the two scans. Rather, they are caused by particle motion induced by the tip as it scans over a particle. Such features have been observed previously for the tip-induced motion of
Figure 2.4  a) CTAB on graphite at 29 °C. Tapping mode phase image size 300 nm x 300 nm. The stripes are spaced apart by 5.3 nm, a little over twice the molecular length of CTAB. b) CTAB on graphite at 19 °C. Tapping mode phase image size 750 nm x 750 nm. The two pronounced diagonal lines are steps on the graphite cleavage plane. The stripes corresponding to half-cylindrical micelles are still barely visible in this large scan. The additional patchy structures are caused by the temperature drop.
particles and clusters on dry surfaces. The particle motion (as evidenced by the orientation of the streaks) occurs along certain distinct directions, namely, the directions either of the surface micelles or of the graphite steps. Apparently, both the micellar orientation and graphite step sites act as preferred sliding directions for these particles. This is analogous to anisotropic frictional forces between clusters and surfaces observed previously in dry sliding by Sheehan and Lieber. Furthermore, we note that most of the streaks in Figure 2.5 originate at step sites (see arrows). Most of the particles are therefore weakly attached to step sites before being moved by the AFM tip. This suggests that steps act as nucleation sites for the particles.

Upon prolonged cooling, we observed the formation of order 100 \( \mu \text{m} \) sized transparent platelets of CTAB by optical microscopy. When the fluid cell was warmed to room temperature, these platelets redissolved and AFM images revealed neat micelles once again. These observations suggest that the particles observed in Figure 2.5 are particles of CTAB that have nucleated predominantly at step sites. However, additional work is clearly necessary to confirm this interpretation.

As a final example, Figure 2.6 shows the effect of slow heating on the dissolution of an adventitious contaminant by a surfactant solution. Since this sequence was obtained in the early uncalibrated trials of the temperature cell, the exact temperatures are unknown. However, it does serve to illustrate that surface phase transitions can be imaged at sub nanometer spatial resolution and \(~10\ \text{s}\) time resolution while heating.
Figure 2.5  a) (left 17 °C) and b) (right 8 °C). CTAB on graphite. Tapping mode amplitude image size 10 μm x 10 μm. Both images were captured in the up scan direction. The micelle directions are shown by the axes in the upper left corner. Arrows point to the nucleation sites of particles on graphite step edges. The particles are moved by the AFM tip either along graphite step edges or along micelle directions.
Figure 2.6a shows a 690 nm x 690 nm image of interfacial aggregates on mica, in a solution of the divalent surfactant $\text{C}_{18}\text{H}_{37}\text{N}^+(\text{CH}_3)_2(\text{CH}_2)_3\text{N}^+(\text{CH}_3)_3\cdot2\text{Br}^-$, or $\text{C}_{18.3.1}$ for short. The double charged and bulky headgroups of this class of surfactant favor highly curved aggregates, leading to micellar cubic phases in bulk solution$^{61}$ and hexagonally packed spherical micelles on mica.$^{54}$ This morphology is also observed in Figure 2.6a (top left and right corners), but here it surrounds a large uniform patch of unknown composition. The lack of lateral structure and the uniform height of this patch (close to the height of the micelle layer) strongly suggest that it is a bilayer, possibly composed of unreacted material from the surfactant synthesis.$^{62}$ Interestingly, the spherical micellar phase coexists with these bilayer patches, and we observe no evidence of transitional aggregate curvatures (such as cylinders) that would indicate surfactant mixing. No substantial changes were observed in this heterogeneous structure over a period of ~1 h at room temperature.

The temperature of the fluid cell was then slowly increased while imaging in the same area of the surface. Initially, the morphology remained unchanged, but at a critical point the patch suddenly began to break up into small roughly circular islands surrounded by a “sea” of the spherical micelle phase (Figure 2.6b and Figure 2.6c). Over a period of 2 h, the spherical micellar phase gradually replaced the bilayer phase Figure 2.6d, with the bilayer islands either diffusing out of view, or desorbing into solution.

A likely explanation for the fast breakup of the uniform patch is a temperature-induced phase transition (e.g., chain melting) in the amphiphiles in this region, leading to
Figure 2.6 Images of an adventitious stain on mica in a solution of the gemini surfactant $C_{18}H_{37}N^+(CH_3)_{2}(CH_2)_{3}N^+(CH_3)_{3}2Br^-$ ($C_{18-3-1}$ for short) (see Ref. Zana^{65}). This surfactant forms spherical micelles on mica. a) An amorphous stain surrounded by spherical micelles at 26 °C (690 nm x 690 nm). Figures b) and c) are the same region at 30 °C, taken 70 and 81 min later, respectively, (690 nm x 690 nm). d) is a zoom of the same region at 30 °C, 196 min after a) (305 nm x 305 nm). The amorphous phase is broken up and “invaded” by the spherical micelle phase.
a sudden penetration of the bilayer by the divalent surfactants. This may be a two-dimensional analogue of emulsification, i.e., the breakup of large oil drops into smaller droplets by surfactants.

2.3.1 Improved heat sink

The improved performance of the water bath for the heat sink led to the development of an actively water-cooled heat sink (see Figure 2.7). This new heat sink offered improved cooling performance for the cell, and a lower profile. The low profile allowed the stock Dimension 3100 base chuck to be used, which greatly simplified use of the cell. The water flowing through the heat sink did not cause any visible noise in the image, partly due to the smooth water flow from the centripetal water pump, and partly due to the ability to use the Dimension 3100 base chuck vacuum hold the heat sink firmly in place. The apparent design trade off was the high thermal expansion coefficient of the aluminum water cooled heat sink, however, the recirculating water maintained it's temperature constant to within a few degrees. Using a temperature controlled water bath for the cooling water could allow the heat sink temperature and therefore the cell temperature to be reduced, and would eliminate the small drift due to heat sink thermal expansion. Ceramic screws were used to connect the cell to the heat sink, to reduce the flow of heat from the heat sink to the cell. The Pt-RTD was moved to the mounting flange to more accurately measure the temperature of the fluid.
A new fluid cell was machined from titanium, which has superior thermal conductivity and corrosion resistance compared to the type 303 stainless steel cell. Performance data is shown in Figure 2.8.
Figure 2.7 Improved performance water-cooled aluminum heatsink.
Figure 2.8 Temperature of Ti fluid cell with water cooled aluminum heatsink as a function of applied power to thermoelectric element.
CHAPTER 3: SURFACTANT AGGREGATES AT A FLAT, ISOTROPIC HYDROPHOBIC SURFACE*

ABSTRACT

We report results of surfactant aggregate morphologies at an amorphous hydrophobic surface whose roughness is small compared to the size of a micelle. Direct imaging by atomic force microscopy shows that single-chain ionic, nonionic and zwitterionic surfactants, which form spherical micelles in solution, form globular aggregates consistent with half-micelles at an amorphous hydrophobic surface. This result is consistent with the expected isotropy of chain-surface interactions.

3.1 Introduction

The self-assembly of soluble surfactants in free solution has been experimentally investigated and theoretically modeled for several decades, but the direct determination of surfactant aggregation at interfaces is comparatively new. Atomic force microscopy (AFM), using soft repulsive interactions, has in the past few years imaged the aggregate structures of a variety of surfactants (ionic, nonionic, and zwitterionic) at a variety of solid surfaces (hydrophilic and hydrophobic) in contact with aqueous micellar solutions. Most investigations have used atomically

* This chapter was published as Wolgemuth, J. L.; Workman, R. K.; Manne, S. "Surfactant aggregates at a flat, isotropic hydrophobic surface", Langmuir 2000, 16, 3077-3081.
flat model surfaces, often the ordered cleavage planes of layered solids such as mica and graphite.

On crystalline hydrophobic surfaces, early results\textsuperscript{53} showed that interfacial self-assembly was determined almost entirely by the crystalline anisotropy of the substrate. AFM images revealed aggregates in the form of parallel stripes oriented perpendicular to an underlying symmetry axis and spaced apart by roughly twice the length of a surfactant molecule. These were interpreted as half-cylindrical micelles, where the bottom row of molecules is oriented horizontally along a symmetry axis. This basic morphology has since been observed for a variety of charged\textsuperscript{53,54,68} and uncharged surfactants,\textsuperscript{66,69,72} over a surprisingly wide range of surfactant geometries. Surfactants capable of cylindrical curvature (i.e., exhibiting a bulk hexagonal phase) have generally self-assembled into oriented half-cylinders on crystalline hydrophobic surfaces. This high degree of surface control has been attributed to the anisotropy of interaction between the horizontal alkane tail and the crystalline surface.\textsuperscript{1} As long as the tail exceeds a certain minimum length (found to be \textasciitilde 10 carbon atoms\textsuperscript{88,72}), the linear contact area between the tail and surface enhances the direction sensitivity of the interaction, leading to easy adsorption directions along the symmetry axes.

In contrast to the above, little work has been reported on aggregate phases at isotropic hydrophobic surfaces. These are important for several reasons. As model surfaces, they impose a simpler boundary condition on self-assembly, facilitating the future comparison of theory to experiment. Furthermore, comparing aggregation at amorphous vs. crystalline surfaces serves to distinguish between the influence of simple
hard-wall confinement and specific interactions with the surface lattice. Finally, amorphous hydrophobic surfaces may shed light on surfactant behavior at the air-solution interface, which is also amorphous and hydrophobic.

Grant et al.\textsuperscript{72} have recently reported AFM results of nonionic surfactant aggregation at an amorphous hydrophobic surface, namely a silica surface to which diethyloctylchlorosilane (DEOS) had been covalently attached. They observed repulsive forces consistent with the expected range of steric/entropic interactions of the ethyleneoxide headgroups. Imaging with these forces revealed a featureless adsorbate layer consistent with a uniform monolayer. Here we report the self-assembly of single-chain surfactants at amorphous silica surfaces hydrophobized by covalent attachment of trimethylchlorosilane (TMCS). This silanating agent permits the preparation of an amorphous hydrophobic surface while introducing only a small roughness (equivalent to a methyl group) to the original silica surface. This avoids grafted alkyl chains (such as the octyl chain of DEOS), which can potentially intercalate surfactant molecules and give rise to a more pliable interface.\textsuperscript{75} Thus our choice of TMCS was dictated mainly by the end goal of a flat, amorphous, and rigid hydrophobic interface.

Our results show that single-chain surfactants give rise to discrete globular aggregates, roughly consistent with hemispherical or hemi-ellipsoidal micelles, at the TMCS-coated silica surface. Since the same surfactants form spherical micelles in solution, the perturbation of spontaneous curvature is smaller for isotropic hydrophobic surfaces than for crystals.
3.2 Experimental Section

The amorphous native oxide layer on silicon wafers was used as the foundation for preparing amorphous hydrophobic surfaces. Chips from a Si(100) wafer were washed in isopropanol, blown dry with dry nitrogen (>99.995%), and placed in a plastic petri dish. A few drops of TMCS (Fluka, >99%, volume ~50 µl) were placed on a cover slip inside the petri dish, a few centimeters from the Si chips. The petri dish cover was left slightly open and the TMCS allowed to evaporate. When evaporation was complete (~30 minutes), the Si chips were rinsed in three consecutive baths of ethanol (in order to remove unreacted TMCS and physisorbed dimers) and blown dry with dry nitrogen. These samples were stored covered until use. They exhibited a static contact angle of 80 ± 3°, measured using a side-mounted optical microscope equipped with a video display. Some surfaces were cleaned by an alternate published technique of immersion in a solution of NH₄OH and H₂O₂, followed by exposure to an ultraviolet lamp; both sets of samples gave similar AFM results.

Commercial surfactants were used as received from Fluka (>98% purity); the dimeric surfactant (described below) was a kind gift of G.D. Stucky et al. Solutions were prepared using Nanopure water directly decanted from a commercial system (Barnstead, resistivity 18.3 MΩ·cm). Surfactant concentrations were typically a few times the critical micelle concentration (CMC). Five types of single-chain surfactants were used: the cationic dodecyltrimethylammonium bromide (DTAB, CMC 16 mM); the dimeric C₁₆H₃₃N⁺(CH₃)₂(CH₂)₃N⁺(CH₃)₃•2 Br⁻ (termed C₁₆:₃:�, CMC ~3 mM); the anionic sodium dodecylsulfate (SDS, CMC 8 mM); the zwitterionic 3-(N,N-dimethyldecylammonio)
propanesulfonate (DDAPS, CMC 2.2 mM); and the nonionic octa(ethylene glycol) monododecyl ether (C_{12}E_{8}, CMC 0.05 mM). All of these surfactants form spherical micelles in free solution. The double-chain surfactant didodecyldimethylammonium bromide (DDAB, CMC 0.15 mM), which forms bilayers and vesicles in solution, was used as a control.

We used a commercial AFM (Digital Instruments, Dimension 3100) operating in soft contact (or precontact) mode. In this mode, the repulsive (electric double layer or steric/entropic) force signature associated with the surfactant adsorbate is itself used as the contrast mechanism during AFM scans. Force curves were obtained before and after each image to ensure that the imaging force originated from the surfactant layer and not from hard contact with the sample surface. Images were obtained using commercial V-shaped cantilevers (Digital Instruments, type DNP-S), specifically the long thin variety with a nominal spring constant ~0.06 N/m. Imaging scan rates were in the range 3-5 Hz, and all images were unprocessed except for slope removal along the fast scan axis. All data were recorded at room temperature (27 ± 2°C).

3.3 Results and Discussion

The amorphous native oxide on silicon wafers typically shows disordered topographic undulations with elevations of a few angstroms and lateral peak spacings of order ~20 nm. These features are generally unavoidable; however, since their lateral extent is large (and vertical extent small) in comparison to micelles, they have not seriously interfered with previous AFM investigations on bare silica surfaces.
The TMCS-coated surfaces (Figure 3.1) showed topography similar to bare silica, indicating that the surfaces were not significantly roughened by the covalent attachment.

Immersion in surfactant solution gave rise to long-range repulsion between tip and sample, similar to force curves previously reported for both charged and uncharged surfactants. Approach curves for the surfactants are shown in Figure 3.2. Repulsive interactions were roughly exponential and extended out to separations of around 10 nm. Forces reached values of order ~1 nN before rupture of the interfacial surfactant layers. Aggregate images were obtained by using a force setpoint below the rupture force; most images were re-checked at the lightest possible imaging forces to guard against tip-induced disruption of surfactant aggregates. Adsorbate features were also correlated between successive scans to ensure reproducibility.
Figure 3.1 200 x 200 nm AFM image (contact mode) of TMCS-coated silica surface. The measured rms roughness of this entire area is 0.1 nm, and the average height of the undulations is 0.46 nm. These values are much smaller than typical micelle sizes (>4 nm). The FFT (inset) shows no pronounced periodicities.
Figure 3.2  AFM approach curves on TMCS-coated silica for each surfactant used in this study (see text). The measured jump-in distances are listed in Table 3.1. Images in Figure 3.3 were obtained by maintaining a force setpoint in the repulsive precontact region of the force curve.
The interfacial aggregate shape should be consistent with the range of spontaneous curvature accessible in solution. Therefore double-chain surfactants such as DDAB serve as a useful control, since they can only form locally flat aggregates. AFM images of adsorbed DDAB on TMCS-coated silica (Figure 3.3a) show a layer which is featureless, except for the underlying sample topography, at all imaging forces. This is consistent with the expected flat monolayer, with tails pointing towards the substrate.

In contrast, single-chain ionic, nonionic and zwitterionic surfactants appear to show globular aggregates on TMCS-silica (Figure 3.3b-f). These are visible as small closely-spaced bumps superimposed on the larger-scale surface texture. Fast Fourier transforms (FFTs, inset) of these images allows us to quantify the aggregate morphology. Whereas the FFT of the DDAB image (Figure 3.3a) shows only a diffuse center spot (similar to the bare surface), FFTs of the single-chain surfactants express prominent periodicities that usually correspond well to the expected size range of micelles, as summarized in Table 3.1. Thus the cationic DTAB and the zwitterionic DDAPS (Figure 3.3b and c) both show FFT peaks at a little over 4 nm, agreeing well with expected micelle diameter for these C12 surfactants. The dimeric C16-3-1, with its longer 16-carbon chain and its doubly charged headgroup, gives rise to larger periodicities of 6.7 nm (Figure 3.3d), consistent with larger micelles. The nonionic C12E8 (Figure 3.3e) also shows comparatively large spacings of 5.8 nm, as expected from its bulky ethyleneoxide headgroup. The anionic SDS (Figure 3.3f) is the only exception, showing FFT
Figure 3.3 200 x 200 nm AFM images of adsorbed surfactants on TMCS-coated silica with fast Fourier transforms (FFTs, inset). a) AFM scan of the double-chain surfactant DDAB (0.3 mM solution, 2 x CMC) showing a surface that is virtually featureless, except for the underlying surface topography. b) AFM scan of the cationic surfactant DTAB (32 mM solution, 2 x CMC) showing globular and short linear aggregates over the underlying surface topography. The inset Fourier transform shows periodicities in the range 4.4 ± 0.3 nm. c) The zwitterionic surfactant DDAPS (10 mM solution, 4.5 x CMC) also shows globular aggregates with an ill-defined periodicity in the range 4.3 ± 0.3 nm. d) The AFM scan of the dimeric surfactant C_{16-3-1} (3.0 mM solution) shows similarly globular structures with periodicities of 6.7 ± 0.4 nm. e) The nonionic surfactant C_{12}E_8 (0.3 mM solution, 6 x CMC) shows globular or short linear segments with periodicities of 5.8 ± 0.5 nm. f) The anionic surfactant SDS (50 mM solution, 8 x CMC) shows globular aggregates at a comparatively large periodicity of 9 ± 2 nm.
Table 3.1 Surface Periodicities and Jump-in Distances for Surfactants on a Methylated Silica Surface

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Expected Diameter (nm) $^a$</th>
<th>Micelle Periodicity from FFTs (nm)</th>
<th>Jump-in Distance from Force Curves (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTAB</td>
<td>4.0</td>
<td>4.4 ± 0.3</td>
<td>2.7</td>
</tr>
<tr>
<td>DDAPS</td>
<td>4.3</td>
<td>4.3 ± 0.3</td>
<td>2.7</td>
</tr>
<tr>
<td>C$_{12}$E$_8$</td>
<td>5.1</td>
<td>5.8 ± 0.5</td>
<td>3.5</td>
</tr>
<tr>
<td>C$_{16}$-3-1</td>
<td>6.0</td>
<td>6.7 ± 0.4</td>
<td>3.7</td>
</tr>
<tr>
<td>SDS</td>
<td>3.8</td>
<td>9 ± 2</td>
<td>3.0</td>
</tr>
</tbody>
</table>

$^a$ Micelle diameters were determined by doubling the length of the surfactant molecule (head + tail). The tail length was calculated from Tanford's formula (Tanford, C. *The Hydrophobic Effect*, Wiley: New York, 1973). For symmetric headgroups (SDS and DTAB), accepted values for ionic diameters were used; for short linear headgroups (DDAPS and C$_{16}$-3-1), the average segment conformation was assumed to be approximately halfway between perpendicular to the tail and fully outstretched; for C$_{12}$E$_8$ the headgroup size was assumed to be twice the Flory radius $R_F = l n^{3/5}$, where $l$ is the monomer length for a (CH$_2$-O-CH$_2$) segment and $n = 8$. (For further discussion see Evans, $^63$ pp. 110 and 290.)

periodicities of 9 ± 2 nm, which are anomalously large in comparison to its micelle diameter of ~4 nm. SDS spacings were also fairly variable between samples, with some samples adsorbing no SDS at all. These discrepancies are discussed below.

The images and FFTs also show that the aggregate phases are not well ordered. In some cases (Figure 3.3b, c, and d) the FFTs show a nearly featureless ring, indicating an amorphous arrangement with a well-defined nearest-neighbor separation. In other cases (Figure 3.3e and f), discrete but broad peaks are visible, suggesting some degree of local order in the way aggregates pack on the amorphous surface. The observed order is far weaker than for crystalline surfaces$^{54}$ and may be caused solely by inter-aggregate repulsive forces.
While AFM results have a high degree of lateral sensitivity, they must be compared to other techniques with high vertical sensitivity in order to arrive at a plausible aggregate morphology. Ellipsometry has shown that surfactants adsorb as a monolayer or sub-monolayer equivalent on hydrophobized silicon. Neutron reflectometry has also revealed a sub-monolayer adsorbed thickness, indicating that chains must on average be tilted away from the surface normal. When these are considered together with the AFM images, the most plausible aggregate structure that emerges is discrete half-micelles roughly in the form of hemispheres or hemi-ellipsoids. Such a morphology is perfectly consistent with the way in which the measured aggregate periodicity scales with expected micelle sizes (Table 3.1).

We also observe from Figure 3.2 that the jump-in distances for force curves (tabulated in the last column of Table 3.1) also increase with increasing micelle size. Although the absolute values of the jump-in distances should be interpreted with extreme caution, since the aggregate morphology on the tip surface is unknown before or after hemifusion, certainly the trend of increasing jump-in distances with increasing micelle size is also consistent with the proposed morphology of hemispherical micelles.

The scaling of aggregate periodicity with micelle size fails only in the case of SDS, where the measured lateral spacing is typically much greater than the micelle diameter and is not very reproducible between samples. We believe the reason lies with SDS having the same charge as ionizable SiOH groups left behind on the silica surface. There are two possible reasons for unreacted surface sites. First, they can result from suboptimal reaction conditions; the measured contact angles for the surfaces used herein
are somewhat smaller than those reported in a recent systematic study of alkyldimethylsilane monolayers. Second, it has recently been pointed out that even when reaction conditions have been optimized, steric hindrance prevents monofunctional silanes such as TMCS from reacting with all of the hydroxyl groups on a silica surface, since the trimethylsilyl group is too bulky to match the surface density of SiOH groups. For these reasons, while reaction with TMCS makes the surface generally hydrophobic, some negative charge probably still exists, inhibiting SDS adsorption and giving rise to more open interaggregate spacings than for other surfactants. The putative role of surface charge is also consistent with control experiments on the cleavage plane of mica (not shown); on this highly negative surface, no SDS adsorption is observed even for solution concentrations up to ~100 times the CMC.

3.4 Conclusion

Previous results showed that single-chain surfactants that aggregate into spherical micelles in solution self-assemble as half-cylinders at the crystalline hydrophobic interface, due to anisotropic interactions between the surface and tailgroup. The present results on amorphous surfaces indicate that when this anisotropy is removed, spontaneous curvature reasserts itself, and interfacial aggregates become roughly hemispherical. Since similar morphologies occur over a wide range of headgroup types (both charged and uncharged), interfacial adsorption seems to be driven by hydrophobic interactions between the surface and tailgroups. When combined with the usual intermolecular interactions, this gives rise to an arrangement of globular half-micelles, with lateral
periodicities that scale with expected micelle size. These results may serve as a useful
guide for theoretical studies and molecular dynamics simulations of surfactant behavior
at unstructured hydrophobic walls.\textsuperscript{81,82}
CHAPTER 4: PATTERNED THIN WATER FILMS ON MICA

Patterned water films were formed on the surface of mica by contact with clean, patterned poly(dimethylsiloxane) stamps in ambient humidity. Capillary condensation of ambient atmospheric water in the stamp channels allowed transport of potassium from the mica surface to the stamp, which locally modified the wettability of the mica surface. The resulting mica surface was imaged with contact-mode atomic force microscopy, revealing 3 Å-tall patterns. The pattern disappeared as the relative humidity was decreased (<25% RH) but reappeared as the relative humidity was increased above ~35%. The pattern also disappeared as the relative humidity was increased above ~70% but again reappeared when the humidity was subsequently decreased to ~35%. This high-humidity treatment often resulted in patterned nm-tall islands on the mica surface, which are believed to be a potassium compound (possibly potassium bicarbonate). Such regularly patterned films may be useful as models of heterogeneous surfaces that can be used for fundamental wetting studies and as templated reaction spaces for aqueous materials synthesis.

4.1 Introduction

Physically adsorbed water on surfaces can cause local corrosion cells on metals and the dissolution of mineral surfaces. Water can also drastically alter imaging forces in atomic force microscopy (AFM) and affect resolution in scanning probe

* This chapter was published as Workman, R. K.; Manne, S. "Patterned thin water films on mica", Langmuir 2002, 18, 661-666.
lithography. Muscovite mica is a model substrate that is widely used in AFM and surface force apparatus studies, primarily because it can be easily cleaved to give large, atomically flat, step-free surfaces of known composition. The adsorption of atmospheric water at mica surfaces is well known and is believed to be well understood. The adsorbed water films generally give featureless AFM images; however, AFM has been used to induce and locally image capillary condensed water features in contact mode and by scanning polarization force microscopy (SPFM). These SPFM experiments also followed the growth of water films on a freshly cleaved mica surface with increasing humidity. The initially smooth mica surface began to form 2D islands that quickly converted to a featureless layer at ~25% relative humidity (RH). This layer was reported to be significantly less than monolayer on the basis of sum-frequency generation vibrational spectroscopy experiments. With further increases in humidity, a second adsorption regime was identified, with water forming thicker islands on mica. These islands often had polygonal boundaries aligned with the underlying mica lattice and grew together to form a featureless monolayer at >80% humidity.

Here we report the formation of micropatterned, stable, thin water films on mica. These patterned films were formed by microcontact printing of clean, patterned poly-(dimethylsiloxane) (PDMS) stamps on the mica surface at ambient humidity. Microcontact printing (μCP) is a simple technique for creating patterns of molecules on surfaces down to length scales of less than 100 nm. μCP is most often used to stamp patterns of covalently self-assembled monolayers onto surfaces; the most commonly studied systems are alkanethiols on gold and (less frequently) alkylsilanes on silica. Such
covalently bonding systems are relatively insensitive to adsorbed water on the substrate because of the strong interaction between the “ink” and the substrate. For non-covalently bonding inks such as lipids or proteins, however, the strength of water-substrate interactions is comparable to the strength of ink-substrate interactions. μCP of non-covalently bonding molecules, therefore, should depend more sensitively on the presence of adsorbed water. Capillary condensation in the stamp channels has been recognized as a problem in μCP, even for covalently bonding molecules, because of undesired transport of the ink molecules in the condensed-water layer.

This work was motivated by our own preliminary efforts with μCP of lipids and polymers on mica, which revealed a great variability in the fidelity of the stamped patterns. To our surprise, we found that printing with clean patterned control stamps also produced clear patterns on the mica surface. Here we show that these patterns are created by local capillary condensation of atmospheric water in the channels of the PDMS stamp pattern. These thick water films redistribute the naturally occurring potassium ions on the mica surface, creating a long-lived pattern of adsorbed water films of varying thicknesses.

4.2 Experimental Section

PDMS stamps were formed using Sylgard 184 (Dow Corning) on silicon calibration grating masters. The gratings were Silicon-MDT model TGG01 (3 μm pitch, 1.8 μm-tall linear grating), and model TGX01 (3 μm-pitch square grating; squares are 1 μm tall and 1 μm wide). The stamps were cured at ~65 °C for more than 12 h. The
cleaning procedure was as follows: stamps were soaked in distilled, deionized water (Barnstead Nanopure, >18 MΩ·cm) for several hours before being shaken and soaked in methanol for several minutes. They were then dried for more than 1 h at 65 °C, soaked in hexane for >1 h, and finally dried at 65 °C for >1 h. We found that the patterns produced by the stamp were not sensitive to the cleaning procedure; similar results occurred when using only a detergent solution to wash and deionized water to rinse. The replica stamps had diameters of ~2 mm. Care was taken to leave the edges of the grating replicas “open” so that when the stamp was placed on a surface atmospheric gases could freely enter the channels. The replicas have protruding areas that contact the sample and are surrounded by voids, as seen in Figure 4.1. The protruding areas of the square grating in Figure 4.1a are completely surrounded by void space that is open to the atmosphere, and the voids of the linear grating in Figure 4.1c form channels that are open to the atmosphere at the stamp edges.

The water patterns were created simply by placing a clean PDMS stamp onto freshly cleaved mica for 5-15 min. The surface was then imaged by contact-mode AFM (Digital Instruments Dimension 3100) using V-shaped silicon nitride levers with a nominal spring constant of 0.12 N/m. The imaging force was typically 1-2 nN.

RH was coarsely controlled during AFM imaging by flowing dry nitrogen into the AFM chamber to lower the humidity or by flowing nitrogen saturated with water vapor to increase the humidity. To achieve RH ≥ 50%, it was necessary to place beakers of warm water in the chamber. This action typically resulted in a rapid rise in RH to >70%. The
Figure 4.1  a) Tapping-mode AFM image of a PDMS 3 μm-period square-grating replica showing a continuous network of voids surrounding discrete protruding squares. Squares are ~1 μm wide. b) Cross section of the grating in a perpendicular to a protruding square face. c) Tapping-mode AFM image of a PDMS 3 μm-period line-grating replica. d) Cross section of the grating in c).
ambient laboratory humidity varied from ~15-45%; this variation had a large impact on the stamped-pattern contrast. The very low-humidity stampings (<10%) were carried out in a glovebox purged with dry nitrogen or dry compressed air; the stamped surface then was taken to the AFM in a desiccator. The humidity was measured with an Omega HX-93 humidity meter (± 2% accuracy).

Elemental identification of the PDMS stamps was performed by Rutherford backscattering spectrometry (RBS). RBS allows elemental identification of surfaces by measuring the number and energy of backscattered ions from the target sample. The energy of a backscattered ion is proportional to the atomic mass of the near-surface atoms.

4.3 Results and Discussion

When a replica of the 3 μm-pitch square grating (Figure 4.1a and b) is placed on a freshly cleaved mica surface at an ambient humidity of ~25-45%, a pattern similar to that shown in Figure 4.2 is formed. Figure 4.2 shows a contact mode AFM image of the mica surface after a 3 μm-pitch square-grating replica was placed on mica for 15 min at 25% RH. Because the darker areas are the discrete phase, they can be identified unambiguously as the areas of contact between the stamp and the surface (compare Figure 4.1a and Figure 4.2a). Figure 4.1a shows a height difference of 2.5-3 Å between the dark holes where the stamp was touching and the surrounding brighter region. Figure 4.2b shows the lateral force image of the same area, indicating higher friction in the channel regions.
Figure 4.2 Contact-mode AFM image of a mica surface after a 3 μm-pitch square-grating replica was in contact with it for 15 min at 25% RH. a) Height image showing dark squares 2.5 Å lower than the surrounding regions. The squares correspond to the places where the PDMS was touching the mica surface. The height image z-range is 1 nm. b) Friction image showing lower friction region where the PDMS contacted the mica (the friction z-range is 0.1 V).
Similar results occurred for the linear-grating replica (shown in Figure 4.1c and d). Figure 4.3 is a contact-mode AFM image of the mica surface after a PDMS replica of a 3 μm-pitch linear grating was placed on the mica surface for 6 min at 35% RH. The narrow, dark stripes are the regions where the PDMS stamp contacted the mica surface, and the brighter, wider stripes correspond to the capillary channel regions on the stamp. The brighter regions are ~2.5-3 Å taller than the dark stripes or the holes in the bright regions. The image contrast was stable for at least several hours at ambient humidity (~35%). When the imaging force was kept in the ~1-2 nN range, no significant changes in the images occurred. Very high force scanning for several hours, however, created dark “scan squares” (not shown) at the same topographic level as that of the original dark stripes. Stamping times of <5 min at RH = 20-35% produced no easily discernible patterns.

The capillary channel regions, in addition to having higher overall topography than the contact regions, also display “holey” or dewetted appearances in Figure 4.2a and Figure 4.3. This dewetted morphology is not observed in areas of mica outside the stamped regions, which appear featureless and smooth. Structures similar to those in the channel regions of Figure 4.3 have been seen previously by Xu et al.90 In their experiments, the tip of a SPFM was lightly touched to a mica surface under ambient humidity conditions, causing capillary condensation of water around the contact region. This water island was then imaged in SPFM mode. These islands were found to disappear at low humidity (<20%) but occasionally to reappear when the humidity was increased.
Figure 4.3 Contact-mode AFM image of the mica surface after a 3 μm-pitch linear-grating replica was placed on the mica surface for 6 min at 35% RH. The bright regions are 2.5 Å taller than the holes or the dark, diagonal stripes. The dark stripes are where the PDMS was touching the mica surface. The image z-range is 1 nm.
Intriguingly, they reported that these structures could not be imaged in contact mode, perhaps because the relatively stiff (0.58 N/m) tips used for SPFM imaging disturb the water structures. The tips used in our experiments were nearly 5 times softer than the SPFM tips; however, they may still slightly disturb the adsorbed water films. For example, we were unable to observe reproducibly the polygonal boundaries of the water films related to the underlying mica lattice, as previously reported in SPFM images.\textsuperscript{89,90}

If the humidity in the chamber was decreased below 20% RH during imaging, the pattern contrast began decreasing until ultimately no pattern was visible. When the humidity was increased back to \(~35\%\)RH, the pattern became partially visible again, although the stamped patterns were often not as well defined. Figure 4.4 illustrates the effects of prolonged exposure to low humidity on the pattern contrast. In this experiment, the 3 \(\mu\)m-pitch linear grating replica was placed on the mica surface for 15 min at 35\% RH. Figure 4.4a is a contact-mode AFM image captured after directing a stream of dry nitrogen at the sample for \(~5\) min. The image looks similar to the image shown in Figure 4.3, except with a 4-5 Å height difference between the narrow, dark stripes (contact areas) and the wide, brighter stripes (channel areas). After 10 min of exposure to the dry nitrogen stream, however, the contrast is much reduced (Figure 4.4b). The height difference between the dark stripes and the brighter network is now typically 2.5-3 Å. The holes in the bright stripes are also much larger, and the water network is disconnected.
Figure 4.4 Effect of humidity on pattern contrast. A linear grating replica was placed on mica for 15 min at 35% RH to create this pattern. The z-range of both images is 1 nm. a) The contrast is 4-5 Å between the dark stripes and the bright areas. A stream of dry nitrogen was directed at the sample for 5 min before obtaining this image. b) After 10 min exposure to the dry nitrogen stream, the average contrast between the dark and bright areas is reduced to 2.5-3 Å.
Similarly, if the humidity in the chamber was increased to >70%, the pattern contrast also disappeared (Figure 4.5). When the humidity was subsequently reduced to ~35%, the pattern contrast returned. Exposure to humidity greater than ~40%, however, often caused the growth of many large, flat particles in the stamped region. These tablets seemed to nucleate at the edges of the stamp channels during stamping and grow into the contact regions. Figure 4.6a shows ~50-100 nm-wide, 5-10 Å-tall particles (bright specks indicated by arrows) visible at the interface between the dark and bright regions immediately after a linear replica was stamped for 15 min at 35% RH. This sample was subsequently exposed to 69% RH for 10 min and left in a container with ambient humidity of ~30% overnight. The following day the sample appeared as shown in Figure 4.6b. The particles were 200 nm wide and were consistently 1 nm tall. Similar particles have been seen on mica previously\textsuperscript{95} and were believed to consist of a potassium compound that is a reaction product of the surface K\textsuperscript{+} ions and ambient gases. Table 4.1 shows the solubilities of the three possible potassium compounds that may form from reactions of potassium ions with ambient water and carbon dioxide.\textsuperscript{96} Potassium bicarbonate has the lowest solubility and is therefore the likeliest aqueous precipitate.

<table>
<thead>
<tr>
<th>Formula</th>
<th>solubility (M)</th>
</tr>
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<tbody>
<tr>
<td>KOH</td>
<td>20</td>
</tr>
<tr>
<td>K\textsubscript{2}CO\textsubscript{3}</td>
<td>8.0</td>
</tr>
<tr>
<td>KHCO\textsubscript{3}</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Table 4.1 Solubility of Possible Potassium Compounds Formed with H\textsubscript{2}O and CO\textsubscript{2}\textsuperscript{96}
Figure 4.5 Contact-mode AFM image of the same area shown in Figure 4.4. The relative humidity was 63% at the top of the image and 69% at the bottom. The image z-range is 2 nm.
Figure 4.6 Contact-mode AFM images of a mica surface (a) immediately after contact for 15 min at 35% RH (image size 6.3 μm x 6.3 μm) and (b) after surface in (a) was exposed to 69% RH for 10 minutes and then left overnight at ~30% humidity (image size 12 μm x 12 μm). The 0.5 nm-tall, 50-100 nm-wide particles (arrows) that are visible along the dark stripes in (a) grew to 1 nm tall and up to 200 nm wide in (b). The z-range is 1 nm in both images.
It is not immediately apparent why the tablets grow only in the dark regions. A rough volume calculation of the particles of Figure 4.6b shows that they contain only about 5% of the available potassium (2.1x10^{14} potassium ion/cm^2 are available on the mica surface). The central role of mobile surface ions in pattern formation was corroborated by data showing the uptake of potassium by the PDMS stamp. Figure 4.7 shows Rutherford backscattering spectrometry (RBS) of a patterned PDMS grating replica removed from a mica surface after contact for 15 min at ambient humidity (~30%). Two controls are also shown for comparison: a PDMS replica that has never been in contact with mica and a flat (untextured) PDMS pad that was in contact with mica for 2 days. The RBS spectrum shows the clear presence of potassium on the PDMS grating replica that was in contact with mica but not on either of the controls. This result shows that surface potassium ions are clearly transferred to the stamp upon contact, but the transfer mechanism is not simply contact between PDMS and mica. Evidently, a channel structure and water diffusion within the channel are necessary to transport the potassium to the stamp. 

The potassium ions removed from the mica surface by the stamp and those sequestered in the potassium carbonate islands are probably replaced with hydrogen ions from the capillary water layer for charge balance. An X-ray photoelectron spectroscopy (XPS) study of native and ion-exchanged micas has shown that immersion for several minutes in deionized water followed by rinsing is sufficient to completely remove
Figure 4.7  RBS data of line-grating replicas. A clean replica is shown by the black triangles. The red squares show the presence of potassium from a replica that was contacted with mica for 15 min at ~30% humidity. The blue circles are for a flat PDMS stamp placed on mica for two days. This flat stamp had no potassium, implying water in the channels is necessary for potassium transport to the stamp. The bottom plot is a zoom on the region of the RBS spectrum corresponding to potassium. The RBS data was normalized to the silicon energy region just below the surface of the clean grating replica.
potassium ions from the mica surface and presumably replace them with hydrogen ions. In our experiments, the potassium transport to the stamp surface and to the islands may create, to some extent, a locally ion-exchanged mica in the channel regions. Such differences in surface potassium ion concentrations may account for the topographic differences observed in Figure 4.2-Figure 4.4.

To confirm the importance of humidity, stamps were also placed in contact with mica at very low relative humidity (<10%). In these experiments, clean stamps were baked at 70 °C for 15 min and then transferred via a desiccator to a glovebox with RH < 10%. The mica was cleaved at RH < 10% and the stamp was placed on the mica surface for 40 min. The mica sample (with the stamp) was exposed to RH = 42% for <1 min during transfer from the glovebox to the AFM. Images showed no patterns on the mica surface stamped under these low-humidity conditions. The role of mobile surface ions was also confirmed by stamping clean PMDS replicas on oxidized silicon wafers; these experiments produced no visible pattern under dry or ambient conditions. These experiments verify the importance of both water and the redistribution of potassium to the formation of the patterns.

We can also rule out, for several reasons, leached contaminants from the PDMS as the cause for the observed patterns. This explanation is inconsistent with the absence of patterns for dry-atmosphere stamping on mica or for ambient- or low-humidity stamping on oxidized silicon. Moreover, the patterns on mica disappear when the humidity is reduced below ~20% and partially reappear when the humidity is brought back to ~35%. The stamped patterns were insensitive to the stamp-cleaning procedures. Perhaps most
convincing is that the stamp contact regions are topographically lower than the surrounding channel regions, whereas the opposite would be expected if contaminants were leaching out of the stamp. Finally, the mica lattice can be clearly imaged in the contact regions, indicating that the surface is native mica.

Although the contact and channel regions show a striking friction contrast, with the friction higher in the channel regions (Figure 4.2b) than in the contact regions, the reasons for this behavior are not clear at present. On the basis of our model, it would seem that the native potassium mica in the contact regions has lower friction than does the partially hydrogen-exchanged mica in the channel regions. This explanation is complicated by the fact that the higher-friction regions also have a thicker water layer than the lower-friction regions, which alone may account for the difference in friction caused by increased capillary forces or viscous drag. It is not obvious why the channel regions, which are potassium-depleted and partially hydrogen-exchanged, would have a thicker water layer than the contact regions that are composed of native mica. One possible explanation is that the hydration radius of hydrogen ions (9 Å) is larger than that of potassium ions (3 Å). Further experimentation with ion-exchanged micas may shed light on these issues.

4.4 Conclusions

The presence of a stamp with capillary channels can create a long-lived pattern of varying water thickness that is possibly due to a localized exchange of hydrogen ions for potassium ions on the mica surface. Particles believed to be potassium bicarbonate were
observed on the mica surface after stamping and exposure to high humidity; these particles were reminiscent of particles previously seen on mica. The localized water patterns that form should be useful for studying basic wetting processes on mica and confined-geometry chemical reactions or as a template for growth of other structures. Other surfaces with mobile ions should also be able to be patterned in this way, and ambient gases other than water vapor and carbon dioxide may be effective for some surfaces.
CHAPTER 5: DETECTION OF A DIFFUSIVE 2D GAS OF AMPHIPHILES BY LATERAL FORCE MICROSCOPY*

ABSTRACT

Sparsely adsorbed amphiphiles with high surface mobility play a central role in surfactant spreading and in the nucleation and growth of self-assembled monolayers. Here we show that lateral force microscopy (LFM) can directly visualize a gas phase of adsorbed long-chain alcohols and fatty acids. The 2D gas originates from the edge evaporation of dense monolayer domains, transferred to a mica surface by microcontact printing. Monolayer corrals act as 2D containers, eventually saturating the enclosed area with the trapped gas phase. Scratching a small hole in the corral allows the gas to leak out of its container, and monitoring this transport process provides a rough estimate of the surface diffusion constant. Our results demonstrate that friction measurement and mapping can detect amphiphile densities down to 1% of a monolayer, making this technique useful in studying the early stages of monolayer formation.

* This chapter was published as Workman, R. K.; Schmidt, A. M.; Manne, S. "Detection of a diffusive two-dimensional gas of amphiphiles by lateral force microscopy", Langmuir 2003, 19, 3248-3253.
5.1 Introduction

When an adsorbent is immersed in amphiphile solution, the first step in the self-assembly process is the fast adsorption of isolated and non-interacting molecules that can diffuse freely along the surface. Several probe microscopy studies have recently demonstrated that surface diffusion and molecular attachment in this "gas phase" play a central role in the nucleation of condensed islands and the gradual evolution of a coherent self-assembled monolayer. The coexistence of 2D gas and condensed phases during self-assembly has been observed in such disparate systems as alkanethiols on gold, alkylsilanes on silica, and alkylphosphonic acids on mica and sapphire, suggesting that the condensation of a dense monolayer from a 2D gas is a general feature of the self-assembly process. Probe microscopy observations at varying concentrations and temperatures have led to the identification of detailed 2D phase progressions and the quantification of triple points, surface diffusion coefficients, and the minimum island size for monolayer nucleation. Many of these authors have noted surprising similarities between the phase behavior of self-assembled monolayers and that of Langmuir monolayers at air-water interfaces, despite the greater rigidity and stronger interfacial forces associated with solid surfaces.

Amphiphile surface diffusion also controls the spontaneous dewetting of a surfactant solution following its initial wetting of a solid surface, a phenomenon termed autophobing. Recent work has shown that autophobing is caused by rapid surfactant diffusion along a leading precursor film of water (< ~1 nm thick), followed by surfactant adsorption ahead of the visible contact line, thereby creating a hydrophobic barrier.
against spreading.\textsuperscript{117-119} \textit{Ex-situ} condensation figures, combined with ellipsometry, neutron reflectivity and surface force measurements, have led to the identification of several distinct zones of surfactant adsorption density, starting from dense monolayers deep in the solution, to liquid-like expanded monolayers near the contact line, to isolated and randomly oriented molecules in the precursor region.\textsuperscript{119}

In previous work, the diffusive gas phases of adsorbed amphiphiles were invisible to both scanning tunneling microscopy (STM)\textsuperscript{101-103} and atomic force microscopy (AFM),\textsuperscript{104-116} and their presence was inferred from their effects on adjacent (visible) condensed phases. For instance, the continued growth and ripening of condensed alkanethiol domains, observed \textit{after} shutting off the flow of new adsorbates from the environment, implied the slow diffusion of a surface gas phase and attachment at island edges.\textsuperscript{102,106} Surface diffusion constants and minimum stable islands have been calculated from a quantitative analysis of monolayer island sizes as a function of time.\textsuperscript{113,115} Although the imaging of isolated, \textit{strongly} adsorbed molecules is routine by STM and achievable by noncontact AFM,\textsuperscript{120,121} the detection of weakly adsorbed and diffusive molecules at ambient conditions poses a greater challenge. While other techniques (e.g., fluorescence probes and reflection interference contrast microscopy) can probe 2D diffusivity in liquid-like films such as lipid monolayers and bilayers, applying these to lower-density gas phases seems problematic.

Here we show that lateral force microscopy or LFM\textsuperscript{122,123} (also known as friction force microscopy or FFM) can detect a 2D gas phase of adsorbed amphiphiles. The gas originates from the 2D evaporation of dense monolayer domains of docosanol transferred
to a mica surface by microcontact printing, similar results have been achieved also with stearic acid and stearylamine. LFM image analysis allows us to quantify the effective surface coverage by the measurement of a relative friction coefficient, as described below. Finally, scratching a small opening in a previously enclosed and vapor-saturated area enables us to monitor surface diffusion in real time as the gas phase leaks out of this area.

5.2 Experimental Details

The gas-phase saturation of monolayer corrals was discovered while investigating the molecular transfer of alkyl derivatives onto mica by microcontact printing. Polydimethylsiloxane (PDMS) stamps were fabricated using Sylgard 184 compound (Dow Corning) on a commercial grating master (Silicon-MDT model TGG01), resulting in linear stamps with a 3 µm pitch. The detailed stamp topography and extensive cleaning procedure have been described previously. Stamps were inked in 860 µM solutions of docosanol in toluene for 30 s and were stamped on freshly cleaved mica for 30 to 300 s. Uneven transfer across the stamp area, combined with cross-channel monolayer bridges due to fingering, occasionally created enclosed and isolated monolayer corrals. These corrals were imaged over several hours in ambient air (relative humidity 20±3%), using a commercially available AFM/LFM system (Digital Instruments, Dimension 3100) and V-shaped silicon nitride cantilevers of stiffness ~0.3 N/m. Constant-force imaging was performed using the following typical scan parameters: scan angle 90°, scan rate 2 to 3 Hz, and imaging force 1 to 3 nN. Adsorbed
amphiphile gases were observed in at least five independent experiments, all using different cantilevers.

5.3 Results and Discussion

For short stamping times (~30 s), the docosanol transferred as isolated islands, elongated parallel to the stamp channels, as shown in Figure 5.1a and b (AFM and LFM images of the same area). The two prominent monolayer regions of Figure 5.1a and b show similar morphologies—a long central island, from which fingers of docosanol spread outward, connect with neighboring bars, and then spread parallel to these bars. This complex motif (typical of short stamping times) suggests radiative diffusion from a point-like source in the stamp, to be discussed in a future publication. Here we simply note that the fingering instability occasionally creates enclosed monolayer corrals, four of which are visible in Figure 5.1a and b. The transferred features show much lower friction than the mica substrate (Figure 5.1b), indicating the transfer of a docosanol monolayer with the OH group facing the mica and the hydrocarbon chain facing outward. The measured heights of the transferred features (1.8 ± 0.3 nm) fall short of the calculated length of docosanol (2.9 nm), to the same degree as observed with other self-assembled monolayers. These discrepancies have been attributed to chain tilt and monolayer compression by the nonzero imaging force.
Figure 5.1  a) and b) Respective AFM and LFM images obtained 15 minutes after the transfer of docosanol to a mica surface by microcontact printing. Although the stamp consists of regularly spaced bars with a 3 μm periodicity, docosanol monolayers (bright islands in a) and dark islands in b) appear only occasionally. Four completely enclosed corrals are visible, three in the left transferred pattern and one in the right. The interiors of these corrals are indistinguishable from their exteriors in both images. c) and d) Respective AFM and LFM images of the left pattern from a) obtained 21 h after the transfer. The intact corrals (1 and 2) now show distinct LFM contrast between the interior and exterior. The arrows show the corral segment which is cut in Figure 5.2. Image sizes are 50 μm for a) and b) and 15 μm for c) and d); z-ranges are 5 nm for a) and c), 100 mV for b), and 200 mV for d).
Figure 5.1a and b show that, shortly after stamping, the areas enclosed by the monolayer corrals are topographically and frictionally indistinguishable from the exterior, indicating the presence of bare mica in both regions. Over the next several hours, however, corral interiors show increasing frictional contrast from the exteriors, eventually developing a spatially uniform friction value *intermediate* between the low-friction boundary and the high-friction exterior. (This occurs whether or not the initial sample area is scanned by AFM during this intervening time, and it occurs also in sample areas far from the initial scan area, indicating that the effect is not tip-induced.) The intermediate friction contrast is illustrated in Figure 5.1c and d, which show a close-up of three corrals from Figure 5.1a and b, 21 h after the stamping. Corrals 1 and 2 remain enclosed, whereas region 3 has developed a small (~100 nm) opening due to monolayer rearrangement and 2D evaporation. Correspondingly, *only the interiors of corrals 1 and 2 exhibit intermediate friction*, whereas region 3 is frictionally indistinguishable from the mica substrate. Although a very slight topographic contrast could sometimes be observed between corral interiors and exteriors, this was always much less pronounced than the frictional contrast and was in many cases unobservable.

To further test whether a complete enclosure was necessary for frictional contrast, we deliberately scratched an opening in corral 1 by scanning at high force at the position indicated by the arrow in Figure 5.1c and d. As shown in Figure 5.2, the area formerly enclosed by corral 1 in time reverts to the higher friction typical of mica, whereas the adjacent corral 2 (still intact) retains lower friction in its interior. The evidence therefore points to a diffusive, hydrophobic, and low-density surface phase that can be trapped by
corrals but becomes infinitely diluted by the large substrate area once a diffusion path is provided. The obvious candidate for this surface phase is mobile docosanol molecules created by 2D evaporation of the monolayer islands.

Such a process is expected to involve two distinct steps: the detachment of an individual molecule from the edge of the monolayer, followed by random diffusion of the molecule on the mica surface. Several lines of evidence suggest that detachment from the monolayer is the rate-limiting step. First, the “filling” of monolayer corrals with the 2D gas requires >3 h after stamping, whereas the “emptying” of corrals is largely complete <0.5 h after scratching an opening (see below). Second, monolayer edges adjacent to open areas always show a sharp change in friction between the monolayer and mica, with no evidence of an intervening 2D gas, suggesting that molecules diffuse quickly once detached. Third, the intermediate friction inside a corral is spatially uniform throughout the corral, again indicating rapid diffusion and mixing after detachment. This uniformity may be violated for a short time after scratching an opening; Figure 5.2a shows a darker patch near the newly created opening that suggests a higher docosanol concentration at that location, probably due to by partial “vaporization” of monolayer during the scratching process. However, the concentration evens out again in ~0.5 h (Figure 5.2b and c).
Figure 5.2 LFM data (selected from a sequence of 15 images) showing the diffusion of trapped adsorbate through a cut, which was created by scanning at high force over the corral 1 segment indicated by arrows in Figure 5.1. a) 16 minutes after the cut, the amphiphile gas has begun to diffuse past the original border (arrow). b and c) 66 and 244 minutes (respectively) after the cut, the friction contrast between the exterior and (former) interior has diminished considerably. However, the contrast is still measurable by suitably averaging the signal over each region, as shown in the section box. The signals e, f, and g, corresponding respectively to mica, monolayer and amphiphile gas, are obtained by averaging across the width of the box (dotted lines). d) Section profile along the length of the box, where each point in the profile is obtained by averaging across the width of the box in c). Although the friction contrast between interior and exterior is barely visible in the LFM image, it is clearly resolved and quantified by the averaged section. Image sizes are 6.0 \( \mu \text{m} \) for a) and 10 \( \mu \text{m} \) for b) and c); the z-range is 100 mV for all images. The substrate region of each image was manually flattened and planefit to remove overall tilt; artifacts were avoided by carefully excluding the corral region from the flatten and planefit procedure.
The area fraction and diffusivity of the 2D gas can be estimated directly from the LFM images. In earlier work, Peach et al. quantified the fractional surface coverage $X$ of spatially homogeneous submonolayer films by the measurement of friction loops. In this work, the presence in a single LFM image of bare mica ($X=0$), solid monolayer ($X=1$) and 2D gas ($X$ unknown) simplifies the analysis and allows us to calculate $X$ directly from averaged image sections (Figure 5.2d). Assuming that friction is proportional to normal force, the LFM signal $f = K\mu N$, where $\mu$ is the coefficient of friction, $N$ is the imaging force, and $K$ depends on instrumental factors such as optical lever magnification and photodiode sensitivity. Accordingly, the change in friction signal between mica and the monolayer, and that between mica and the 2D gas (see Figure 5.2d), may respectively be expressed

$$\Delta f_1 = K(\mu_{\text{mica}} - \mu_{\text{monolayer}})N$$

$$\Delta f_2 = K(\mu_{\text{mica}} - \mu_{\text{gas}})N.$$ 

The 2D gas may be approximated as a partial monolayer whose nonpolar chains occupy an area fraction $X$ of the corral interior. The frictional force due to the 2D gas is therefore

$$\mu_{\text{gas}}N = X\mu_{\text{monolayer}}N + (1 - X)\mu_{\text{mica}}N.$$ 

Using this in the expression for $\Delta f_2$ gives

$$\Delta f_2 = KX(\mu_{\text{mica}} - \mu_{\text{monolayer}})N,$$

from which

$$\frac{\Delta f_2}{\Delta f_1} = X.$$
To first order, therefore, the ratio of the two differences in friction signal (from mica to monolayer and from mica to amphiphile gas) is the fraction of the enclosed area taken up by nonpolar chains during imaging. It is important to note that $X$ is the area fraction of alkane coverage and not the number density relative to the monolayer. This is because an isolated chain can adopt a prone conformation (especially as the imaging tip scans over it), making its area coverage many times that occupied by a chain in a dense vertical monolayer. Assuming that the chain conformation is strictly horizontal in the gas phase, the adsorbate number density relative to the monolayer is

$$\frac{\sigma_{\text{gas}}}{\sigma_{\text{monolayer}}} = \frac{X / a_{\text{horizontal}}}{1 / a_{\text{vertical}}} = 0.14X$$

where the projected areas for horizontal and vertical orientations were calculated directly from Tanford’s formulas.\(^{127}\)

Figure 5.3 shows the time evolution of the area fraction $X$ in corral 1, as calculated from $\Delta f_1$ and $\Delta f_2$ values measured in the averaged sections illustrated in Figure 5.2c and D. The surface coverage in corral 2 is also shown for comparison. Both corrals start from an amphiphile area fraction of around 0.35 (or a number density ~5% of a monolayer), corresponding to an average occupation area $a_{\text{gas}} = 3.4 \text{ nm}^2$ per molecule. The 2D saturation vapor pressure $\Pi$ for docosanol on mica can now be calculated from $\Pi a_{\text{gas}} = k_B T$ (where $k_B$ is Boltzmann’s constant and $T$ is temperature). The result $\Pi \approx 10^{-3}$ N/m is somewhat larger than the range of surface vapor pressures measured for Langmuir monolayers at the air-water interface.\(^{129}\)
Figure 5.3  Plot of the surface coverage $X \approx \Delta f_2/\Delta f_1$ vs. time for corral 1 (open circles) and corral 2 (closed circles) from Figure 5.2. Values of $\Delta f_2$ and $\Delta f_1$ for each image were determined from averaged sections along the section box illustrated in Figure 5.2c and d.
 Whereas the surface coverage of the intact corral 2 remains constant, that of corral 1 decreases quickly in the ~0.5 h after scratching an opening and much more slowly thereafter. We believe that the initial decrease is due to the diffusion of the original amphiphile gas, and the leveling-off is due to further monolayer evaporation caused by a sudden drop in the 2D gas pressure. A careful comparison of the images in Figure 5.2 shows definite signs of new monolayer evaporation, mainly the necking down and pinching off of dendritic fingers formerly enclosed by the corral. (Some of the new evaporation could also be tip-induced, although it is then difficult to understand why a similar evaporation is not observed at the outer boundary of the corral.) Assuming that the initial drop in surface coverage is due to pure surface diffusion, we can estimate a rough value for the diffusion coefficient $D$. Using the simplest applicable model, we can approximate the corral as a small source of length $l$, from which molecules diffuse unidirectionally outward in 1D. Letting $n(t)$ be the number of molecules in the source region as a function of time, the solution to Fick's Law for 1D diffusion out of a point-like source yields a source concentration

$$\frac{n(t)}{n_0} = \frac{1}{\sqrt{\pi D t}},$$

where $n_0$ is the initial number of molecules in the source. Rearranging gives

$$\frac{n(t)}{n_0} = \frac{X(t)}{X(0)} = \frac{l}{\sqrt{\pi D t}}.$$

The points corresponding to the initial drop in $X(t)$ in Figure 5.3 yield a good fit for a $t^{1/2}$ dependence, and the fit parameter (along with the corral length $l = 3.7 \, \mu m$) gives a diffusion coefficient $D \approx 0.003 \, \mu m^2/s$. By contrast, the Stokes-Einstein expression yields
a self-diffusion coefficient six orders of magnitude larger in bulk liquid. The smaller value at the surface is consistent with greater confinement and with attractive forces between molecules and surface sites.

Because of the many approximations used above, this value of $D$ should only be considered an order-of-magnitude estimate, one which is undoubtedly affected by environmental factors such as temperature and relative humidity (here 28 °C and 20% respectively). Nevertheless, it is instructive to compare $D$ to other values measured for similar systems. Reported values of surface diffusion coefficients include ~0.3 μm²/s for octadecylphosphonic acid on mica during solution-phase self-assembly; 112,113,115 ~1 to 10 μm²/s for lipids in supported bilayers in aqueous media; 131-133 and ~0.1 to 1 μm²/s for lipids in supported bilayers in air at 55% relative humidity. 134 These values are understandably larger than that reported here, because solvent environments and high humidity impart greater mobility to adsorbed molecules. An experimental situation more analogous to ours is a recent report by Salmeron et al. 106 showing the slow ripening (in air) of hexadecanethiol monolayer islands on gold, mediated by the surface diffusion of a fixed quantity of hexadecanethiol adsorbed as a 2D gas. Although they do not report a value for $D$, an order-of-magnitude estimate of ~10⁻⁶ μm²/s can be calculated from the change in island size (~200 nm in 24 h). Our estimate of $D$ for docosanol on mica therefore falls in the appropriate range—larger than for alkanethiols on gold in air (characterized by strong molecule-surface interactions), but smaller than for solvent-mediated surface diffusion.
In addition to docosanol, 2D gas phases were also observed with stearic acid and stearylamine corrals transferred to mica, indicating the generality of this phenomenon. Unlike the docosanol corrals, the stearic acid and stearylamine corrals became saturated with the gas phase within a few minutes of the pattern transfer, indicating a much faster evaporation rate for these shorter-chained molecules. Figure 5.4 shows AFM and LFM images near the edge of a stamped pattern of stearic acid, where enhanced fingering causes frequent bridging of stearic acid monolayers across neighboring stamped bars. The resulting labyrinthine pattern contains several enclosed corrals, as well as many regions that are nearly enclosed. A careful comparison of Figure 5.4a and b reveals that all identifiably enclosed regions exhibit the “intermediate friction” signal associated with a gas phase, whereas all identifiably open regions lack this contrast. (Many regions cannot be unambiguously classified as closed or open, owing to the finite image size.) In some cases, even tiny openings (~30 nm) are enough to render an almost-enclosed region frictionally indistinguishable from mica. In all cases, the gas phases in enclosed corrals are invisible to AFM.

Why do sparsely adsorbed amphiphiles exhibit such high contrast in LFM but not in AFM? The explanation almost certainly involves the orientational freedom of the tailgroups in the gas phase, giving them a dominant horizontal orientation as they are scanned by the AFM tip. The friction associated with a layer of horizontal alkane chains is similar to that for a vertical layer; the frictional difference between methylene and methyl groups is small compared to the contrast with the hydrophilic mica surface.
Figure 5.4  a) and b) Respective AFM and LFM images of stearic acid monolayers on mica, showing labyrinthine patterns near the edge of a stamped region. Every identifiably closed corral (e.g., region 1) shows intermediate friction in its interior. Every identifiably open region (e.g., region 2, which has a small opening indicated by the arrow) shows the same friction signal as the mica substrate. Image sizes are both 30 μm; z-ranges are 3.0 nm for a) and 200 mV for b).
Thus the LFM contrast between mica and a docosanol monolayer can essentially be achieved by a sparse horizontal layer with a number density only 14% that of the monolayer (from Eq. (6)). For low adsorption densities, therefore, the AFM height contrast is essentially magnified by a factor of $(0.14)^4 \approx 7$ in the LFM friction contrast. Judging from the noise level of Figure 5.2d (sections a and c), it should be possible for LFM to detect surface coverages down to $X_{\min} \approx 0.04$, corresponding to a number density only $\sim 0.6\%$ that of a vertical monolayer.

5.4 Conclusions

We have shown that LFM can detect low-density, diffusive films of amphiphilic molecules and can monitor their collective diffusion on the substrate. Monolayer corrals of docosanol and stearic acid, transferred to mica by microcontact printing, evaporate and trap their own saturated gas phase. LFM images in air reveal high friction outside the corral (bare mica), low friction on the corral boundary (amphiphile monolayer), and intermediate friction inside the corral, corresponding to the amphiphile gas. Assuming that the LFM signal inside the corral was a weighted average of the alkane and mica values, we calculated values for the surface coverage that compared reasonably with the expected surface vapor pressures of Langmuir monolayers. Scratching an opening in a corral allowed us to monitor the surface coverage as a function of time and estimate the surface diffusion constant. More quantitative measurements, using designed corrals of different shapes and sizes, are planned in the future.
CHAPTER 6: MOLECULAR TRANSFER AND TRANSPORT IN NON-COVALENT MICROCONTACT PRINTING

ABSTRACT

Microcontact printing is commonly used to create patterned films of molecules covalently bonded to substrates (e.g., thiols on gold). Here we describe microcontact printing of several types of non-covalently bonding molecules on mica. Due to the weaker interaction of the molecules with the substrate, environmental factors such as temperature and relative humidity play an important role. The vapor pressure of the inks also had a large impact on the fidelity of the stamped patterns. Fingering instabilities were observed for monolayers of octadecanol, docosanol, stearylamine, and stearic acid stamped at moderate relative humidity. The strength of the ink-surface interaction and the fidelity of the stamped pattern generally increased with the headgroup-surface contact area. These stamped monolayer films shed light on molecular transfer and two-dimensional spreading mechanisms.

6.1 Introduction

Microcontact printing is a simple way of depositing a patterned monolayer of molecules on a surface. A patterned elastomeric replica is inked with a solution of the desired molecules and briefly placed in contact with a sample, leaving behind the desired pattern of ink molecules. This technique has been used to pattern surfaces in
technological applications such as ultrathin resists,\textsuperscript{137} templated crystal growth,\textsuperscript{138,139} and controlled wetting.\textsuperscript{35}

Microcontact printing of covalently bonding molecules such as alkanethiols on gold\textsuperscript{136,140,141} and other metals\textsuperscript{142,143} and alkyl silanes onto silicon\textsuperscript{94,144-146} have been extensively studied. As the size of stamped features were reduced below \( \sim 1 \ \mu \text{m} \), effects due to the nature of the ink\textsuperscript{140} and the stamp\textsuperscript{147} were found to be important, which led to a general interest in the mechanism of transfer of the molecules from the stamp to the surface. There are many paths ink molecules may take during stamping\textsuperscript{140} (see Figure 6.1). This is a complicated system dependent on temperature and humidity, as well as ink, stamp and substrate intermolecular forces. The effect of humidity on molecular transfer processes has also been observed in dip pen nanolithography,\textsuperscript{148,149} where these effects have been actively explored.

Stamping of non-covalently bonding molecules to surfaces has been relatively unexplored, with the notable exceptions of lipid bilayers\textsuperscript{3-6} and proteins.\textsuperscript{4,7-10} The relatively weak interaction between non-covalently bonding molecules and surfaces allows one to investigate phenomena such as monolayer film spreading,\textsuperscript{150,151} precursor films,\textsuperscript{117,152,153} and surface diffusion.

Here we have studied microcontact printing of several long-chain fatty acids, long-chain alcohols, and an alkane, alkylamine, alkanethiol, lipid and a triglyceride on mica. Mica was used because it is a well-characterized atomically smooth model surface. The various ink molecules were selected to investigate the headgroup-surface interactions while keeping similar tailgroup interactions.
Because environmental factors were found to play an important role, the effects of humidity, temperature and (in some cases) ink concentrations were investigated. The headgroup was found to have the strongest effect on the patterned films. Molecules without a polar headgroup (alkanes) did not stamp at all onto mica; all molecules with a polar headgroup did stamp, and the fidelity of the stamped pattern generally improved with increasing headgroup area. Relative humidity, and therefore the amount of adsorbed water on the mica surface, was found to have a strong effect on the stamped pattern. For example, some types of molecules transferred to the surface under ambient humidity, but virtually no transfer occurred under very dry conditions. Surface water drastically decreased the sticking coefficient of vapor phase transported molecules and often prevented the direct transfer of molecules from the stamp contact area to the surface. Instead, many types of ink molecules were transported from the stamp along a water meniscus. Water meniscus transport resulted in a fingering instability,\textsuperscript{152,154-157} for some molecules under moderate humidity conditions, but never for dry conditions.

The effect of temperature was investigated for an alkane, alcohol and a triglyceride. The vapor pressure of the ink molecules was also found to play an important role in the fidelity of the stamped patterns, consistent with the experiments of alkanethiols on gold.\textsuperscript{140}
Figure 6.1 Schematic of the possible paths ink molecules take from the stamp to the surface (see also Delemarche et al.\textsuperscript{140}). Ink molecules are represented by the red dots and water in blue. Path "v" represents vapor phase transport from the stamp surface, path "m" is along a capillary-condensed water meniscus, and path "t" is transfer directly from the stamp to the surface in the contact region. The contact region is the area where the stamp makes contact with the surface and the channel region is the area between the contact regions.
6.2 Experimental Section

Sample Preparation and Characterization: Poly(dimethylsiloxane) (PDMS) stamps were formed using Sylgard 184 (Dow Corning) on a silicon calibration grating master (Silicon-MDT model TGG01, 3 μm pitch, 1.8 μm tall linear grating). All stamps were cured at ~65 °C for more than 12 hours. The cleaning procedure was as follows: soaking in distilled and deionized water (Barnstead Nanopure, >18 MΩ-cm) for several hours, then shaking and soaking in methanol for several minutes and then drying for more than 1 hour in air at 65 °C, followed by soaking in hexane for > 1 hour, and finally drying at 65 °C for > 1 hour. The stamp area was roughly 1.75 mm². In all experiments, stamps were inked by immersing in toluene or ethanol solution for 30 seconds. The stamp was blown dry under a stream of N₂ for 30 seconds immediately after removing from the inking solution. The stamps were then left at room temperature for at least 1 hour before stamping to assure the stamp surface was free of solvent. Stamps were placed by hand on freshly cleaved mica and left under its own weight. Stamps that didn’t appear to “wet” the surface were gently tapped on top with tweezers.

Tetracosane (>99%), 1-Hexadecanol (99%), tristearin (>98%), stearic acid (~99%) (Fluka), 1-Tetradecanol (97%), 1-Octadecanol (99%), 1-Docosanol (98%), and octadecylamine (97%) (Aldrich) were used as the ink molecules. Toluene (Mallinckrodt AR grade), Ethyl Alcohol (Aaper Alcohol and Chemical, “Absolute – 200 proof”), and Nanopure water (>18 MW-cm) were the solvents used to make the inking solutions.
Atomic force microscope images were captured using a Dimension 3100 (Digital Instruments, CA) using silicon nitride probes with a quoted nominal spring constant of 0.12 N/m. Friction measurement sensitivity was the default 1V/V, with a scan angle of 90 degrees. Images larger than ~25 x 25 μm typically required a 3rd order plane fit and a 1st order flatten. Laser interference from the mica surface occasionally caused large-scale features that were removed using FFT filtering. Care was taken not to modify any features associated with the stamped patterns.

Low temperature stamping and imaging was achieved with a custom built heating/cooling stage, described previously. The low to moderate humidity stamping (RH = 11-51%) was done in the local laboratory environment and the very low humidity stamping (RH <10%) was done in a chamber purged with dry air. Mica samples were cleaved in the dry chamber for low humidity experiments. Temperature was measured with a 100Ω platinum RTD and relative humidity was measured with an Omega Engineering HX93 (accuracy ±2%).

6.3 Results

More than 40 experiments were performed, and most experiments showed some variations in the stamped pattern morphology across the ~1 mm diameter stamped region. For each stamping location, several ~100 μm sized areas were scanned, and the area with the most common morphology were picked for further images. The results presented here represent the overall trends in non-covalent stamping as a function of temperature, humidity, headgroup, and chain length.
We will first present results by organized by headgroup, then discuss general trends in the discussion section.

Stamping alkanes. In contrast with the amphiphiles discussed below, we never observed coherent monolayer films of alkanes stamped onto any substrate. We attempted to stamp 9.2 mM tetracosane (melting point 51 °C) in toluene onto mica. Several 30 second and one minute stampings were tried on mica at room temperature with a relative humidity of 32-36% with no lines visible in height or friction. To see if chain mobility was important, we next tried heating a thin stamp inked with 9.2 mM tetracosane to 70 °C, and then contacting freshly cleaved mica mounted on a sample puck to the hot stamp for less than 5 seconds. Again, no lines were visible on the mica surface. To assure tetracosane was actually on the stamp, a stamp was immersed in molten tetracosane followed by blowing the excess tetracosane off with a stream of dry nitrogen. The resulting stamp was very difficult to place on the mica surface due to a greater attraction between the tweezers and the stamp vs. the stamp and the mica and required many attempts. Finally, a large downward force with a second pair of tweezers left the stamp on the surface. This crude process left many visible chunks of tetracosane on the surface; however, no lines were visible in the AFM images.

As a final attempt, we also tried stamping tetracosane onto other substrates. A 1 minute 15 second and 1 minute 30 second stamping of 9.2 mM tetracosane on a polystyrene surface at room temperature and 60 °C, respectively, showed no lines. A two minute stamping on MoS₂ also showed no lines. A 9 minute stamping at 65 °C on
graphite revealed extremely faint lines in friction, but nothing visible in height (not shown).

**Stamping long-chain alcohols**

Long-chain alcohols stamped onto mica under ambient humidity. The fidelity of the patterns increased with increasing chain length. Spreading seems to occur by fingering, with increased mobility with decreasing chain length. The spreading only occurs during stamping, with little or no spreading (except for surface diffusion) after stamping.

**Docosanol:** Docosanol stamped from an 860 μM toluene solution at room temperature for 5 seconds showed monolayer islands that spread out along the contact edges and into the channels (Figure 6.2). The green lines drawn on Figure 6.2a represent the stamp contact regions. Each of the individual islands was apparently created by a localized docosanol source on the stamp. The ~2 nm tall stamped features show lower friction than the mica substrate (Figure 6.2b), suggesting the docosanol monolayer is oriented with the OH group facing the mica and the hydrocarbon chain facing upward.

The 5 seconds of stamp contact is not enough time for many of the spreading fronts to reach across the channel or spread under the contact regions, however, a 30 second stamping provides ample time (Figure 6.3). Each source spread from the surface of the stamp channel along a capillary-condensed water meniscus to the mica surface. This docosanol film on the meniscus soon developed a surface tension driven fingering instability that rapidly spread across the channel towards the opposite contact region (see discussion). In most cases a long central finger extended all the way to the adjacent
Figure 6.2  860 μM docosanol stamped for 5 sec at 18% RH a) 45 μm height image, 5 nm z-range. b) Friction image of area in a), 100 mV z-range.
contact area and spread along neighboring stamp contact areas (Figure 6.3b). The
docosanol also simultaneously spread along the local contact region, and additional
fingering instabilities developed and spread outward.

Careful examination of the isolated three- or (occasional) four-bar features in
Figure 6.3 reveals the details of their formation. A long central bar is connected to
shorter adjacent bars by a single finger located midway along its length. The central bar
has fingers extending outwards all along its length, but the size of the fingers decreases
towards the ends of the bar, and the bar typically splits into “rails” at the ends. These
attributes indicate a central localized source of docosanol spread quickly along the central
contact edges and somewhat more slowly under the contact region, leaving the rails at the
ends. The central finger also spread quickly to the adjacent contact edges, and provided
the sole source of molecules to form the adjacent bars.

A longer stamping time of 5 minutes, shown in Figure 6.4, created continuous lines
that appear to be a continuation of the process seen in Figure 6.2 and Figure 6.3. Here
the spreading docosanol sources have traveled far along the contact edges, forming
“rails” on either side of the stamp contact region. Extensive fingering crossing the
channels also has provided molecules to spread along adjacent rails.

Stamping under very dry conditions (<1% RH) gave very little transfer of
docosanol, even for stamping times of 30 minutes (Figure 6.5). A typical 100 μm scan
contained only two such small islands, suggesting the docosanol OH headgroup
Figure 6.3 860 μM docosanol stamped for 30 sec at 18% RH a) 90 μm height image shows partial lines 2.3 nm tall, with some spreading from the edges (see discussion) (z-range 3 nm). b) 25 μm zoom on the lines in the upper left of a), 4 nm z-range.
Figure 6.4  860 μM Docosanol stamped for 5 minutes at 19% RH. (25 μm image, 5 nm 2-range).
Figure 6.5  100 μm height image of 860 μM docosanol stamped for 30 minutes at < 1% RH (z-range 4 nm).
interaction with dry mica is not as strong as the docosanol-docosanol and docosanol-
stamp interaction. Additionally, it can be inferred from Figure 6.2 - Figure 6.5 that the
docosanol ink is not homogeneously distributed on the stamp surface.

Octadecanol: Repeated attempts were made to stamp up to 1 mM octadecanol in
toluene at room temperature, but no lines were found. However, 10 mM inks did produce
lines that spread quickly during stamping (Figure 6.6). In some cases, stamped lines met
in the channel region after only 5 seconds stamping time (Figure 6.6b and Figure 6.6c).
The very irregular edges of the 30 second stamping lines (Figure 6.6a) compared to the 5
second stamping lines are not understood. One curious feature of the 5 second and 1
second lines is the asymmetry of opposite edges of a stamped line. It appears as if the
spreading occurred from one edge of the stamp contact line and not the other. It is also
not understood why higher concentration ink was necessary to produce lines of
octadecanol compared to the other long chain alcohols.

Hexadecanol: Stamps inked with 300 μM hexadecanol in toluene stamped for 60
seconds under ambient conditions (27 °C, RH 28%) produced wide, low contrast lines on
the mica surface (Figure 6.7a). The hexadecanol in the contact regions was comprised
primarily of islands with an apparent height of 4 Å, whereas the hexadecanol islands in
the non-contact regions were typically 2 Å above the background. A low friction contrast
between the island and inter-island regions suggest the presence of hexadecanol
molecules throughout the stamped region (friction image not shown), consistent with
vapor phase transport from the channels during stamping and surface diffusion, as was
Figure 6.6  

a) 10mM octadecanol stamped for 30 seconds at 24 °C, RH = 20% 25 μm region.
b) 5 second stamping of 10mM octadecanol with stamp previously used for a 30 second stamping (27 °C, RH = 20%), 13.7 μm region.
c) Same stamping as in b) in a different 13.7 μm region.
d) 1 second stamping of 10mM octadecanol with same stamp as in b) and c) (13.7 μm region). All images have a height scale of 5 nm.
seen for hexadecanethiol on gold\textsuperscript{140} (see discussion for details). There were no low friction contrast patches or islands between the stamped lines of octadecanol or docosanol.

To observe the effects of temperature on the surface diffusion of the hexadecanol, the mica surface was cooled to 6 °C and then stamped for 30 seconds. The surface was subsequently imaged at 6 °C, showing narrow lines comprised of 1.5 – 1.7 nm tall tablets of hexadecanol (Figure 6.7b). Friction images (not shown) revealed a high coverage of low contrast islands between the stamped lines, not visible in the height image. The presence of islands in between the stamped lines in both the room temperature and low temperature stamping is consistent with vapor phase transport of the hexadecanol ink from the stamp surface.

**Stamping fatty acids.** Stearic acid (C\textsubscript{18}OOH, melting point 69 °C) stamped from a 1mM ink gave an almost completely spread monolayer on the first 30 second stamping (Figure 6.8a), and highly spread lines on the second 30 second stamping (Figure 6.8b). The decreased coverage in the center of the contact areas in Figure 6.8b suggests that the transfer of molecules to the surface begins near the contact edges, then spread both outward into the channel and inward under the contact area. The quantity of ink present on the stamp has a clear impact on the stamped patterns,\textsuperscript{140} as illustrated by the first and second stamping images of stearic acid (Figure 6.8a and Figure 6.8b) and octadecanol (Figure 6.6).
Figure 6.7  a) Hexadecanol on mica stamped for 60 seconds and imaged at room temperature and b) stamped for 30 seconds at 6 °C and imaged at 6 °C. z-range is 1 nm for a), 5 nm for b). Both images are a 25 μm region.
Figure 6.8  a) First 30 second stamping of 1mM stearic acid (50 μm image, height scale 3 nm) (RH = 38%). b) Second 30 second stamping of 1mM stearic acid (RH = 38%, 25 μm image, height scale 3 nm).
Stamping under dry conditions (RH = 2%) for 30 seconds yielded a different morphology. Though imaged under an ambient humidity of 37%, the lines in Figure 6.9a show comparatively little spreading and no fingering. The dry stamped lines have many small (~35 nm) islands of stearic acid in between the lines. This island morphology was not seen in the ambient (RH = 35%) stamping. Figure 6.9b is an image of the same sample as Figure 6.9a 19.5 hours later (at ~35% humidity). There are fewer small islands in the channel regions and the size of the large islands is greater after 19.5 hours (compare Figure 6.9a and Figure 6.9b). The growth of the large islands is apparently at the expense of the solid contact regions in Figure 6.9a, as the total surface coverage remains constant, which also implies the stearic acid molecules do not escape the surface after stamping. A comparison of the width of the stamped lines in Figure 6.9a and Figure 6.9b reveals an increase of ~100 nm in the 19.5 hours between the images, however, it is not understood why the edges of the contact region remain solid after 19.5 hours while the center of the contact region becomes depleted. Figure 6.9c further illustrates the 2D diffusion of stearic acid after 19.5 hours. The stearic acid line at the edge of the stamped pattern (lower left) has partially evaporated out to the semi-infinite mica surface, eroding its outer edge, whereas its inner edge remains intact due to the confinement of gas phase stearic acid on that side.

The striking difference between the dry and moderate humidity stamping illustrates the role of surface water and capillary-condensed water during stamping. The edges of the lines stamped under dry conditions remain straight even after 19.5 hours in 37% humidity; in contrast to the lines stamped in 38% RH for 30 seconds that show
fingered spreading. The low humidity stamped lines show an even coverage of islands between the stamped lines consistent with vapor phase transport; however the 38% humidity stamping showed no evidence of islands between the lines; because the flux of stearic acid to the surface is the same in both cases, the sticking coefficient of stearic acid must be lower or the surface diffusion is more rapid in ambient humidity.

**Stamping triglycerides.** Tristearin stamping on mica was studied extensively. A relatively low concentration of 200 µM in toluene was found to stamp very well at low humidity (~10%). Figure 6.10a and Figure 6.10b show solid bars of tristearin with slightly scalloped edges. The third 30 second stamping (Figure 6.10c) using the same stamp showed holey bars, with the holes going all the way to the mica substrate (supported by the friction image and depth measurements).

Tristearin stamped at moderate humidity (~24%) showed decreased coverage of the stamped lines, changing from solid bars to “dotted bars”, illustrated by Figure 6.11. The lines here are primarily comprised of ~25 nm diameter islands, with the island density higher at the edges of the lines. Each of the islands appears dark (low) in friction, surrounded by the same higher friction value as between the lines.

High humidity (~51%) stamping transferred tristearin only at the edges of the contact regions, producing “rails” of tristearin as seen in Figure 6.12.
Figure 6.9  a) Low humidity (RH = 2%) 30 second stamping of stearic acid on mica. 10 μm scan of the surface under ambient conditions within 1 hour of stamping. b) Nearby region 19.5 hours later. c) Edge of dry stamped region (25.1 μm image) showing 2D evaporation of the edge line (lower left). Z-range is 3 nm for all images.
Figure 6.10  a) Solid, 1.6 nm tall “bars” of tristearin from first 30 second stamping at RH = 10%. (25 \( \mu \text{m} \) height image, 6 nm z-range). b) 5 \( \mu \text{m} \) zoom of image in a) (5 nm z-range). c) “Holey” bars of tristearin from third 30 second stamping with the same stamp as in a) and b) (6 nm z-range). Five \( \mu \text{m} \) height image. d) Friction image same area as c) (50mV z-range).
Figure 6.11 Dotted bars of tristearin stamped for 30 seconds at 24% RH. Ten μm height image on the left (3 nm z-range), friction image on the right (25 mV z-range).
Figure 6.12 "Rails" of tristearin from 30 second stamping at RH = 51%. Twenty five μm height image on the left (5 nm z-range), friction image on the right (75 mV z-range).
While there was some variation in the morphology at a given humidity range (e.g. dotted bars instead of rails at high humidity), the results shown are typical. Tristearin showed little, if any, evidence of fingering, but still transferred at only at the edges of the contact region in high humidity. The large headgroup of tristearin formed continuous bars at very low humidity, in contrast with the single OH group of docosanol which barely stamped at all (Figure 6.5), and the not-quite-solid bars of the larger COOH headgroup of stearic acid (Figure 6.9a).

Triglycerides like tristearin have the unusual property of multiple melting points. Tristearin has four melting points, with the highest temperature of ~70 °C. Because the tristearin stamped at room temperature showed no lateral diffusion or vapor phase transport, we tried stamping in an ambient temperature of 66 °C for 1 minute. Later room temperature imaging showed a highly diffused tristearin pattern (Figure 6.13). It is not known whether the higher concentration regions of Figure 6.13 are the contact regions or the channel regions, but the vapor pressure of tristearin is probably substantially higher this close to its melting point, which could give significant vapor phase flux to the surface, possibly greater than that from the contact regions.

The higher surface diffusion rate at elevated temperatures was also observed for lines of tristearin stamped at room temperature and subsequently heated in-situ. Figure 6.14a shows tristearin stamped under ambient conditions (RH unknown). The sample was then heated to 40 °C. Images of the sample at 40 °C showed the narrow features of the stamped lines disappear first (Figure 6.14b), followed by the larger features, leaving
Figure 6.13 Tristearin stamped for 1 minute at 66 °C. Twenty five μm height image, 5 nm z-range.
an almost featureless surface at 40 °C after about 1.5 hours. Despite the relatively featureless appearance of Figure 6.14b, tristearin is still present on the surface, either in a gas or liquid phase. After 2.5 hours at 40 °C, the surface was cooled then imaged at room temperature (Figure 6.14c). The results are similar to that of Figure 6.13, demonstrating a greatly increased surface mobility just 13 °C above room temperature and 14 °C below its first bulk melting point.163

6.4 Discussion

The common idealized model of microcontact printing is one in which a monolayer of ink from the stamp gets transferred to the surface at all points of contact. Reality is much more complicated due to vapor phase transport of ink from the stamp from the channel regions, surface diffusion of ink during stamping, inhomogeneous ink distribution (in some cases ink crystals on the stamp), competition from surface water, and a water meniscus providing transport of ink to the surface. Many of these issues have been discussed for alkanethiols on gold.140,162,164

The typical stamp inking process consists of simply immersing the stamp into a dilute solution of the ink molecules then blowing off the excess solvent with a stream of compressed gas. The result is assumed to consist of a layer of ink molecules diffused into and deposited on the surface of the PDMS stamp. Our own AFM and optical microscopy images of inked stamps reveal the presence of crystals and large multilayer islands on the stamp surface for some inks; however, the detailed distribution of the ink
Figure 6.14 Thirty second sampling of Inset 2, (c) 72 min. (d) 72 min. (e) 20 min. region at room temperature after heating to 40°C for 2.5 hours. Z-tune is 5 mm for all images.
on the stamp surface is still unknown. Purposely modifying the ink distribution on the 
stamp was used by Cherniavskaya et al.\textsuperscript{165} who inked only the channels of a stamp to get 
ink transfer only at the edges of the contact region. The opposite approach was taken by 
Pompe et al.\textsuperscript{94} who devised a method to only ink the parts of the stamp that will contact 
the sample, greatly reducing the vapor phase transport and lateral spreading of their ink 
during stamping.

To understand how the ink gets from the stamp to the surface, it is useful to look at 
the basic forces involved. We first consider stamping without the presence of water. 
With a constant tail group, inks with greater headgroup-surface interaction strength will 
have lower surface diffusion and therefore greater fidelity. Increasing the tail group 
interaction also will decrease diffusion by increasing intermolecular forces within the ink. 
However, if the ink's tail interaction forces, with itself or the stamp, are much stronger 
than the ink-surface interaction, the ink will not transfer from the stamp to the surface. 
This was certainly the case for the alkane tetracosane, which did not transfer from the 
stamp at all under ambient conditions. Another ink transport mechanism is vapor phase 
transport from the stamp channels. This effect has been studied for alkanethiols on 
gold,\textsuperscript{140} and reported for octadecyltrichlorosilanes on silica,\textsuperscript{166} for example. Table 6.1 
shows the estimated vapor pressure\textsuperscript{167} of the molecules stamped in this paper and for 
comparison, some commonly used alkanethiols. The flux, $F$, due to the vapor pressure 
can be estimated by $F = P/\sqrt{2\pi mkT}$, where $P$ is the vapor pressure of the ink in 
Pascals, $m$, the molecular mass of the ink in kg, $k$, Boltzmann's constant, and $T$ is the 
temperature in Kelvin.\textsuperscript{168} The stamp surface area measured by tapping mode AFM of the
stamp reveal a 1 μm long section of the channel has a surface area of 4.1 μm². One parameter not known is the sticking coefficient of incident ink molecules on the mica surface. For the case of hexadecanol in ambient conditions, height (Figure 6.7a) and friction (not shown) data are consistent with less than a complete monolayer on the surface; resulting in a sticking coefficient less than 0.01 (see Table 6.1).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Estimated vapor pressure at 298K (kPa)</th>
<th>Flux (molecules / m²s)</th>
<th>Incident monolayers (30 second stamping)</th>
<th>Melting point¹⁶⁹ (K)</th>
<th>Boiling point¹⁶⁹ (K)</th>
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<td>3x10¹⁹</td>
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<td>7x10¹⁹</td>
<td>300</td>
<td>292</td>
<td>611¹⁷⁰</td>
</tr>
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<td>7x10⁻⁷</td>
<td>6x10¹⁸</td>
<td>25</td>
<td>303</td>
<td>638¹⁷⁰</td>
</tr>
<tr>
<td>stearylamine</td>
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<td>4x10¹⁸</td>
<td>17</td>
<td>326</td>
<td>620</td>
</tr>
<tr>
<td>octadecanol</td>
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<td>2x10¹⁸</td>
<td>8</td>
<td>331</td>
<td>608</td>
</tr>
<tr>
<td>stearic acid</td>
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<td>5x10¹⁷</td>
<td>2</td>
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<td>623¹⁷⁰</td>
</tr>
<tr>
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<td>3x10¹⁷</td>
<td>1</td>
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<td>663¹⁷⁰</td>
</tr>
<tr>
<td>tetracosane</td>
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<tr>
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<td>2x10¹⁶</td>
<td>0.1</td>
<td>346</td>
<td>649¹⁷⁰</td>
</tr>
</tbody>
</table>

Table 6.1 Estimation of surface coverage from vapor phase transport. Vapor pressure was calculated from the modified Yalkowsky-Mishra equation (Equation 12 in Myrdal¹⁶⁷) using melting and boiling points given in this table. Incident monolayers is calculated from Flux x (stamp surface area + sample surface area) x stamping time / (5x10¹⁸ molecules/ m²²).

The presence of water significantly complicates the idealized stamping mechanism. Water competes effectively with the stamped molecules for the mica surface. Increasing the relative humidity to ~90% after stamping causes the stamped patterns on mica to rapidly spread, destroying the pattern. The water displaces the
molecules, giving them high mobility (equivalent to reducing the headgroup-surface interaction strength, which increases surface diffusion). This helps explain why the center of the stamp contact area usually remains free of molecules at moderate humidity. Surface water under the contact regions reduces the headgroup-surface interaction strength so the ink remains on the stamp and doesn’t directly transfer to the mica surface. The ink instead spreads inward from the edges of the contact region\textsuperscript{140} or along the surface of a water meniscus\textsuperscript{162,164} to the mica surface. The effect of surface water preventing transfer in the contact area has also been shown in covalently bonding systems with dip-pen nanolithography for alkanethiols on gold\textsuperscript{162} and gold complexes on silica,\textsuperscript{171} and with microcontact printing for perflourinated monochlorosilanes on silica\textsuperscript{94} and alkylsilanes on silica.\textsuperscript{165} Surface water also reduces the vapor phase transport of ink molecules to the channel regions; compare, for example stearic acid stamped under ambient conditions (Figure 6.8b) versus dry conditions (Figure 6.9a).

It would be desirable then to tune the properties of the ink to meet the requirements of stamping. A low vapor pressure and low surface diffusion rate is desirable for high fidelity, which leads eventually to solid inks. However solid inks may crystallize on the stamp surface after inking, interfering with conformal contact and adversely affecting homogeneous transfer rates across the patterned area. Instead, it may be useful to have a slightly branched tail group to lower the melting point, but keep the gas phase and surface diffusion rates low.

Since most of the Figure 6.2 (docosanol) or Figure 6.12 (tristearin) features originated from the edges of the contact regions, it seems likely that the ink molecules
came from the channel regions. The non-uniform distribution of stamped features in Figure 6.2 suggests that the docosanol ink came from localized high concentration regions in the channels. While inking only the channel regions was the intention of Cherniavskaya et al.\textsuperscript{165} by using ink solvents that dewet the stamp surface, this effect may also occur unintentionally, even for ink solvents that wet the stamp. The non-reproducibility of non-covalent stamping in general may be caused, in part, from the non-homogenous distribution of ink on the stamp, particularly for solid inks.

Fingering Instability

The fingering patterns seen in Figure 6.3, 6.4, 6.6, and 6.8 have been observed on a macroscopic scale by others.\textsuperscript{152-154} In their work, a surface water film (created controlled by relative humidity) was necessary to produce fingering.\textsuperscript{117,152-154,172} We also observed a strong dependence on relative humidity. A two dimensional fingering instability was observed when octadecanol, docosanol, stearylamine, and stearic acid were stamped under moderate relative humidity, but were never seen for stamping under dry conditions. For the former case, the fingering patterns form within the 30 second duration of stamping, and the patterns remain stable in ambient conditions at least for a period of hours. This leads us to conclude that capillary condensed water in the stamp channels creates the conditions necessary for fingering. Because the stamp channels are open to the environment, a pressure driven instability is ruled out. The fact that all of these fatty acids, alcohols and amines spread freely at the air-water interface lead us to propose the Marangoni effect as the driving force for the instability.\textsuperscript{152,154-157} Figure 6.15
Figure 6.15 Marangoni driven fingering mechanism. a) Ink molecules spread along the water meniscus. b) A perturbation in the concentration at the spreading front induces a local line tension gradient, causing flow from adjacent regions of lower line tension. This flow results in further stretching of the higher line tension region, which maintains the line tension gradient and causes further expansion. The expanding high line tension region becomes an expanding finger of water, dragging with it the ink molecules.
schematically illustrates the proposed mechanism. Ink molecules spread from the channels along the surface of the capillary-condensed water meniscus (Figure 6.15a). As they spread, a perturbation in the local concentration of ink molecules develops in the spreading front. A localized decrease in ink concentration results in a localized increase in line tension which pulls fluid from the surrounding regions of lower line tension (see for example Nikolov et al.\textsuperscript{155}). The arriving fluid further stretches the higher line tension region, amplifying the effect. This flow continues until the line tension gradient falls below some critical value (due to diffusion or depletion of the ink molecules, for example).

One unresolved issue is how the ink is able to spread under the contact areas, as is evident in Figures 6.2, 6.3, 6.4, 6.6, and 6.8. For the case of alkanethiols on gold, it has been proposed that the alkanethiols attach to the surface at the edge of the meniscus and spread inward towards the contact region by reactive spreading (see for example Schwartz\textsuperscript{162}). For the non-covalently bonding molecules studied, water was easily able to displace the stamped lines at >90% humidity, so it doesn’t seem likely these molecules could spread under a thick water meniscus. However, as the water in the meniscus spreads outward due to the fingering, it becomes thinner, and may become thin enough so that these inks can spread inward towards and under the contact region.

It is interesting to note that fingering was never observed for tristearin inks. According to our proposed fingering mechanism of a Marangoni driven flow, a critical minimum value for the line tension gradient is required to create the fingers. It is possible that tristearin could not create the necessary line tension gradient on the water
meniscus. Another possibility is the stronger headgroup surface interaction of tristearin on mica anchors the meniscus contact line and prevents the creation of fingers. This type of contact line pinning may explain why alkanethiols on gold do not show fingering.

6.5 Conclusion

We have studied the behavior of several non-covalently bonding molecules with microcontact printing on mica. A strong dependence on relative humidity and the type of headgroup was observed, and a surface tension driven fingering instability occurred under moderate humidity conditions for octadecanol, docosanol, stearylamine, and stearic acid. Tristearin, which has the largest headgroup of the molecules studied, did not produce fingering patterns under any humidity conditions. This may be due to the stronger interaction of its headgroup with the mica surface, or due to details of its spreading behavior on water. Most types of molecules studied stamped with higher fidelity under low humidity conditions; however the long chain alcohol docosanol did not stamp onto dry mica. This is likely due to the relatively small interaction of the OH headgroup with the bare mica surface. Temperature was also shown to be an important factor in the surface diffusion rate of these non-covalently bonding molecules. Tristearin stamped with high fidelity at room temperature, but was shown to freely diffuse on the mica surface 13 °C above room temperature but still 14 °C below its first bulk melting point. The short chain alcohol hexadecanol diffused quickly on mica at room temperature, but produced stamped patterns at 6 °C. Hexadecanol also illustrated the importance of vapor pressure on the achievable fidelity of microcontact printing. Despite
the improved stamping at 6 °C, vapor phase transported hexadecanol covered the channel regions, largely washing out the stamped pattern.
CHAPTER 7

CONCLUSIONS

This work has demonstrated the utility of atomic force microscopy, specifically using alternate imaging forces, in understanding the behavior of amphiphilic thin films.

Previous work on single-chain surfactants that aggregate into spherical micelles in solution revealed they self-assemble as half-cylinders at the crystalline hydrophobic interface, due to anisotropic interactions between the surface and hydrocarbon tailgroup. The work presented here on amorphous surfaces indicates that when this anisotropy is removed, the spherical curvature found in solution is reestablished and interfacial aggregates become roughly hemispherical. Since similar morphologies occur over a wide range of headgroup types (both charged and uncharged), interfacial adsorption seems to be driven by hydrophobic interactions between the surface and tailgroups.

While self-assembly is useful for simple surface-wide patterning, it cannot create individual structures of complex shape. To create these types of patterns, microcontact printing is required. Control experiments for the work on microcontact printing of self-assembled monolayer revealed the surprising creation of patterned monolayer water films. The presence of the stamp on the mica surface and the resulting capillary condensed water created 2.5 Å to 5 Å thick water patterns. The patterns disappeared in very low and very high humidity, suggesting a localized exchange of hydrogen ions for potassium ions on the mica surface was responsible for the patterns. These water patterns should be useful for studying basic wetting processes on mica. Other surfaces with
mobile ions should also be able to be patterned in this way, and ambient gases other than water vapor and carbon dioxide may be effective for some surfaces.

LFM was demonstrated to detect low-density, diffusive films of amphiphilic molecules and can monitor their collective diffusion on the substrate. Monolayer corrals of long-chain alcohols and fatty acids, patterned by microcontact printing, act as 2D containers, eventually saturating the enclosed area with their own saturated gas phase. LFM images in air reveal high friction outside the corral (bare mica), low friction on the corral boundary (amphiphile monolayer), and intermediate friction inside the corral, corresponding to the amphiphile gas. Assuming that the LFM signal inside the corral was a weighted average of the alkane and mica values, we calculated values for the surface coverage that compared reasonably with the expected surface vapor pressures of Langmuir monolayers. Scratching an opening in the 2D container allowed us to monitor the surface coverage as a function of time and to estimate the surface diffusion constant. Our results suggest that friction measurement and mapping can detect amphiphile densities down to 1% of a monolayer, making this technique useful in studying the early stages of monolayer formation.

The behavior of self-assembled monolayers that do not form covalent bonds with the substrate were studied using microcontact printing and force microscopy. Commonly studied self-assembled monolayers, such as alkanethiols on gold, form covalent bonds with the substrate. This strong interaction dominates the weaker intermolecular forces in the self-assembling film. The weak interaction of non-covalently bonding molecules have with the substrate allows more details of the intermolecular forces within the self-
assembled monolayer and with the substrate to be observed. We found a strong
dependence on relative humidity and the type of headgroup on the resulting patterns. A
surface tension driven fingering instability was observed for octadecanol, docosanol,
stearylamine, and stearic acid stamped under moderate humidity conditions. Tristearin,
which has the largest headgroup of the molecules studied, did not produce fingering
patterns under any humidity conditions. This may be due to the stronger interaction of its
headgroup with the mica surface, or due to details of its spreading behavior on water.
Most types of molecules studied stamped with higher fidelity under low humidity
conditions; however the long chain alcohol docosanol did not stamp onto dry mica. This
is likely due to the relatively small interaction of the OH headgroup with the bare mica
surface. Temperature was also shown to be an important factor in the surface diffusion
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room temperature, but was shown to freely diffuse on the mica surface 13 °C above room
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patterns at 6 °C. Hexadecanol also illustrated the importance of vapor pressure on the
achievable fidelity of microcontact printing. Despite the improved stamping at 6 °C,
vapor phase transported hexadecanol covered the channel regions, largely washing out
the stamped pattern.
APPENDIX: LIST OF PUBLICATIONS


REFERENCES

17. Levitz, P.; Van Damme, H.; Keravis, D. "Fluorescence Decay Study of the Adsorption of Nonionic Surfactants at the Solid-Liquid Interface. 1. Structure of


48. Thermoelectric cooler Melcor HT4-12-30L, heat sink Thermalloy 2333BTCM.
49. 100 Ω, α=0.003 85, Omega Engineering Part No. F3105.
50. The Dimension 3100 sample chuck was replaced with a custom Invar sample chuck, in order to accommodate the height of our heat sink. The custom chuck was 12.1 mm thick vs the 17.6 mm thickness of the Dimension chuck. It should be noted, however, that the standard Dimension chuck could be used if the
temperature stage were just 2.5 mm shorter. Removing this height from the heat sink should not affect the performance significantly.

51. Temperature was measured at the top of the fluid cell. The temperature difference between the top of the cell and the sample surface was found to be up to ~1 °C.

52. A coil of rigid copper tubing (OD 1/8 in.) was first tried as the heat exchanger, but vibrations from the pump were coupled too strongly to the stage to permit imaging. Flexible tubing provides less efficient heat removal, however, it did not couple any vibration to the stage.


57. CTAB (≥99%) was obtained from Fluka and was used as received. All solutions were prepared in Nanopure water with resistivity ≥18.3 MΩ.


98. RBS allows elemental identification of surfaces by measuring the energy of elastically backscattered ions from the target sample.


130. Using a viscosity of ~0.01 poise (typical of long-chain alcohols) and a random-coil radius of 0.5 nm gives a diffusion coefficient $D=k_B T/6\pi \eta R \approx 4 \times 10^3 \mu m^2/s$.


170. Boiling point of alkanethiols extrapolated from 3rd order polynomial fit to boiling points of C1-C14 thiol series given in the CRC Handbook of Chemistry and Physics, 3rd Electronic Ed. The boiling point of docosanol was extrapolated from a 3rd order polynomial fit to C6-C20 (even number of carbons) alcohol series from the CRC. The boiling point used for stearic acid is the decomposition temperature listed in the CRC, however Stull, D. R. "Vapor Pressure of Pure Substances - Organic Compounds", Industrial and Engineering Chemistry 1947, 39, 517-540, lists the boiling point at 643K.