X-ray Investigations of Mixed Charge Amphiphilic Systems

BY

MIROSLAV N. MIHAYLOV B.S. (Sofia University Sofia Bulgartia) 2004 M.S. (University of Illinois at Chicago) 2008

THESIS

Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics in the Graduate College of the University of Illinois at Chicago, 2015

Chicago, Illinois

Defense Committee:

Mark L. Schlossman, Chair and Advisor Anjum Ansari Serdar Ögüt Richard Cavanaugh Vivek Sharma , Chemical Engineering UIC Copyright by

Miroslav N. Mihaylov

2015

To my wife Elina A. Vitol.

ACKNOWLEDGMENTS

I want to thank my committee members Prof. Ansari, Prof. Ogut, Prof. Cavanaugh and Prof. Sharma for their time, interest and valuable comments and suggestions about my thesis.

The person that I owe the most is my thesis advisor, Prof. Mark Schlossman. He guided me through the difficult experiments and the entire cycle of the thesis work with knowledge and understanding. I learned a lot from him and it has been a privilege to work beside him as his PhD student.

I am indebted to our research group postdoctoral researchers Dr. Wei Bu - without him the data acquisition would have been immensely difficult, Dr. Mrinal Berra for having numerous discussions with me about data analysis and computational methods, Dr. Sabina Tatur for sharing her knowledge on the experimental techniques with Langmuir troughs.

I am grateful to all my colleagues in Prof. Schlossman's group, especially Dr. Binyang Hou, Dr. Hao You, Dr. Chiu-Hao Chen, Daniel Amoanu, Urmee Shainas, Jaesung Yoon and especially Numan.

I would also like to thank a number of individuals from the Advanced Photon Source at the Argonne National Laboratory: Binhua Lin for her assistance at the beamline, Mati Meron for many helpful discussions, Mark Rivers for providing his technical expertise on implementing the EPICS control system and Ivan Kuzmenko.

I also want to thank my family for their support and patience throughout the years of my graduate studies.

ACKNOWLEDGMENTS (Continued)

I would like to express my gratitude to the Physics department Machine Shop. Special thanks to Bob for always being available to help. Kevin Lynch, Richard Frueh and Tony - thank you! Last but not least I want to thank to all the people in the physics office: Melissa Mattingly, James Nell and Derrick Stanley.

TABLE OF CONTENTS

CHAPTER

11	Liquid surfaces and interfaces
1.1	Surfactant systems
1.2	Catanionic surfactants
1.0	Motivation and techniques
1.4	Motivation and techniques
EXPE	RIMENTAL APPARATUS
2.1	Langmuir Trough
2.1.1	Trough
2.1.2	Surface pressure Balance
2.1.3	Surface Density Control
2.1.4	Calibration Procedures
2.1.5	Water Subphase Handling
2.1.6	Enclosure
2.1.7	Cleaning Procedures and assembly
2.1.7.1	Cleaning metal parts
2.1.7.2	Cleaning teflon parts
2.1.7.3	Assembly and final cleaning
2.2	X-ray Source and Reflectometer
2.2.1	X-ray Source
2.2.2	Liquid Surface Reflectometer
X-RAY	SCATTERING FROM LIQUID INTERFACES
3.1	X-rays interaction with matter
3.2	Born Approximation
3.3	Electron Density Profile
3.4	Grazing Incidence Diffraction
3.5	Parratt's formalism: Matrix Recursive Method
МАТЕ	BIALS AND METHODS
4 0 1	Chemicals
402	Solvent Preparation
403	Sample Preparation
404	Spreading Procedure
4.1	Isotherms
ISOTH	IERM DATA

TABLE OF CONTENTS (Continued)

CHAPTER

PAGE

	Control Experiment Arachidic Acid Isotherm
5.2	Characteristics of Individual Components
5.2.0.1	C18TAB Surface Pressure
5.2.0.2	PIP2 Surface pressure
5.2.1	Composite system (PIP2 C18TAB) Isotherms
5.2.1.1	Pressure Time dependence
5.2.1.2	Isotherm Data
X-RAY	DATA RESULTS AND ANALYSIS
6.1	Summary of the X-ray data
6.2	AA x-ray data and analysis
6.3	X-ray Reflectivity Measurements on PIP2/C18TAB monolayers
6.3.0.3	2 Slab Model
6.3.1	3 slab model
6.3.2	Subphase pH dependence
6.4	GID
6.5	Out of plane Bragg Rod intensity analysis
6.6	Conclusion
ELEC 7.1	RON DENSITY ANALYSIS Interfacial area per molecule
7.2	Molecule Groups
7.2.1	C18TAB molecule groups
7.2.2	PIP2 molecule groups
7.2.3	PIP2 C18TAB 2 Slab Model
7.3	Conclusion
APPEN	DICES
App	endix A
ADD	endix B
r r	ondix C
App	
App App	endix D
App App App	$\begin{array}{c} \text{endix } \mathbf{D} \\ \text{endix } \mathbf{D} \\ \text{endix } \mathbf{E} \\ \end{array}$

LIST OF TABLES

TABLE		PAGE
Ι	Calculated area per molecule for selected values of surface pressure	
	at room T \ldots	61
II	X-ray Reflectivity Samples Summary	68
III	Best Fit parameters	69
IV	Best Fit parameters	73
V	Best Fit parameters 3 Slab Model	76
VI	Number of electrons in the molecular groups from the surfactant	
	molecules	86
VII	Number of electrons in the molecular groups from the surfactant	
	molecules	87
VIII	Trough opening as a function of motor coordinate values	103

LIST OF FIGURES

FIGURE		PAGE
1	Perspective view of the trough assembly	6
2	Surface Pressure Sensor-Holding Stage Assembly	8
3	EPICS medm screen for the trough.	11
4	Voltage for four different mg weights on the film balance	13
5	Linear fit and data voltage values for four milligram weights.	14
6	Voltage to surface tension conversion.	15
7	Compression of the residual impurities on the "clean" water surface.	16
8	Assembly trough and enclosure	18
9	Sideview of the trough without the enclosure	19
10	APS Storage Ring Diagram	24
11	Scattering geometry Side View	25
12	Liquid Surface Reflectometer at ChemMatCARS APS	26
13	X-ray beams imprints on the pilatus area detector	27
14	Kinematics of Scattering	29
15	Penetration Depth	32
16	Kinematics of Scattering by two scatterers separated by distance r	33
17	Fresnel and Born Approximation compared	36
18	ED Profile of a rough surface compared to ideally flat	39
19	Hexagonal packing real and reciprocal space	40
20	GID Scattering Geometry	41
21	Close packing structure and diffraction patterns	43
22	Parratt layers	46
23	PIP2 molecular diagram	50
24	C18TAB molecular diagram	51
25	Spreading procedure technique requires some practice and steady han	d 53
26	Wilhelmy plate force diagram	55
27	Surface tension while and after spreading of 200 $\mu l \ 0.5 \ mM \ AA$	58
28	Arachidic Acid isotherm	59
29	$\pi - T$, Barrier position and 2D Gas law as a function of time	64
30	Spreading of PIP2:C18TAB 3:1 solution 50 $\mu l \ 0.5 \ mM$	66
31	PIP2/C18TAB mixture Isotherm	67
32	AA Reflectivity	70
33	X-ray Reflectivity of PIP2/C18TAB	72
34	Electron Density Profile	74
35	30% Chi-squared Error bars values for $XR_{7,1}$ best fit parameters	75
36	X-ray Reflectivity of PIP2/C18TAB	77
37	GID Data	78
38	PIP2/C18TAB mixture Isotherm	80

LIST OF FIGURES (Continued)

FIGURE

PAGE

39	Bragg Rod Intensity along Qz
40	2 slab model parameters 84
41	Catanionic system molecular arrangements
42	GUI XR data Visualization 9
43	GUI Mlayer
44	GUI subtraction from linear background
45	Barrier position as a function of the motor coordinate 10
46	Chi-square distribution function for $\nu = 3,5$ and $10 \ldots 10$
47	Probability of exceeding the χ^2 values versus the Reduced Chi-square 10
48	Chi-square hypersurface for $m=2$ 104
49	χ^2 along a given parameter dimension a_i
50	XXX Medm GUI Click-flow diagram

LIST OF ABBREVIATIONS

$\mathbf{L}\mathbf{M}$	Langmuir Monolayer
SP	Surface Pressure
XR	X-ray Reflectivity
GID	Grazing Incidence Diffraction
BR	Bragg Rod
BA	Born Approximation
ED	Electron Density
LVDT	Linear Voltage Differential Transducer
ERF	Error Function
AA	Arachidic Acid
C18TAB	Trimethyloctadecylammonium Bromide
PIP2	Phosphatidylinositol-4,5-diphosphate C-16
EPICS	Experimental Physiscs and Industrial Control System
MEDM	Motif Editor and Display Manager
GUI	Graphical User Interface

SUMMARY

The liquid vapor interface is of a fundamental importance for a wide range of applications from physics, chemistry and biology to material science and nanotechnology. Soft matter thin films composed of mixture of cationic and anionic surfactants are of great interest because of their unique interfacial properties that arise from the strong electrostatic interactions between the oppositely charged headgroups. In order to exploit these properties a better understanding of the molecular scale structure of these catanionic systems is needed. Surface sensitive synchrotron X-ray scattering techniques at room temperature were used to study structural properties of a catanionic system composed of the phospholipid PIP2 and Trimethyloctadecylammonium bromide. Through a series of surface pressure versus time and surface pressure area isotherm measurements it was established that the catanionic mixture is more surface active compared to its individual components. Furthermore, the surface pressure - area isotherm of the mixed charge system was monotonous without any phase transition indicating that the film is in a liquid expanded phase. The monlayer stability compression-decompression cycles showed that the formed Langmuir film was stable over the course of many days. Specular X-ray reflectivity measurements determined the electron density profile in the direction normal to the interface averaged over the inplane region of the interface. X-ray reflectivity, normalized to the Fresnel reflectivity of an ideal flat interface, was fit to a model system consisting of 2 layers. The occupancy of the components obtained from the electron density profile analysis gave an estimate which was in excellent agreement with the macroscopic calculation from the molecu-

SUMMARY (Continued)

lar weight, amount deposited and available area of the film. Another independent technique, Grazing Incidence Diffraction, probed for an inplane ordering of this two dimensional structure. It showed highly ordered domains composed of untitled acyl chains with hexagonal unit cell. Bragg rod analysis of the variation of the scattered intensity along the specular direction was in agreement with the findings from the X-ray reflectivity analysis.

X-ray data showed a stable ordering of this soft matter system with the same regularity as that of a solid crystal. What makes this type of ordering so special is that none of the individual components of the system on their own can form such a state but, because of their cooperative and collective behavior, it becomes possible to achieve a very stable configuration in this catanionic system.

CHAPTER 1

INTRODUCTION

1.1 Liquid surfaces and interfaces

The liquid surface is an important system to study with numerous applications in the field of physics, chemistry, biology and wide array of industrial applications and nanotechnology. For physicist the boundary of two immiscible fluids represents a quasi two dimensional system attractive for studying rich phase transitions and critical phenomena processes. The liquidair and liquid-liquid interfaces present an outstanding playground for chemical self-assembly of surfactant molecules. Phospholipid monolayers are often used as a idealized model system for the membrane of biological cell (1) (2) and the structures at the liquid-air interface in the lungs (3). The surfactants are widely used in the industry applications such as detergent products, cosmetics, food industry (4) , hydrometallurgical production of precious metals and rare earth materials (5) (6) and drug delivery systems (7). Basic physical understanding of these surfactant systems is of a great importance in order to develop these applications.

1.2 Surfactant systems

The expression **amphiphilic** refers to a molecular structure with two distinct components one of which is soluble and the other one insoluble in a given solvent environment. Assuming the "aquacentric" point of view, **surfactants** are amphiphilic materials that exhibit simultaneously some solubility in water and some affinity for non-aqueous environments. A common hydrophobic group in surfactants is the hydrocarbon chain with a typical length of 10-22 carbon atoms(8),(9),(10). The hydrophobic strength of the tail group is determined by its length and if long enough the surfactant molecule becomes insoluble in water. These insoluble molecules naturally prefer the air-water interface and can form a two dimensional film - Langmuir Monolayer LM.

Lipids are surfactants that generally consist of a polar head group and one or two hydrocarbon chains. In aqueous environment they tend to assemble in bilayer sheets with the hydrophilic heads on the outside and hydrophobic tails on the interior of the film. Lipids play an important role in biological applications. All biological cell membrane are composed of a lipid bilayer with a large number of associated and embedded proteins. The typical thickness of the LM is 2-5 nm but they can expand laterally to macroscopic distance which can safely describe these LM systems as thin sheets with a length scale large compared to its thickness.

LM are prepared by depositing a known number of amphiphilic molecules at the surface of an aqueous subphase. The molecules are dissolved in a volatile water insoluble solvent such as chloroform that would evaporate quickly in a matter of minutes upon spreading.

LM is an attractive model system to study ordering and phase transitions in two dimensions. They have been a subject of extensive research over the past century. Surface pressure as a function of the molecule area refereed as $\pi - A$ isotherm has been the standard measurement on LM. In 1891 A. Pockles reported her isotherm measurements of the steric acid (11). Later lord Rayleigh 1899 experiments suggested that these layers must be with a thickness of a single molecule (12). Irving Langmuir regarded by many as the father of the surface science gave the modern understanding of the LM structure at molecular level (13).

The field has undergone a revolution in the last two decades with the introduction of the synchrotron x-ray sources and the development of novel x-ray scattering techniques allowing to directly probe the molecular arrangement of the LM at these soft condensed matter interfaces. Als-Nilsen Pershan 1983 and Braslau et al. 1985 carried out one of the first x-ray diffraction studies on the surface structure of a liquid (14) (15) (16). Kjaer et al. and Dutta et al. 1987 observed the LM structures at molecular scale via x-ray diffraction experiments (17) (18).

Additionally the development of new optical techniques such as fluorescence microscopy, polarized fluorescence microscopy and Brewster angle microscopy showed us the structure in LM at larger length scales (19) (20) (21) (22).

1.3 Catanionic surfactants

A Catanionic surfactant consists of a pair of oppositely charged amphiphiphiles. Mixtures of cationic and anionic surfactants are of great interest because of their phase behavior and interfacial properties (23) (24) (25). These mixtures are appearing to be more surface active compared to the single components. The phase behavior and microstructural evolution study by Kathleen et al. (23) and Tah et al. (26) revealed that the surfactant geometry strongly affect the micro structure present in the anionic and cationic surfactant mixtures.

Wang et al. (27) characterized the pressure area isotherms of a set of mixed charge surfactant LM made of compounds with different chain number and length. They established that the number of alkyl chains and their length are governing the phase behavior of these films.

The pressure area isotherms for many of mixed charge surfactant systems are monotonous without any sharp phase transitions (27) (28) (29) (30).

X-ray structural measurements on catanionic systems reported by D. Vaknin and Wei Bu (29) indicated closely packed and highly ordered composite system. B. Stripe et al. (31) grazing incidence diffraction experiments on floating monolayer of catanionic surfactant gave an insight into the mechanism of oriented crystallization in biology. Monica Olvera de la Cruz's group did significant amount of numerical calculations and molecular dynamic simulations on systems composed of binary mixtures of oppositely charged components (32) (33) (34) (35) (36).

1.4 Motivation and techniques

Despite the numerous ongoing research on catanionic system (37) (38) there have not been many reports on their structural measurements. In this work, we use anionic and cationic amphiphiles of unequal charge to explore the structure of a monolayer composed of electrically neutral mixture of the two. In principle, the strong electrostatic interaction between the -3 charge phospholipid (phosphatidylinositol (PtdIns) which consists of two saturated C14 chains with PIP2 headgroup) and +1 (cetylammonium bromide) head groups of the co-assembled amphiphiles increases their cohesion energy and favors the formation of a flat, laterally correlated ionic structure. The in-plane ordering of this structure is determined with surface diffraction. Pressure area isotherms exhibited behavior similar to the one from other catanionic systems and different mixture with PIP2 (39). PIP2 phospholipid present in the biological cell membrane and plays an important role in cell signaling processes. It is highly charged and it's interaction with the surface counterion might have a particular physiological relevance (40).

CHAPTER 2

EXPERIMENTAL APPARATUS

2.1 Langmuir Trough

All experiments were performed with a custom made Langmuir trough enclosed in an aluminum box. The trough was originally designed and built by Shwartz et. al. (41)

Some of the original components had to be rebuilt due to corrosion damage while the electronics components completely replaced and some parts interfacing the electronics were modified. The entire design of the trough and the encapsulating chamber allows operation while preserving maximum clean environment. Monolayer surface density was controlled, and temperature and surface tension were measured remotely via the EPICS control system (42).

2.1.1 Trough

Langmuir Trough is quarter inch deep milled from a solid piece of Teflon with a base bolted to a hard-coated anodized aluminum plate. The Teflon block was fly-cut while attached to the aluminum base in order to ensure maximum flatness of the top edge required for good contact with the barrier. On Figure 1 is shown the Langmuir Trough assembly. A solid Teflon barrier placed across the short edge of the trough is allowed to move along the surface in the direction of the long edge. When moving the barrier all the film molecules are on one side but the water flows freely under it thus the area of the film can be set to a specific value. In order to provide



Figure 1. Perspective view of the trough assembly

maximum clean environment the trough is placed in a aluminum sealed chamber with Kapton windows at the horizontal level of the trough at the path of the x-rays.

There are two o-ring sealed glass windows for visual inspection of the interior of the trough: a small window on the short side of the chamber and a larger one on the the top lid with the size of the trough allowing for inspection of the entire trough surface at all times. The top window is held shut by four De-Sta-Co clamps allowing easy removal for aspiration of the the aqueous surface.

The bottom wall of the chamber was anodized as well in order to reduce the corrosion damage from the spilled water and the humid environment of the box. A vapor saturated Nitrogen or Helium is flushed trough the chamber for two main reasons. This vapor environment prevents the change of the liquid surface level due to the evaporation of the water from the trough. Furthermore the Helium environment can minimize the background scattering from air which is crucial for the X-ray measurements.

2.1.2 Surface pressure Balance

Custom built Wilhelmy plate type surface pressure balance was used to measure the surface tension. The balance consists of a leaf spring made from spring steel, a Linear Voltage Displacement Transducer (LVDT) and paper plate made of filter paper. Figure 2 shows the assembly of the surface pressure sensor with the holding stage.

LVDT is a device used for measuring absolute linear position. The transformer is made of three solenoidal coils placed next to each other. The electronics measures the difference of voltage across the top and the bottom half of the coil. This difference signal is linearly



Figure 2. Surface Pressure Sensor-Holding Stage Assembly

proportional to the position of the centered cylindrical ferromagnetic core for some range of displacement of the core inside as long as the core does not approach the fringing fields of the solenoids. We used AC LVDT Schaevitz 050HR connected to the signal conditioner model LDM 1000. The output voltage of the signal conditioner was read with Keithley 2000 multimeter. That voltage was converted to surface tension via the software described later in this section.

The wetting of the vertically inserted paper is at zero contact angel thus the force exerted is just the surface tension times the perimeter of the contour that is in contact with the water. Since the filter paper is very thin that perimeter is taken simply to be twice the length of the plate. A custom made tool was utilized for cutting the Wilhelmy paper plates with reproducible fixed width. It is made of a one inch thick aluminum block on both sides of which is bolted a American Line 0.09 Single Edge cutting blade. It was important to change the blades regularly in order to ensure proper operation of the cutter. The cutting of the paper plates is accomplished by placing the filter paper on the top of a clean alpha wipe over a softer plastic film underneath. With a quick motion of the knife tool keeping the blades slightly inclined the paper strip was cut. Then by pressing the both ends of the paper strip with another quick motion the square paper plate was obtained. The side of the square with the most sharp cut edge was used to be the one that is in contact with the water. A precise measurement of the plate width on a set of used paper plates was performed with optical comparator. The average width of the paper plate was established to be $25.65\pm0.03 \ mm$. The paper plate is rigidly mounted via Kel-f clamp on a thin Kel-f rod which is attached to the core of the LVDT.

The top of the core is attached to a piece of stainless steel wire hanging freely on the leaf spring. Thus any change of the surface tension affects the vertical displacement of the ferromagnetic core which is being read as a voltage from the signal conditioning electronics that is part of the LVDT. The leads of the LVDT are taken outside the box via LEMO connector ensuring proper sealing of the chamber. The LVDT is rigidly attached to a custom built holding stage while the spring leaf is clamped to a vertically adjustable part of the stage in order to allow for precise centering of the core in the vertical position. A Dovetail Translation Stage DT12 from Thorlab is utilized for that need. For adjustments of the core to the center of the LVDT the holding clamp is loosened and the spring is centered while looking at the hanging core from above. It was important that the core does not contact the inside of the LVDT. Also the core had to be grounded for a moment after each assembly by touching it with the tip of a small screwdriver that is also in contact with some of the metal parts of the trough. The setup is mounted on a vertical translation stage allowing to adjust the bottom edge of the paper plate. Before use these translation stages ware disassembled and degreased.

2.1.3 Surface Density Control

The teflon barrier is rigidly attached to the translation stage as shown on Figure 1. The movement of the barrier across the surface is adjusting the area available to the deposited surfactant. The translation stage was designed to run without lubrication and with negligible backlash. It consists of two stationary pieces bolted to the base of the trough that move a central piece along two gold-coated stainless steel rods 3/8 in diameter. The trough barrier is held onto the center moving piece. The piece itself was driven by a 3/8 16 lead screw that was held by teflon sleeves in the center of each piece. The lead screw went through two nuts that were attached to the opposite side of the moving sections. The nuts could be rotated against one another on the lead screw so reducing the backlash to less than 0.001 which corresponds to $0.005 \text{ Å}^3/molecule}$ in the isotherm measurements. The lead screw and nuts are made of

Kel-F. The trough was mounted on the top of the two stationary end pieces. The lead screw was attached to the stepper motor by a stainless steal flexible coupling in order to reduce the transmission of vibration from the motor and to account for any eccentricity of the plastic lead screw. A motor was mounted on the outside of the trough where the opening across the trough



Figure 3. EPICS medm screen for the trough.

chamber was sealed via Teflon sleeve in a similar way to the ones from the lead rods. We used a motor Animatics Smart Motor SM1720M. Animatics SmartMotor series are integrated with encoder, an amplifier and controller with RS232 communication.

Driving the motor and reading the voltage out of the Keithley was done via the EPICS control system. A custom software IOC and custom graphical user interface MEDM (Motif Editor and Display Manager) was built to fit the needs of the experiment. Figure 3 shows the control GUI screen. More details about the control software are given in Appendix D.

2.1.4 Calibration Procedures

A proper calibration is required every time after the pressure sensor is cleaned or moved. In order to do that the Wilhelmy plate holding clamp is replaced with a small pan on which a calibration weights of 100 and 200 mg are added after one another while the voltage is recorded for approximately 5 minutes each. On Figure 4 is illustrated the voltage versus time graph for the duration of the placement of the different weights. The conversion factor from volts to surface tension units is given by

$$\frac{9.8}{C \times 2L_w} \tag{2.1}$$

where $L_w = 25.65 \pm 0.03 \ mm$ is the length of the paper plate and C has units of Volts per milligrams and is determined from the linear fit of the voltage and the corresponding weights as shown on Figure 5.

Autocorrelation of the time series shows a correlation length of roughly one time interval of two consecutive measurements (43). This means that the time points in the time series are



Figure 4. Voltage for four different mg weights on the film balance

independent and therefore the error for each of the weights can be estimated with the usual formula.

$$\sigma_v = \sqrt{\sum_{i=1}^{N} \frac{(x_i - \bar{x})^2}{N(N-1)}}$$
(2.2)

The error is roughly the same for all of the weights and it is of the order of 10^{-6} or smaller. The uncertainty of the slope coefficient of the linear fit is of the order of 10^{-12} (44) hence the error in the the surface tension measurement is contributed only by the uncertainty of the paper plate perimeter which is approximately $3 \times 10^{-5} m$ which is no greater than $2 \times 10^{-3} mN/m$.



Figure 5. Linear fit and data voltage values for four milligram weights.

Figure 6 shows the MEDM screen with the settings for the conversion from volts to surface tension.

2.1.5 Water Subphase Handling

The water was obtained from a Millipore (45) Mili-Q UV+ system fed by Milli-RO system. and was stored in a four liter Pyrex bottle with a Teflon valve on the bottom. The top of the bottle had another Teflon valve which allowed the venting of the air through the air filter attached to the valve. The bottle was connected with the trough via Teflon tubing and nylon feed-through. The end of the tubing is connected to the feed-through that is going through the side wall of the trough enclosure. Another shorter tubing is attached to the inner side of the feedthrough and ending slightly above the water surface level at the back end of the trough . That



Figure 6. Voltage to surface tension conversion.

allowed adding the water to the trough while keeping the chamber closed reducing the exposure to exterior contamination. A pipette attached to aspirator pump was used for removing the liquid from the trough and to aspirate the surface clean of any residual contaminants. The tip of the pipette was bent downwards to allow for easy aspiration of the liquid. Typically the pipette will be fed through the small side-door or the smaller Ultra-Tor fitting attached to the side door in order to reduce the contamination of the inner parts of the trough and particularly the water surface. In order to prepare a clean water surface, the water in the trough was flushed several times by consecutive fill-ups and aspirations while keeping constant air flow of ultra high purity gas going through the chamber. The barrier is kept at maximum open position throughout most of the time. The final fill up of the trough is done with the highest possible meniscus of the water. After waiting for at least 20 minutes in order to allow for the remaining impurities to adsorb at the water-vapor interface the barrier is compressed to it's maximum closed position corresponding to a compression factor of 5. The water surface is aspirated lowering it significantly to a level very close above the edge of the trough walls. Then the barrier is moved to maximum open position trough enclosure is sealed and the surface pressure should have equilibrated. The cleanliness of the water surface is tested with what is called a blank isotherm Figure 7. The surface is considered clean if the change in surface pressure is less



Figure 7. Compression of the residual impurities on the "clean" water surface.

than 0.1 mN/m when the surface compressed by a factor of 4. Estimated number of impurities particles via the two dimensional ideal gas law approximation gave an estimate of 10^{13} which is three orders of magnitude less compared to the number of molecules typically being deposited for the LM experiment (41).

2.1.6 Enclosure

The main body of the trough is enclosed in a rectangular aluminum chamber with side windows sealed with capton tape. Figure 8 shows the final assembled trough with the enclosure. The base of the enclosure is made of aluminum quarter inch thick plate that was hard coat anodized. All around the edges of the bottom plate there is a o-ring groove ensuring the proper sealing of the the chamber. The rectangular box of the trough has flanges on the top and the bottom. The bottom flange is pressing on the o-ring while the top flange has it's own o-ring groove that is sealing the top lid. The top lid is another rectangular plate of aluminum quarter inch thick that is also hard coat anodized. A large window right above the trough was cut. It was covered by a rectangular glass piece 5x10 inches and sealed via o-ring and DE-STA-CO 2005-U Horizontal Handle Hold Down Action Clamp. On the short side of the box where the surface pressure balance is there is a small hinged door with a glass window that is also sealed with o-ring. The door was used for the operation of the surface pressure balance and aspiration of the water subphase. The trough was placed on a kinematic mount tilt stage allowing the proper leveling.



Figure 8. Assembly trough and enclosure

2.1.7 Cleaning Procedures and assembly

The usage of consistent cleaning procedures was found to be very important in achieving a clean environment for the trough studies. Typical workflow in the cleaning consists of dissembling the chamber, putting the surface pressure balance aside and removing the teflon partsthe trough and the barrier. All the parts are cleaned thoroughly and then inserted and sealed





in the box as quickly as possible, in order to minimize their exposure time to the air in the room.

2.1.7.1 Cleaning metal parts

All the metal parts from bolts, washers and barrier holder to the trough base, the aluminum enclosure and lid were regularly cleaned. Smaller parts were degreased by immersing them in trichloro-ethylene and washing them with acetone and methanol afterwards. At the end they were rinsed with clean water from the Millipore system. Larger pieces ware cleaned with acetone, and methanol or chloroform in a fume hood.

2.1.7.2 Cleaning teflon parts

The trough and the barrier ware cleaned by immersing them in a bath of sulfuric acid with amonium persulfate dissolved in it at concentration 18 g/l. After at least 30 minutes the teflon parts were rinsed thoroughly with clean water from the Millipore system. On separate occasions the trough and the barrier were cleaned just with alpha wipe soaked with chloroform. The corners were cleaned by pressing the alpha wipe with a Q-tip or a dull screwdriver.

2.1.7.3 Assembly and final cleaning

After all the components were cleaned the box was assembled and sealed. After rinsing the trough multiple times with water from the Millipore system it was quickly transferred to the box mounting stage. The trough was filled with water immediately from via the integrated water storage system previously described. The barrier was assembled with the metal part and quickly placed in the trough. After that the water in the trough is exchanged at least 3 times. The draining of the water was done via opening the side door and aspirating with

pipette connected to a vacuum pump. In order to avoid any dust from the external air in the lab to enter the inner parts of the chamber a vapor saturated ultra pure nitrogen gas was let run in the chamber thus creating a small outward gradient of the air flow.

2.2 X-ray Source and Reflectometer

In this section we justify the need of synchrotron x-ray source. X-ray measurements were carried out at the Liquid Surface Reflectometer at Beamline 15 at the Advanced Photon Source in Argonne National Laboratory. We provide a general design, features and parameters of the conditions under which we collected the data with the reflectometer.

2.2.1 X-ray Source

In general the soft matter systems interacts weakly with the x-rays. Assuming we want to measure structure with atomic resolution under a = 5 Å on the Langmuir Monolayer systems at the water-air interface ($Q_c \approx 10^{-2}$ Å⁻¹) the specular scattered intensity is proportional to

$$I \propto \left(\frac{Q_c}{2Q}\right)^4 \approx 10^{-10} I_0 \tag{2.3}$$

This number is further reduced by additional three orders of magnitude due to the effects from the thermally excited capillary waves. The signal from the grazing incidence diffraction is of the order of 10^{-8} of the incidence radiation. Third-generation light source at the Advanced Photon Source (APS) at Argonne National Lab provides high brilliance and highly monochromatic X-ray beam with intensity of $10^{10} - 10^{12}$ photons per second thus allowing us to collect data for a single Q point in a matter of seconds to few minutes. Furthermore the angular range corresponding to the momentum of transfer needed to explore the structure at the atomic level resolution is accessible only at the synchrotron facilities. The production of the high brilliance x-ray starts with the electrons emitted from a cathode heated to $\approx 1100C^{\circ}$ accelerated by high V AC in the LINAC to 99.999% of the speed of light Figure 10. From the LINAC the electrons are injected into the booster synchrotron and are accelerated by an electric field and four RF cavities from 450 MeV to 7 Gev in 500 ms further increasing their speed to over 99.999999%. The 7 Gev beam is injected into the 1104 meter circumference storage ring. The storage ring is a circular vacuum chamber encompassed by electromagnets that are focusing and bending the electron beam. That sequence of magnets produces very small beam with extremely small angular divergence.

Around the ring there are forty straight sections also called sectors. Thirty five of which are equipped with insertion devices providing the source of x-ray radiation to the user experiments. The liquid surface reflectometer instrument used in our scattering experiments is located in sector 15.

2.2.2 Liquid Surface Reflectometer

X-ray scattering experiment were carried out on beamline 15-ID at ChemMatCARS at the APS ANL with the liquid surface reflectometer described in detail elsewhere (46) (47) (48) (49). Measurement techniques described elsewhere (50) (51) (5) (52) (53) (54).

X-ray reflectivity and grazing incidence diffraction were measured with a Pilatus 100K area detector using monochromatic x-rays of energy 10 keV. XR experiment geometry is illustrated on Figure 11. Liquid surface reflectometer is shown on Figure 12

The monochromatic x-ray beam is deflected by the crystal monochromator to the desired angle corresponding to the particular wave-vector transfer. The beam size and, angular accep-


Figure 10. APS Storage Ring Diagram

tance of the detector are defined by a sets of horizontal and vertical slits placed on the path of the x-ray beam. The incident beam size is defined by the **S1** slits and it's variation of intensity is being monitored by an ionization chamber **monc**. The beam reflects from the sample onto the two dimensional pixel detector **PILATUS 100K** situated 550 mm away from the center of the sample. The pixel size of the PILATUS is $172\mu m \times 172\mu m$ with an active area 33.5 mm×83.8 mm. To limit the angular acceptance of the detector in order to reduce the various sources of background scattering two sets of slits are placed: **S4** - at 210 mm away from the



Figure 11. Scattering geometry Side View

sample and S5 - directly in front of the detector. The scattering signal detected by a pixel on the area detector corresponds to a specific value of the reciprocal space.

On Figure 13 is shown a typical pattern of the reflected and transmitted x-rays beams on the fraction of the area detector. The reflected beam intensity is determined by integrating over a region 15×15 pixels and the background signal is defined as averaged intensity over two similar rectangular regions placed horizontally on both sides of the reflected region.





Figure 13. X-ray beams imprints on the pilatus area detector

CHAPTER 3

X-RAY SCATTERING FROM LIQUID INTERFACES

After a short introduction to the interaction of X-rays with matter we provide a brief description of the surface sensitive X-ray scattering techniques used for studying the Langmuir films at the liquid-vapor interface. These techniques allow us to determine the in-plane and out of plane structure with near atomic level resolution. We will describe the scattering geometry, specular reflectivity in terms of the Born Approximation, Grazing Incidence Diffraction (GID) and Bragg Rods and Diffuse off-specular Reflectivity.

3.1 X-rays interaction with matter

The index of reffraction of condensed matter for X-rays with wavelength of $10^{-1} - 10^0$ Å is slightly less than 1 and is given by 3.1

$$n = 1 - \delta + i\beta \tag{3.1}$$

where δ and β are of the order of 10^{-5} and 10^{-8} respectively

$$\delta = \frac{2\pi\rho r_e}{k^2} \text{ and } \beta = \frac{\mu}{2k}$$
(3.2)

Here $k = \frac{2\pi}{\lambda}$ is the X-ray wave number for an X-ray with wavelength λ , ρ is the electron density of the medium, r_e is the classical electron radius and μ is the linear absorption coefficient of the medium.

The kinematics of surface X-ray scattering is illustrated on Figure 14. The liquid surface is in the x-y plane, with the normal pointing upwards in +z direction. (46), (55) The incident X-ray wave vector $\mathbf{k_i}$ makes an angle α_i to the surface and scattering is observed at α_s and in-plane angle ϕ w.r.t. the y-axis. The wave will be partially reflected and partially refracted within the plane of incidence spanned by the $\mathbf{k_i}$ and the vector normal to the surface. Specular reflection is observed at $\alpha_i = \alpha_s ta=0$ with wave-vector transfer \mathbf{Q}

$$\mathbf{Q} = \mathbf{k}_{\mathbf{s}} - \mathbf{k}_{\mathbf{i}} = Q_z \hat{\mathbf{z}} \tag{3.3}$$



Figure 14. Kinematics of Scattering

Similarly specular refraction is observed at $\alpha_t = \alpha_i$. Measurement of the reflection as a function of α_i can be expressed as a function of the wave-vector transfer $\mathbf{Q}_{\mathbf{z}}$. Features of the electron density with length scale d along the normal direction of the interface would cause interference effects that would appear as oscillations with period $2\pi/d$ in the Q_z dependence of the reflectivity. In general the components of \mathbf{Q} expressed in the angles of the scattering geometry is given by

$$Q_z = k(\sin \alpha_i + \sin \alpha_s)$$

$$Q_{xy} = k\sqrt{\cos^2 \alpha_i + \cos^2 \alpha_s - 2\cos \alpha_i \cos \alpha_s \cos \phi}$$
(3.4)

Expressed in more convenient form for calculations

$$Q_z = 2k \sin \frac{\alpha_i + \alpha_s}{2} \cos \frac{\alpha_s - \alpha_i}{2}$$

$$Q_{xy} = 2k \sqrt{\sin^2 \frac{\alpha_i + \alpha_s}{2} \sin^2 \frac{\alpha_s - \alpha_i}{2} + \cos \alpha_i \cos \alpha_s \sin^2 \frac{\phi}{2}}$$
(3.5)

By imposing the boundary conditions at the interface requiring continuity of the wave amplitude and its first derivative we can derive the Snell's law

$$\cos(\alpha_i) = n\cos(\alpha_t) \tag{3.6}$$

The incident and transmitted angles are small and we can expand the cosine terms in 3.6 from which and we can derive two important results, the critical angle of total external reflection and the penetration depth. Since the index of refraction of X-rays is slightly less than unity the condition for total external reflection is easily achieved for grazing incident angles satisfying the condition $\alpha_i < \alpha_c$ where

$$\alpha_c = \sqrt{2\delta} \tag{3.7}$$

Typical values for α_c are below 0.5° or few milli-radians.

Expanding 3.6 and using 3.7 yields

$$\alpha_i^2 = \alpha_t^2 + \alpha_c^2 - 2i\beta \tag{3.8}$$

The intensity of the transmitted wave can be decomposed into two terms

$$A_t e^{ik\alpha_t z} = A_t e^{ikRe(\alpha_t)z} A_t e^{-kIm(\alpha_t)z}$$
(3.9)

where the imaginary part corresponds to the absorption in the medium. We can define the quantity penetration depth Λ as the distance for which the intensity falls off by 1/e.

$$\Lambda = [2kIm(\alpha_t)]^{-1} = [2\frac{2\pi}{\lambda}Im(\sqrt{\alpha_i^2 - \alpha_c^2 + 2i\beta})]^{-1}$$
(3.10)

On Figure 15 is illustrated the penetration depth Λ in water at wavelength $\lambda=1.38$ Å. For incident angles below the critical angle the incident wave is totally reflected, while the refracted wave becomes evanescent traveling along the surface. The amplitude of this evanescent wave de-

cays exponentially with the depth. For $\alpha_i < 0.5\alpha_c$ the penetration depth is nearly independent of the X-ray wavelength and is approximately 50Å.

The evanescent wave can provide us with the in-plane structure information via diffraction from surface layers with thickness of the order of 50Å. This diffraction is called Grazing Incidence Diffraction (GID) (56), (57), (58), (59), (60).



Figure 15. Penetration Depth

3.2 Born Approximation

Consider the interaction of X-rays via Thomson scattering where material is simply characterized by its electron density ρ . A charged particle is accelerated by the electric field of the incident X-ray and re-radiates. For the case of the atoms considered in soft-condensed matter the scattering from the light electrons is more efficient than the one for the heavy nuclei . In the kinematic approximation which considers only the single scattering and multiple scatterings are negligible an electron only sees the incident wave. Waves scattered by two electrons separated by distance r only differ by a phase factor $e^{i\mathbf{Q}\cdot\mathbf{r}}$ (61)



Figure 16. Kinematics of Scattering by two scatterers separated by distance r

In the continuous limit taking the sum over all of the electrons the total scattered amplitude is proportional to

$$\int dr \rho(r) e^{i \mathbf{Q} \cdot \mathbf{r}}$$

and the scattering cross section proportional to the intensity squared is given by

$$\frac{d\sigma}{d\Omega} = \left| r_e \int dr \rho(r) e^{i\mathbf{Q}\cdot\mathbf{r}} \right|^2 \tag{3.11}$$

where the proportionality factor r_e is the classical electron radius. For scattering from homogeneous ideally flat surface the electron correlations are the same within a given x-y plane and varies only in the direction normal to the surface. Furthermore for large values of z the electron density is constant equal to the bulk value of the respective phase. Integrating by parts 3.11 we get

$$\frac{d\sigma}{d\Omega} = \left|\frac{r_e}{iQ_z^2}\int dr \frac{\partial\rho(r)}{\partial z} e^{i\mathbf{Q}\cdot\mathbf{r}}\right|^2$$

The total intensity scattered into the detector can be obtained by integrating the differential scattering cross section over the solid angle to the detector's angular acceptance $\Delta\Omega$.

$$I = \frac{I_0}{A_s sin\alpha} \int_{\Delta\Omega} d\Omega \frac{d\sigma}{d\Omega}$$

Normalizing to the incident intensity gives us the reflectivity coefficient within the Born Approximation (BA)

$$R = \frac{I}{I_0} = \frac{1}{A_s sin\alpha} \int_{\Delta\Omega} d\Omega \frac{d\sigma}{d\Omega}$$
$$R = \frac{16\pi^2 r_e^2 \rho_s^2}{Q_z^4} = \left(\frac{Q_c}{2Q_z}\right)^4$$
(3.12)

Where Q_c is the critical momentum of transfer.

$$Qc = 4\sqrt{\pi r_e \rho_s} \tag{3.13}$$

Expressed as a function of the critical incidence angle α_c using the geometry equation 3.5

$$Qc = 2k\sin\alpha_c \tag{3.14}$$

The condition for total external reflection takes place when $Q_z \leq Q_c$

Specular reflection of an ideal flat surface is given by the Fresnel law of optics. Fresnel reflectivity is the square modulus of the reflectance coefficient as a function of the momentum of transfer in the z direction. In the limit of small angle of incidence and ignoring absorption it reduces to (62)

$$R_F(Q_z) = \left| \frac{Q_z - \sqrt{Q_z^2 - Q_c^2}}{Q_z + \sqrt{Q_z^2 - Q_c^2}} \right|^2$$
(3.15)

For large values of Q_z the Fresnel reflectivity is in agreement with the reflectivity from the BA 3.12 as shown on Figure 17. For small values of $Q_z \rightarrow 0$ BA diverges and is inaccurate for $Q_z < Q_c$ which is a reflection of the fact that for scattering near the critical angle the multiple

35

scattering events are dominant a major assumption of the BA. A higher order approximation accounting for the multiple scattering is the Distorted Wave Born Approximation (DWBA)



Figure 17. Fresnel and Born Approximation compared

3.3 Electron Density Profile

X-ray reflectivity technique is commonly used to characterize the interfaces relevant to the soft condensed matter. By measuring the XR and fitting the BA reflectivity normalized by the Fresnel we can determine the ED profile across the interface which in turn can be related to the molecular arrangements in the film floating on the interface (46).

$$\frac{R(Q_z)}{R_F(Q_z)} = \left| \frac{1}{\rho_0 - \rho_s} \int \frac{d \langle \rho(z) \rangle}{dz} e^{-iQ_z z} dz \right|^2$$
(3.16)

Where $\frac{d\langle \rho(z) \rangle}{dz}$ is the derivative of the electron density (ED) profile averaged over the in-plane coherence length of the X-rays. The Electron Density Profile describes the variation in ED in the direction normal to the interface. Far from the interface the ED values are constrained between the two bulk values ρ_0 and ρ_s which are the ones for the air and the water respectively. The ED profile is given by

$$\langle \rho(z) \rangle = \frac{1}{2} [(\rho_0 + \rho_s) - (\rho_0 - \rho_s) f(z))]$$
(3.17)

Where f(z) is a monotonic function satisfying the condition

$$\lim f(z) = \pm 1|_{z \to \pm \infty} \tag{3.18}$$

and furthermore has to transition into a step function for the case of ideally flat interface. The most common choice for this f(z) is the error function ERF where $erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$ is the error function and is used to model the fluctuations of the interface due to capillary waves.

If we model the interface as N layers of homogeneous electron density each with with it's own interfacial width L and fluctuation of the smooth surface σ due to the capillary waves. We can refine the model 3.17 to accurately represent the film at the interface as a composite of N + 1 interfaces. (63)

$$\langle \rho(z) \rangle = \frac{1}{2} \left[\sum_{i=0}^{N} (\rho_i - \rho_{i+1}) \left(1 + erf(\frac{z - D_i}{\sqrt{2\sigma_i}}) \right) \right] + \rho_s \tag{3.19}$$

Where $(\rho_i - \rho_{i+1})$ is the change of the ED, σ_i layer roughness of the ith layer. And the quantity D_i is the distance from the surface to the interface between i and i+1 layers.

$$D_i = \sum_{j=1}^i L_j \tag{3.20}$$

The averaged normal derivative is given by the Gaussian form.

$$\frac{d\langle \rho(z)\rangle}{dz} = \sum_{i=0}^{N} (\rho_i - \rho_{i+1}) \frac{1}{(2\pi\sigma_{i+1}^2)^{1/2}} e^{-\frac{(z-D_i)^2}{2\sigma_{i+1}^2}}$$
(3.21)

Equation 3.16 takes the form

$$\frac{R(Q_z)}{R_F(Q_z)} = \left| \sum_{i=0}^{N} \frac{\rho_i - \rho_{i+1}}{\rho_0 - \rho_s} e^{-iQD_i} e^{-Q^2 \sigma_{i+1}^2/2} \right|^2$$
(3.22)

On Figure 18 is shown the two layer ED Profile with nonzero roughness compared to the one from ideally flat interface (dashed line).



Figure 18. ED Profile of a rough surface compared to ideally flat

3.4 Grazing Incidence Diffraction

In 3D crystals, diffraction from a set of planes with interplanar spacing d takes place when the Bragg law is obeyed, namely when these two conditions are met:

- 1. The scattering vector length Q equals the reciprocal of the interplanar spacing $Q = 2\pi d^*$
- 2. The normal to the planes bisects the angle between the incident and the outgoing beam

 $Q = |\mathbf{k_s} - \mathbf{k_i}| = \frac{4\pi}{\lambda} \sin \theta$, $d^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ where $\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*$ are the reciprocal vectors of the unit-cell vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$ and $\mathbf{h}, \mathbf{k}, \mathbf{l}$ are the Miller indices of planes with spacing d_{hkl} . On Figure 19 is shown the real and reciprocal space latices. The notation for the Lattice planes specified by the their respective Miller indices in parentheses (h k l) with negative values indicated by over-striking (64).



Figure 19. Hexagonal packing real and reciprocal space

The scattering in 3D crystals takes place only when the scattering vector Q coincides with (h,k,l) points of the reciprocal 3D lattice Figure 20. For 2D crystals there is no restriction on the z component of the scattering vector, hence the Bragg scattering extends as continuous Bragg rods (BR) trough the 2D reciprocal lattice points. The finite thickness of the 2D crystal causes the BR to extend over a finite Qz region. From the analysis of the intensity distribution over that Qz interval we can obtain information on the molecular size and tilt in the crystalline

part of the LM. By combining the methods of GID and XR, the structure of the Langmuir films can be accurately characterized.



Figure 20. GID Scattering Geometry

Any periodicity of the molecules on the interface give rise to a peak of the scattered intensity. The intensity along a particular (h,k) BR is modulated with the square of the molecular form factor. The form factor of a rod with cylindrical shape molecule is a disc perpendicular to the molecular axis. The intersection of the Bragg rod with the reciprocal disc gives rise to the diffraction maximum. The variation of this intensity in the Q_z direction has is proportional to the structure factor amplitude and is approximated by (57)

$$I_{BR}(Q_z) \sim |T(Q_z)|^2 |F(Q_z)|^2$$
(3.23)

Where $T(Q_z)$ and $F(Q_z)$ are the transmission coefficient and cylindrical structure factor respectively (65)

$$T(Q_z) = \frac{2Q_z}{Q_z + \sqrt{Q_z^2 - Q_c^2}} F(Q_z) = \frac{\sin(Q_z H/2)}{Q_z H/2}$$
(3.24)

The intensity reaches it's maximum when the scattering vector $(\mathbf{Q}_{xy}, \mathbf{Q}_z)$ is perpendicular to the molecular axis. When molecules are in the plane perpendicular to the **hk** plane the maximum intensity of the BR will occur at the horizon at $Q_z = Q_c$. For the case when the molecules are tilted w.r.t. that plane the maximum would occur at a finite Q_z that will depend on the molecule tilt.

The intensity along the BR for the 3 main packing arrangements of the surfactant molecules are shown on Figure 21. On the left side is shown the lattice in reciprocal space. From top to bottom the lattice structures are hexagonal untitled, distorted hexagonal untitled and hexagonal tilted.



Figure 21. Close packing structure and diffraction patterns

3.5 Parratt's formalism: Matrix Recursive Method

In general the idealized interfaces cannot be approximated as step. A more accurate approach describing the continuous electron density profile would consider the multiple graded interfaces that are rough and thick between the two infinitely thick bulk medias. This model is accounting for the multiple scattering across those layers by applying the boundary condition of the propagated wave at each interface. Introduced by Kiessig in 1931 (66) and later by Parratt in 1954 (67) who developed the theory presented here in the matrix formalism of dynamical theory of reflection. Good description of this calculation can also be found in (46), (68), (69), (65), (70).

Consider plane wave polarized in the direction orthogonal to the plane defined by the incident and reflected x-rays. Medium is divided into N layers where each layer is considered to have uniform electron density. For this example we will consider the upper medium to be air. Going downwards each layer has index $1 \le j \le N$. Derivations of the matrix recursive method are under the following conditions.

- S polarized waves- polarized in the direction normal to the incidence plane
- Ignoring absorption i.e. the imaginary part of the index of refraction $\beta = 0$
- No back reflection from the substrate since the x-rays penetrate only few microns
- Relativistic effects are not considered. Expected some small corrections for heavy atoms

For each interfacial layer we consider transmitted and reflected waves with amplitudes A^+ and A^- Figure 22. The electric field E^- for the downwards traveling wave in the jth layer is given by

$$\mathbf{E}^{-} = A^{-} e^{+(\omega t - k_{x,j}k - k_{z,l}z)} \mathbf{\hat{e}}_{\mathbf{v}}$$
(3.25)

Where the wave vector components for layer j are given by

$$k_{x,j} = k_j \cos \alpha \tag{3.26}$$

$$k_{z,j} = -k_j \sin \alpha = -\sqrt{k_j^2 - k_{inx,j}^2}$$
(3.27)

The x component is conserved and is equal to $k_x, j = k \cos \alpha$ while the z component is simply kn_j . Substituting these expressions and expanding the cosine for small angles the equation above becomes.

$$k_{z,j} = -k\sqrt{\frac{q}{2k} - 2\delta_j} \tag{3.28}$$

From 3.2 taking the ratio of δ_j/δ and remembering that $\delta = 1/2\alpha_c^2$ and $Q_c = 2k\alpha_c$ we can derive the expression for δ_j as a function of ρ_j

$$\frac{\delta_j}{\delta} = \frac{\rho_j}{\rho_{sub}} \tag{3.29}$$

$$\delta_j = \frac{\rho_j}{2\rho_{sub}} \left(\frac{Q_c}{2k}\right)^2 \tag{3.30}$$



Figure 22. Parratt layers

For each layer we will have the superposition of incident and reflected waves giving and the electric field at layer j is

$$E_j(x,z) = (A_j^+ e^{ik_{z,j}z} + A_j^- e^{-ik_{z,j}z})e^{+i(\omega t - k_{x,j}x)}$$
(3.31)

We introduce the shorthand notation for the upward and downward components of the electric field at layer j

$$U(\pm k_{z,j}, z) = A_j^{\pm} e^{\pm i k_{z,j} z}$$
(3.32)

Taking the combination of the two equations that arise from the conditions of continuity of the tangential component of the electric field and the continuity of the electric field derivative at depth Z_{j+1} it can be derived

$$\begin{bmatrix} U(k_{z,j}, Z_{j+1}) \\ U(-k_{z,j}, Z_{j+1}) \end{bmatrix} = \begin{bmatrix} p_{j,j+1} & m_{j,j+1} \\ m_{j,j+1} & p_{j,j+1} \end{bmatrix} \times \begin{bmatrix} U(k_{z,j+1}, Z_{j+1}) \\ U(-k_{z,j+1}, Z_{j+1}) \end{bmatrix}$$
(3.33)

Where the refraction matrix $\mathscr{R}_{j,j+1}$ in the equation above transforms the electric field across two adjacent layers and the indices $p_{j,j+1}$ and $m_{j,j+1}$ are given by

$$p_{j,j+1} = \frac{k_{z,j} + k_{z,j+1}}{2k_{z,j}}$$

$$m_{j,j+1} = \frac{k_{z,j} - k_{z,j+1}}{2k_{z,j}}$$
(3.34)

Similarly we can define the translation matrix \mathscr{T}_j which is transforming the magnitude of the electric filed in layer j.

$$\begin{bmatrix} U(k_{z,j}, z) \\ U(-k_{z,j}, z) \end{bmatrix} = \begin{bmatrix} e^{-ik_{z,j}h} & 0 \\ 0 & e^{-ik_{z,j}h} \end{bmatrix} \times \begin{bmatrix} U(k_{z,j+1}, z+h) \\ U(-k_{z,j+1}, z+h) \end{bmatrix}$$
(3.35)

Applying the above two transition across all the layers we get

$$\begin{bmatrix} U(k_{z,0}, Z_0) \\ U(-k_{z,0}, Z_1) \end{bmatrix} = \mathscr{R}_{0,1} \mathscr{T}_1 \mathscr{R}_{1,2} \mathscr{T}_2 \cdots \mathscr{R}_{N,sub} \begin{bmatrix} U(k_{z,sub}, Z_{sub}) \\ U(-k_{z,sub}, Z_{sub}) \end{bmatrix}$$
(3.36)

The product of all the 2 \times 2 matrices above gives the 2 \times 2 transfer matrix $\mathcal M$

$$\begin{bmatrix} U(k_{z,0}, Z_1) \\ U(-k_{z,0}, Z_1) \end{bmatrix} = \begin{bmatrix} M_{1,1} & M_{1,2} \\ M_{2,1} & M_{2,2} \end{bmatrix} \times \begin{bmatrix} U(k_{z,j+1}, Z_{sub}) \\ U(-k_{z,sub}, Z_{sub}) \end{bmatrix}$$
(3.37)

Since the reflection is defined as the ratio of the reflected to the incident electric fields and there is nor reflection back from substrate $U(k_{z,sub}, Z_{sub}) = 0$ the the from the matrix equation above we get

$$r = \frac{U(k_{z,0}, Z_1)}{U(-k_{z,0}, Z_1)} = \frac{M_{1,1}}{M_{2,2}}$$
(3.38)

Numerical approach for the Parratt's Matrix Recusive method with Mathematica is outlined in the appendix A.4.2.

CHAPTER 4

MATERIALS AND METHODS

4.0.1 Chemicals

Arachidic Acid (AA $C_{20}H_{40}O_2$, CAS Number 506-30-9) was purchased from Sigma Aldrich and used as received. Chloroform also from Sigma Aldrich was used for preparing the spreading solution of AA.

Phosphatidylinositol-4,5-diphosphate C-16 (PIP2 $C_{41}H_{78}O_{19}P_3 \cdot Na$ PtdIns-(4,5)-P2(1,2dipalmitoyl)) Figure 23 was purchased from Cayman chemicals (Item Number 10008115) in 100 microgram vials and was stored at all times in the freezer at -20 C° .

Trimethyloctadecylammonium bromide(C18TAB $CH_3(CH_2)_{17}NBr(CH_3)_3$ CAS Number 1120-02-1) purchased from Sigma Aldrich and it was used without further purification Figure 24.

4.0.2 Solvent Preparation

Solvent stock solution for both components was prepared from chloroform/methanol/water 1:1:0.1 mixture. Ultrapure water from a Millipore (45) Mili-Q UV+ system was used for preparing all solutions.

The following materials were used for preparing of the solvent solution.

- Two 50 ml volumetric beakers
- One 5 ml volumetric beaker for the water



Figure 23. PIP2 molecular diagram

- One 250 ml volumetric flask for mixing the three solvent components
- One 100 ml volumetric flask for preparation and storing the C18TAB solution
- Teflon tape used for sealing the flasks and PIP2 vial
- Two 100 μl Hamilton syringes one for each of the methanol and chloroform
- One 50 or 100 ml beaker for transfer the Chloroform



Figure 24. C18TAB molecular diagram

Fill one of the 50 ml beakers with methanol and the other beaker with chloroform. Then pour them both into the 250 ml flask. Upon shaking the flask two to five times to ensure proper mixing of the methanol chloroform, slightly less than 5 ml of water is added. Repeat that procedure two times. It is important that the water is poured into the flask in a very small stream and closely observing the mixing since the over saturation of the water can be easily achieved. The third time we add the chloroform and methanol in the amounts of 25 ml and observe even greater caution while adding the final 2 - 3 ml of water. The prepared solvent flask was closed with the glass stopper, sealed with the teflon tape and stored in the freezer at -20C°.

4.0.3 Sample Preparation

Separate Hamilton syringes were used for each of the components. Before and at the end of each use the syringes were cleaned by drawing chloroform trough the needle. The chloroform was drawn from a small clean beaker dedicated for that purpose alone. Also before each use needle of the syringe is run trough a stream of chloroform to remove any small dust particles that might have accumulated on the exterior of the needle.

Both solutions were prepared at concentration of 0.5 mM and mixed together in the PIP2 vial. Forty minutes prior to the preparation the PIP2 vial was taken out of the freezer in order to allow for its temperature to equilibrate with that of the room temperature. In order to prepare a 0.5 mM solution of PIP2 a 208 μl of the solvent solution are injected into the PIP2 vial by punching the needle of the syringe through the stopper. It would take on average 20 minutes for the PIP2 to dissolve.

The C18TAB solution is prepared via dissolving the weighted amount into the stock solution in a 100 ml flask. Both solutions are being mixed in the PIP2 vial by injecting (3:1) 824 μl 0.5 mM of C18TAB solution into the already dissolved PIP2. The prepared mixed solution was sealed with teflon tape and stored at -20 C° . It was taken out of the freezer 20 minutes before use.

Before mixing both solutions were prepared at concentration 0.5 mM and mixed together in the PIP2 vial. The prepared mixed solution was sealed with teflon tape and stored at -20 C° .

4.0.4 Spreading Procedure

The sample is deposited via a separate graduated 100 μl Hamilton syringe that was used for that purpose only. The same cleaning procedure as with the other syringes was employed. The syringe has 12 inch needle that is encased in a piece of glass capillary tubing. While flowing vapor saturated nitrogen or helium through the trough chamber the solution was deposited trough a small (of an inch diameter) port on the side of the chamber. The solution was added to the aqueous surface drop by drop hanging from the end of the needle to the water surface by carefully touching the drop to the surface without submerging he needle tip Figure 25.



Figure 25. Spreading procedure technique requires some practice and steady hand

The isotherm measurements start approximately fifteen to thirty minutes after the spreading in order to allow for the solvent to evaporate thus leaving only the surfactant molecules at the interface.

4.1 Isotherms

The most standard and frequent measurement on Langmuir Monolayers (LM) is the measurement of the surface pressure π as a function of the area per molecule A and is known as a compression π -A isotherms. The first isotherm measurements were conducted by Agnes Pockels in 1891 (11) and later Irving Langmuir in 1917 (13) gave the modern understanding of the structure of LM at the molecular level. The π -A isotherms are the two dimensional analogue of p-V isotherm curve. Thermodynamic phase transitions of the LM are expressed in the isotherm as discontinuities in the surface pressure behavior or regions of constant pressure for a range of area per molecule. π being the two dimensional analog of the hydrostatic pressure is given by the difference in surface tension between the pure water subphase ($\gamma_0{=}72.8~{\rm mN}~{\rm m}$) and the one with the deposited surfact ant on it. $\pi=\gamma_0-\gamma$ A is the occupied area per molecule and is calculated from the number of molecules spread at the interface divided by the area of the interface. The area is controlled by variation of the fraction of the water surface accessible to the monolayer. Typically the area is reduced at a constant rate by moving a barrier across the water surface and the surface pressure is measured continuously via surface film microbalance. The most common technique for measuring surface pressure is the Wilhelmy plate, particularly its paper version introduced by Gaines (71). It measures the force F exerted on a hydrophilic paper plate typically made of filter or chromatography paper that is always wet while in contact with the aqueous phase Figure 26.



Figure 26. Wilhelmy plate force diagram

The interfacial tension is calculated from

$$\gamma = \frac{F}{p\cos\theta} \tag{4.1}$$

where p is the perimeter of the paper plate. Since the paper completely wets we achieve a zero contact angle and the surface tension simply becomes 4.1

$$\gamma = F/p.$$

The surface tension is continuously monitored while reducing the available surface of the monolayer. That is accomplished by slowly moving a teflon barrier across the short edge of the trough driven by an external stepper motor.

CHAPTER 5

ISOTHERM DATA

5.1 Control Experiment Arachidic Acid Isotherm

Significant effort was put into rebuilding an experimental Langmuir Trough including replacement of some of its components and developing a new data acquisition system. We needed a known and well behaved test system in order to verify and extensively test the experimental apparatus prior to conducting the intended experiments. We chose the Arachidic Acid (AA) for our control measurements.

The 0.5 mM solution of AA in chloroform was deposited via 100 μl Hamilton syringe in a series of drops each with volume 2-5 μl . No change within 0.1 mN/m in surface pressure was observed during spreading or at the end of the spreading of the AA solution. On Figure 27 is illustrated the surface tension for the duration shortly after the spreading of 200 μl of 0.5 mMAA.

Compression of the film at a constant rate of 0.4 square angstroms per molecule per minute began 20 minutes after spreading of the AA solution to allow for evaporation of the chloroform. The number of molecules and hence the area per molecule were calculated from the molecular weight and the amount spread.



Figure 27. Surface tension while and after spreading of 200 μl 0.5 mM AA

Figure 28 shows the obtained surface pressure versus molecular area ($\pi - A$) isotherm of AA spread on a neutral pH and buffer free water. The isotherm of this well-studied system (57), (72),(73),(74) possesses the typical features characteristic of fatty acid isotherms.

Initially spread at high area per molecule of the order of 100 square angstroms without any significant change (within 0.1 mN/m) in surface pressure. This is considered a 2D gas phase that is well described by a 2D ideal gas law. With decreasing the area per molecule the monolayer transitions into the so called liquid expanded phase where the head groups are still



Figure 28. Arachidic Acid isotherm

disordered at the liquid vapor interface. That is the region with area per molecule smaller than 26 Å² Typically at that phase the system does not give any X-ray diffraction signal. With further compression the monolayers goes into the tilted condensed phase which is characterized by densely packed and ordered head groups all the tails aligned in the same direction. Right around the crossectional area of the acyl chains which is approximately 20 Å² the systems transitions into the untitled condensed phase followed by collapse of the monolayer. Pressure
point of 20mN/m is in good agreement with the area of the acyl chain in the rotator phase (75),(76), (77).

Applying the 2D ideal gas law for the surfactant molecules on the surface we can extrapolate the area per molecule for a given surface pressure.

$$\frac{A_{trough}}{N} = \frac{k_B T}{\pi} \tag{5.1}$$

On Table I are shown values of area per molecule for a range of surface pressure at room temperature estimated from 5.1, where the number of particles is calculated for an area with dimensions 4.5x8.5 inches.

X-ray reflectivity measurements were conducted for two values of the pressure in the tilted condensed phase of the isotherm. First one at $\pi = 10 \ mN/m$ and the second at pressure close to the transition point at $\pi = 18 \ mN/m$. We did that by compressing the trough to the desired pressure and after 15 minutes the rate of pressure drop would decrease to under 0.1 mN/m per hour. Overall change in pressure while taking the XR curve is 0.2 mN/m or less for the first and 0.05 mN/m for the second data set.

The area per molecule calculated from the amount spread and the area of the trough differ from the actual values from the isotherm by 4 $Å^2$. This is mainly due to the fact that pH value of the water subphase was not lowered thus some of the surfactant molecules must have dissolved.

$\pi \ [{\rm mN/m}]$	A $[Å^2]$	N $\times 10^{16}$
0.1	4142	0.06
1	414	0.6
3	138	1.8
4	103	2.4
10	41	6
20	20.7	12

TABLE	Ι
-------	---

Calculated area per molecule for selected values of surface pressure at room T

5.2 Characteristics of Individual Components

Each surfactant C18TAB or PIP2 taken by itself does not form a stable monolayer at the water surface, even when deposited in excessive amounts until a significant increase of π is present. Shortly after the spread the π would decrease back to near zero values like it is in the case of PIP2 while C18TAB component deposited by itself would not induce any change in π (78), (26).

5.2.0.1 C18TAB Surface Pressure

Water soluble C18TAB does not adsorb at the liquid vapor interface when deposited by itself (78), (26). Solution of 0.5 mM C18TAB in Chloroform was prepared and spread at an

amount that would correspond to approximately 100 Å² per molecule. Just like with the AA isotherm procedure waited 20 minutes to allow for the solvent to evaporate and started the compression. The surface pressure balance uncertainty in measurement is less than 0.1 mN/m. No change of the surface pressure was observed within that uncertainty.

Another experiment performed where we would deposit enough solvent until a significant change in surface pressure is observed. At first 80 μl and then added additional 300 μl of 1 mM solution amount that correspond to occupancy of less than 10 Å² per molecule. No change within the instrumental uncertainty in the π observed in this case either. As a control experiment in order to eliminate instrumental fault or some other unforeseen experimental flaw we would deposit a AA solution in an excessive amount until π increase was observed. This was done on the same water suphase for which the C18TAB was deposited earlier, to confirm that the trough was working correctly.

5.2.0.2 PIP2 Surface pressure

Single component PIP2 solution prepared as described in 4 was deposited on neutral pH water without any buffer with spreading area per molecule of the order of 100 Å². Twenty minute after the spreading the compression of the trough started at a rate of 0.4 square angstroms per molecule per minute. No change withing $0.1 \ mN/m$ in π was observed. As a control experiment on the same water substrate a solution of AA was spread and later on compressed. Isotherm with the regions characteristic for the AA was observed.

As a separate experiment an excessive amount (200 μl 0.5 mM) of PIP2 solution was deposited until the π increased by 14 mN/m. The corresponding area per molecule calculated from the amount spread and molecular weight of the PIP2 was 43 Å². The time dependence of the surface pressure for that experiment is illustrated on Figure 29. Highest value of the barrier line represents completely open surface. Lowest value corresponds to compression ratio 6:1. Shortly after 20:00 where the surface pressure jumps to 14 mN/m is where the spreading occurred. For the next 3 hours the π decreased by 7 mN/m (Region on the graph between the spreading and 30 minutes before midnight). If allowed to equilibrate further it would have reached an equilibrium value close to 2 mN/m. The quantitative equilibrium value of the π was found by fitting the form $\pi = Ae^{(t-t_0)/\tau}$ and is shown as solid circles on Figure 29 (51)

From the 2D ideal gas law SP of 2 mN/m corresponds to area per molecule 10 times smaller than what was initially spread. Hence over 90% of the deposited PIP2 did not adsorb to the interface.

Upon compression (Region of the graph where the barrier changes to the maximum compression on Figure 29) of the surface with compression ratio 6:1 the surface pressure changed back to 4 mN/m which would start dropping back to zero rapidly though it seems to be stabilizing at a higher pressure. (Region of the graph after 2:00 am).

5.2.1 Composite system (PIP2 C18TAB) Isotherms

A binary system for which individual components are soluble in the subphase can form a stable LM system at the air water interface driven by the electrostatics.

5.2.1.1 Pressure Time dependence

When deposited as a mixture C18TAB:PIP2 with ratio 3:1 they tend to form a Langmuir film that is stable over the course of at least 5 or days. That might be due to the fact that



Figure 29. $\pi - T$, Barrier position and 2D Gas law as a function of time

the anionic PIP2 molecules try to minimize their free energy due to electrostatic repulsion and attract enough cationic C18TAB molecules at the surface thus forming the catanionic structure at the liquid vapor interface. This leads to the increase of surface pressure while the excess molecules dissolve into the aqueous subphase.

In order to create stable conditions for surface pressure measurements the cleanliness of the trough was of a great importance together with maintaining constant vapor saturated gas phase. The vapor saturated gas phases prevents the evaporation of the interface which would alter the surface pressure readings. For the range of pH values (40) 4 to 6 PIP2 has charge close to negative 3 while the C18TAB has +1 charge. All of the experiments reported here are conducted at neutral pH=5.5 aqueous subphase. The 3:1 molecule ratio was chosen in order to study the aggregation behavior of the electrically neutral surface. With this ratio the opposite charged surfactant headgroups are acting as a counterions to each other. Choosing a ratio different than 3:1 produced similar isorthems.

The $\pi - \gamma$ dependence while spreading is very different from what was earlier observed with the Arachidic Acid system.

On Figure 30 is shown the surface tension as function of time for the first 50 μl deposited with overall drop of tension about 20 mN/m. When another 50 μl was deposited the tension dropped further by 4 mN/m. After that it would take over 3 hours for the surface tension to reach an relatively equilibrium value of 50 mN/m where the rate of change is slightly larger than 2 mN/m per hour.

As we can see the slightest amount of deposited surfactant with area per molecule over one thousand square angstroms would result in an increase of π by 2 mN/m or more. That is a great discrepancy from the 2D ideal gas law where such surface pressures are expected at much smaller areas per molecule 200 Å². The 2D ideal gas law is clearly not valid and this behavior of the surface pressure is attributed to long range interactions.



Figure 30. Spreading of PIP2:C18TAB 3:1 solution 50 μl 0.5 mM

The system exhibits coexistence between the 2D gas phase at low surface density and a denser liquid condensed phase that is characteristic with higher surface pressures. This is an evidence of formation of 2D foams (79),(80).

5.2.1.2 Isotherm Data

Figure 31 shows surface pressure molecular area (π -A) isotherm for the catanionic system PIP2/C18TAB 3:1 ratio with a compression speed of 4 Å²/min. The isotherm varies smoothly and lacks any distinct phase transitions. The overall behavior is similar to other pressure area measurements of catanionic structures (26),(81), (82),(27),(28)



Figure 31. PIP2/C18TAB mixture Isotherm

Because of the surface pressure behavior explained in the previous section the isotherm starts from a nonzero $\pi \approx 20 \ mN/m$.

Changing the pH value of the aqueous substrate did not produce any qualitatively different isotherms. PIP2 charge is slightly less than 3 or larger than 3 for aqueous pH values less than 4 or larger than 6 respectively. This must be due to the fact that the system self-adjusts the amount of charges needed to minimize the free energy of the surface as long as we are depositing the binary mixture in molecular ratios close to 3:1. Collapsing point of the isotherm is at $\pi \approx$ 40 mN/m with A ≈ 25 Å²

CHAPTER 6

X-RAY DATA RESULTS AND ANALYSIS

6.1 Summary of the X-ray data

X-ray measurements were conducted on three different samples summarized in Table II

Sample Notation	Description
AA	Arachidic Acid control sample
Sam 1	$\rm PIP2/C18TAB$ 1:3 mol ratio on neutral pH 5.5 subphase 2 separate samples
Sam 2	PIP2/C18TAB 1:3 mol ratio on buffered pH 7 subphase

TABLE II

X-ray Reflectivity Samples Summary

Upon compressing the film to the desired pressure and waiting enough time allowing for the rate of change of SP to be reduced to less than 0.1 and 0.3 mN/m per hour for the AA and PIP2/C18TAB respectively. The higher value for the catanionic system was due to the longer relaxation times of the order of 3 hours compared to 15 minutes for the pure surfactant system.

6.2 AA x-ray data and analysis

Figure 32 illustrates X-ray reflectivity normalized by the Fresnel reflectivity from AA monolayer deposited on the water-vapor interface. The two curves represent different values of π from the liquid condensed phase of the isotherm the second being close to the transition point. Least square fit by a monolayer model consisting of two slabs 3.22 representing the tail and head group respectively are in agreement with previously reported measurements (57),(74),(82). Best fit parameters are shown on table Table III.

$\pi \ [mN/m]$	$ ho_1/ ho_{H_2O}$	$ ho_2/ ho_{H_2O}$	$L_1[\mathring{A}]$	$L_2[\mathring{A}]$	$\sigma[\mathring{A}]$
10	1.19	0.952	4.84	19.9	2.54
17	1.21	0.968	4.8	21.1	2.54

Best Fit parameters

Oscillations in the reflectivity represent interference of the X-ray waves scattered from different parts of the monolayer. Reflectivity curves for both datasets exhibit similar shapes and have peak positions of the second curve which are slightly shifted towards lower Q_z with respect to the first curve. This is an indication of slightly thicker layer which is expected when



Figure 32. AA Reflectivity

we increase the SP and the acyl chains transition from tilted to vertical orientation. After the second XR curve was taken a quick GID measurement was conducted all of which indicated a single peak at $Q_{xy} \approx 1.45 \text{\AA}^{-1}$ and transient peak at $Q_{xy} \approx 1.39 \text{\AA}^{-1}$ with duration of 2 to 5 minutes. This is an indication of compressed monolayer in the collapse region. The lattice parameters (a=4.83,b=5.21 Angstroms) are in good agreement with those found in previously

reported measurements on that system (83),(57) and are close to these typically found in single crystals of few fatty acids (75), (76).

6.3 X-ray Reflectivity Measurements on PIP2/C18TAB monolayers

We took X-ray reflectivity measurements and consecutively Grazing Incidence Diffraction measurements of the catanionic LM of PIP2/C18TAB (1:3 ratio) on aqueous subphase for two different pH values. Figure Figure 33 shows the reflectivity curves normalized to the reflectivity of an ideally flat interface 3.15 for the mixture spread on pure water (pH 5.5) for 3 different values of the surface pressure π as indicated. Solid lines are the best fit calculated reflectivities with the model 3.16.

At low surface pressure the system is in its gas phase and apart from a weak peak at low Q_z values no other features in the reflectivity curve are present. For this case the LM can adequately be described by a single slab model. For the higher values of π two peaks are present which is an evidence that the system can be adequately fit with a 2 slab model. The decrease in the period with the pressure increase indicates that the monolayer gets thicker as we further compress the film.

6.3.0.3 2 Slab Model

Best fit parameters for 2 slab model are summarized in Table IV. Subscripts 1 and 2 in the density and thickness correspond to composite head and tail groups respectively. More detailed analysis of the layer composition and parameters interpretation is presented in the next chapter.

Area/molecule takes into account solution concentration, components molecular weight, amount spread and area of the trough at the position of the barrier for which the measurement



Figure 33. X-ray Reflectivity of PIP2/C18TAB

was conducted. In the Sample solution column XR is shorthand for X-ray Reflectivity dataset. The first subscript indicates the dataset number and the second subscript refers to the solution. As it was already discussed earlier in 3.3 more than one solution exists for a particular reflectivity dataset. Of the two conjugate solutions we chose the one with the tail density that is characteristic for densely packed acyl chains in the rotator phase cite (75),(76). Electron

A/mol $[Å^2]$	$\pi[mN/m]$	DATA _{sam,sol}	$ ho_1/ ho_{H_2O}$	$ ho_2/ ho_{H_2O}$	$L_1[\text{\AA}]$	$L_2[\text{\AA}]$	$\sigma[\text{\AA}]$
115	6	$XR_{1,1}$	$\begin{array}{c} +0.01 \\ 1.03 \\ -0.001 \end{array}$		$19.5^{+0.9}_{-1.0}$		$\overset{+0.05}{3.27^{-0.04}}$
40	22	$XR_{3,1}$	$\begin{array}{c} +0.02 \\ 1.09^{-0.01} \end{array}$	$0.14^{+0.02}_{-0.01}$	$22.5^{+0.7}_{-0.9}$	$11.5^{+1.4}_{-1.2}$	$\overset{+0.1}{3.45^{-0.22}}$
	22	$XR_{3,2}$	$\overset{+0.01}{1.09^{-0.01}}$	$0.93^{+0.04}_{-0.03}$	$13.7^{+1.8}_{-1.5}$	$10.4^{+1.1}_{-0.9}$	$^{+0.25}_{3.25^{-0.23}}$
24	32	XR _{7,1}	$\overset{+0.008}{1.29}\overset{-0.005}{-0.005}$	$\overset{+0.003}{0.47^{-0.005}}$	$13.3^{+0.2}_{-0.3}$	$13.9^{+0.04}_{-0.04}$	$\substack{+0.063\\3.53-0.058}$
	32	$XR_{7,2}$	$\begin{array}{c} +0.008 \\ 1.14 \\ -0.006 \end{array}$	$\overset{+0.011}{0.96^{-0.006}}$	$12.7^{+0.8}_{-0.9}$	$\overset{+0.5}{14.5^{-0.4}}$	$3.51^{+0.08}_{-0.06}$

TABLE IV

Best Fit parameters

densities are normalized to value of bulk water $\rho_w = 0.333e/\text{ Å}^3$. Corresponding electron density profiles described by 3.20 for the highlighted set of parameters in Table IV are shown on Figure 34 and discussed later in the text.

Error bar analysis discussed in details in C.1 produced very low chi-squared values for all of the best parameters found. The chi-squared fits for parameter set $XR_{7,2}$ is shown on Figure 35.

6.3.1 3 slab model

3 slab model solutions were found via the procedure described in A.2. Table V lists two of the solutions for the reflectivity data set with highest surface pressure (XR_7) . In these solutions



Figure 34. Electron Density Profile

the first two layers can be interpreted as a refinement of the head-group layer of the two slab model. First layer accounts for the inositol ring of the PIP2 molecule, the middle layer for the combined C18TAB head group and lower part of the PIP2 head group and the third layer accounts for the tails.

6.3.2 Subphase pH dependence

Figure 36 illustrates the normalized reflectivity curves values of the pH 5.5 and 7 both at the same SP of 20.



Figure 35. 30% Chi-squared Error bars values for $XR_{7.1}$ best fit parameters

$DATA_{sam,sol}$	$ ho_1/ ho_{H_2O}$	$ ho_2/ ho_{H_2O}$	$ ho_3/ ho_{H_2O}$	$L_1[\text{Å}]$	$L_2[\text{Å}]$	L_3 [Å]	$\sigma[\text{\AA}]$
$XR_{7,2}$	1.15	1.13	0.96	5.04	7.54	14.16	3.48
$XR_{7,2d}$	1.15	1.12	0.96	7.13	5.8	13.87	3.47

IADLE V

Best Fit parameters 3 Slab Model

6.4 GID

GID data collected before and after the X-ray reflectivity measurements. The GID measurements reported here are those taken after the X-ray reflectivity since at that time the system surface pressure is at relatively stable equilibrium however the result did not differ much from the measurements taken prior the X-ray reflectivity while waiting for the system to equilibrate. Grazing Incidence Diffraction data below the critical wave vector transfer $Q_c = 0.0217$ Å⁻¹ $Q_z = 0.018$ Å⁻¹ at surface pressure $\pi = 22 \ mN/m$ is presented on Figure 37

The chart at the bottom illustrates the GID pattern versus the in-plane scattering wave vector Q_{xy} integrated over Q_z range from 0 to 0.628 Å⁻¹ The diffraction pattern is relatively simple and similar to what has been reported previously (77). It consists of a single strong Bragg reflection at $Q_{xy} = 1.51$ Å⁻¹. This is an evidence of a close packed hexagonal lattice with constant a=4.8 Å⁻¹ and area per lattice site of 20 Å². The chart on the right illustrates the Bragg Rod intensity integrated over Q_{xy} range from 1.2 to 1.8 Å⁻¹ The intensity peaks at



Figure 36. X-ray Reflectivity of PIP2/C18TAB

 Q_z value equal to the critical wave vector of transfer $Q_c = 0.0217$ Å⁻¹ which is an indication of untitled chains. Since our system is composed of 3 parts single tail surfactants and 1 part double tail surfactants the average number of tails per molecule is n=5/4 and the molecular area becomes 25 Å² which is in good agreement with the area per molecule calculated from the macroscopic quantities Table IV.



Figure 37. GID Data

78

The $\pi - T$ measurements suggest the presence of a long range ordered structure. GID scans were performed for the range of Q_{xy} from 1.3 to 1.9 Å⁻¹ and no other peaks were observed.

The results for higher surface pressure $\pi = 32 \ mN/m$ are presented on Figure 38

As with the lower surface pressure the same strong Bragg reflection at $Q_{xy} = 1.51$ Å⁻¹ is present together with two transient features with average duration of the order of minutes Figure 38. The second in-plane transient peak appearing in the diffraction pattern at $Q_{xy} =$ 1.47 Å⁻¹ is an indication of the original hexagonal packing being distorted with lattice constants a = 4.8 Å⁻¹ and b=4.93 Å⁻¹. Another transient feature is the out of plane peak at Qz=0.5 which can be attributed to tilting of the hexagonal cell (41).

6.5 Out of plane Bragg Rod intensity analysis

The effect of finite molecular size on the scattering intensity along the Bragg Rod is discussed in chapter 3.4. The variation of the scattered intensity along the Q_z direction is proportional to the in plane periodic structure. In this particular case the acyl tails are modeled as cylinders with finite length and their Form Factor has the form 3.24. On figure Figure 39 is shown the Bragg Rod profile along the Q_z direction. Maximum intensity of this is at $Q_z = Q_c$ is an indication that the acyl chains normal to the interface. Least square fit of the intensity to 3.23 finds a chain length of $H = 14.7^{+3.7}_{-1.6}$ Å which is in good agreement with the X-ray reflectivity data analysis.



Figure 38. PIP2/C18TAB mixture Isotherm

80



Figure 39. Bragg Rod Intensity along Qz

6.6 Conclusion

By combining the methods of X-ray Reflectivity and Grazing Incidence Diffraction, the molecular-scale structure of the Langmuir films of the catanionic PIP2/C18TAB was accurately characterized with sub nanometer spatial resolution.

Born Approximation analysis of the X-ray Reflectivity data was used to extract the electron density variation along the direction normal to the interface averaged over the in-plane region of the X-ray footprint of the interface. GID data showed a highly ordered domains composed of untitled acyl chains with hexagonal unit cell and lattice constant of 4.8 Å⁻¹. At higher compressions the hexagonal packing is being distorted and tilted with lattice constants a=4.8 Å⁻¹ and b=4.93 Å⁻¹ The occupancy of the components agrees with the macroscopic calculation from the molecular weight and the amount of surfactants deposited.

X-ray data showed a stable ordering of this soft matter system with the same regularity as that of a solid crystal. What makes this type of ordering so special is that none of the individual components of the system on their own can form such a state but, because of their cooperative and collective behavior, it becomes possible to achieve a very stable configuration in this catanionic system.

CHAPTER 7

ELECTRON DENSITY ANALYSIS

Once we find a set of parameters for the ED profile 3.21 satisfying the Born approximation we need to verify how physical that layer model is. By assigning different atom groups of the molecules to different slabs the occupied area per slab should be the same. A detailed analysis for the area per slab calculations is presented in this section. The results from the slab model are found to be in good agreement with the area of the hexagonal unit cell determined from the GID data analysis.

7.1 Interfacial area per molecule

Best fit parameters by the monolayer model to the normalized reflectivity gives the slab thickness and relative electron density to that of the water Table IV. The area per molecule can be determined from the number of electrons per area in the slabs by assuming which part of the molecule corresponds to which slab. For a two slab solution we can safely assume that the layer at the water phase corresponds to the head-group part of the amphiphiles and the second layer accounts for the tails Figure 40. In order for the model to be physical we expect that the area covered by the head group to be equal to the one covered by the tails. In general the area occupied by slab i in units of square Angstroms is given by

$$A_i = \frac{N_{e,i}}{\rho_w \rho_i L_i} \tag{7.1}$$

where $\rho_w = 0.33$ is the electron density of the water $N_{e,i}$ is the number of electrons in the slab ρ_i, L_i are the relative electron density and the slab thickness respectively. The head-groups are



Figure 40. 2 slab model parameters

in contact the water phase and there must be some water molecules present at the depth of the head-groups. So we would expect that the area per molecule for the head group to be slightly smaller compared to that of the tails. When calculating the number of electrons for the head group a number of water molecules are added. The electron density in the head group is due to a combination of water molecules and the surfactant head groups.

7.2 Molecule Groups

We assume that the separation between the head group slab 1 and the tail group slab 2 occurs at the center of the C-N and C-O bonds for the C18TAB and PIP2 respectively. Furthermore some of the water molecules intercalate into the headgroups. When calculating the number of electrons per slab we considered a composite system with different ratios of C18TAB PIP2 in order to evaluate the possibilities partial dissolving in the aqueous phase for either of the components.

To obtain the number of electrons a simple Wolfram Mathematica function is employed the procedure of which is described in A.9.

7.2.1 C18TAB molecule groups

For a single C18TAB molecule the tail group consists of $CH_3(CH_{22})_{17} = C_{18}H_{37}$ and the trimethyl ammonium head group is made of $N(CH_3)_3 = NC_3H_9$ The number of electrons for each of the molecular groups described is in listed in Table VI

7.2.2 PIP2 molecule groups

Head-group is considered to consist of 3 parts. Oxygen-carbohydrates $(CO_2)_2(CH_2)(CH)$, Phosphorus group connecting the inositol ring CH_2PO_4 and the inositol head group $(CH)_6(OH)_3(PO_4H)_2$. The number of electrons for each of the molecular groups described is listed in Table VI.

C18TAB					
Tail	$C_{18}H_{37}$	145			
Head	NC_3H_9	34			
PIP2					
Tail	$C_{30}H_{62}$	242			
Head	$C_{11}H_{11}O_{11}P_2$	165			
Head Tail	CH_2PO_4	55			
O_2 Chains	$C_4H_3O_4$	59			

TABLE VI

Number of electrons in the molecular groups from the surfactant molecules

7.2.3 PIP2 C18TAB 2 Slab Model

Substituting the best fit parameters for the densely packet monolayer solution $XR_{7,1}$ from Table IV of slab 1 and 2 into equation 7.1 yields the area of the composite head and tail groups summarized in Table VII. The number of electrons of the head group is taken from Table VI is due to a combination of the two surfactant head groups with the respective ratio plus a number of water molecules being added. The area per head group presented in column 3 does not account for these water molecules. The number of water molecules added is justified from constraints on the acyl chain area (75),(84) and from considerations arising from the area of the hexagonal cell calculated from the GID measurements earlier 6.4. That is achieved by matching the area of the tail group to the area of the head group. "Tail area composite system" column 4 represents the composite area of the tail slab. "From GID" column is the product of the "Tails/Molecule" with the area of the primitive cell obtained from the GID data analysis $A = \frac{3\sqrt{2}}{Q_{xy}^2} = 20\text{Å}^2$. Possible molecular arrangements in the 2 slab model are illustrated on

PIP2	C18TAB	Head Area	Tail Area	Per Tail	Tails/	From	Number of water
		composite	composite	$\rm{Area}[{\rm \AA}^2]$	Molecule	GID	molecules to add
		system	system			$[Å^2]$	to headgroup
		$[Å^2]$	$[Å^2]$				
1	3	$80^{\pm 4.9}$	$148^{\pm 4.8}$	$29.6^{\pm 0.96}$	5/4	$25.0^{\pm 0.1}$	$22^{\pm 1}$
1	2	$72^{\pm 4.4}$	$116^{\pm 3.7}$	$28.9^{\pm 0.93}$	4/3	$26.7^{\pm 0.1}$	$20^{\pm 1}$
1	1	$65^{\pm 4.0}$	$85^{\pm 2.7}$	$28.3^{\pm 0.90}$	3/2	$29.6^{\pm 0.1}$	$9^{\pm 1}$
1	0	$58^{\pm 3.6}$	$52^{\pm 1.7}$	$26.0^{\pm 0.85}$	2/1	$40.0^{\pm 0.1}$	$3^{\pm 1}$
0	1	$7^{\pm 0.4}$	$31^{\pm 1.0}$	$31.0^{\pm 0.40}$	1/1	$20.0^{\pm 0.1}$	$115^{\pm 1}$

TABLE VII

Number of electrons in the molecular groups from the surfactant molecules

Figure 41. From the GID the data analysis we established that the area per tail group to be $N_{tails/molecule} \times 20 = 25$ in units of square Angstroms. Adding 22 water molecules to the composite head group would yield similar area of the head group slab. The Brag Rod analysis determined that we have close packing of untitled chain groups 6.5. C18TAB tail has four more carbohydrate links compared to those of the PIP2 where total number of electrons in these four carbon links is 99. Subtracting these 99 electrons from the tail slab yields an area of the composite tail group of 126 Å². This gives an area per single tail close to 25 Å². There are two possibilities for these extra four carbohydrate links.

- They are sticking above the rest of densely packed tails flapping on them forming an extra layer with large roughness that cannot be detected by the Xray Reflectivity measurements.
- The C18TAB molecule is pulled a little further into the aqueous phase. We need to reduce the amount of water molecules intercalated into the head group by 10.
- A combination of the two above

7.3 Conclusion

From X-ray reflectivity data we established that within the context of 2 slab model our system consists of well defined 10 carbon long compact layer and a second layer corresponding to the composite head-group with some associated water molecules. It is not obvious how things are arranged within the head group slab. This model accounts for all of the electrons calculated from the composite molecular structure C18TAB/PIP2 3:1 ratio and is in agreement with the occupied area per molecule obtained from the grazing incidence diffraction analysis.



Figure 41. Catanionic system molecular arrangements

APPENDICES

Appendix A

MATHEMATICA PROGRAMS FOR DATA ANALYSIS

In this section, the numerical expressions used in the calculations employed in the respective Mathematica applications are summarized. Only relevant parts of the code are shown. For the applications with Graphical User Interface, a brief description of their use and features is provided.

A.1 Equations used for the BA calculations

Fresnel reflectivity equation

$$R_f[q, q_{off}, q_c, \lambda, \beta] = \left| \frac{(q - q_{off}) - \sqrt{(q - q_{off})^2 - q_c^2 + \frac{32i\pi^2}{\lambda^2}\beta}}{(q - q_{off}) + \sqrt{(q - q_{off})^2 - q_c^2 + \frac{32i\pi^2}{\lambda^2}\beta}} \right|^2$$
(A.1)

Where each of the supplied arguments is

- q_{off} The instrument offset
- q_c The critical wave vector $Q_c = 4\sqrt{\pi r_e(\rho_{top} \rho_{bot})}$
- $\lambda\,$ The Xray wavelength
- $\beta\,$ The imaginary part of the scattering factor $\beta=\frac{\lambda\mu}{4\pi}$

Box Model Reflectivity Divided by Fresnel for \mathbf{n} layer slab model

$$\frac{R}{R_f}[q,n] = \left| \sum_{i=1}^n \frac{\rho_i - \rho_{i+1}}{r_{bot} - \rho_{top}} e^{-\frac{q^2 \sigma_i^2}{2}} e^{-iq \sum_{k=1}^i L_k} \right|^2$$
(A.2)

Appendix A (Continued)

 $\rho_{bot} \text{ and } \rho_{top}$ The ED bulk values

 ρ_i, L_i and σ_i The ED , layer thickness and roughness for the ith layer

Electron Density Profile

$$\rho[z,n] = \sum_{i=1}^{n} \left[(\rho_i - \rho_{i+1}) \frac{1}{2} \left(1 + erf(z - \sum_{k=i+1}^{n} L_k / \sqrt{2}\sigma_i) \right) \right] + \rho_{top}$$
(A.3)

A.2 Command Line program for mesh Calculation

For more complex models such as the 3 layer the number of possible solutions increases exponentially. Finding all the possible solutions is a challenging task and for that reason we developed a command line routine that is performing a grid calculation for all the possible combinations of the input parameters that are in a physically meaningful range. The fit result after each iteration is stored in a flat SQL database table. A uniqueness of the solution is enforced via the UNIQUE composite index all the parameters. With the typical values of the loop parameters we will arrive at the same solution for a large number of input parameters. With the uniqueness constraint any possible solution is recorded just once. With a simple database queries we can extract only the solutions that are of interest to us.

The MySQL table structure is shown bellow.

-- Table 'mlayer'.'params' -- CREATE TABLE IF NOT EXISTS 'mlayer'.'params' ('id' INT NOT NULL AUTO_INCREMENT, 'ps' INT NULL, 'r1' DECIMAL(5,3) UNSIGNED NULL, 'r2' DECIMAL(5,3) UNSIGNED NULL,

```
'r3' DECIMAL(5,3) UNSIGNED NULL,
'L1' DECIMAL(4,2) UNSIGNED NULL,
'L2' DECIMAL(4,2) UNSIGNED NULL,
'L3' DECIMAL(4,2) UNSIGNED NULL,
's1' DECIMAL(5,3) UNSIGNED NULL,
'chi' DECIMAL(5,2) NULL,
PRIMARY KEY ('id'),
UNIQUE INDEX 'uniq_idx' ('r1' ASC, 'r2' ASC, 'r3' ASC, 'L1' ASC, 'L2' ASC, 'L3' ASC))
ENGINE = InnoDB;
```

The contents of the ASCI file mlayer.m are shown below

```
#!/usr/local/bin/MathematicaScript -script
```

```
Needs["DatabaseLink'"];
JDBCDrivers["MySQL(Connector/J)"];
conn = OpenSQLConnection[ JDBC["MySQL(Connector/J)", "localhost/mlayer"],
"Username" -> "root", "Password" -> ""
];
```

```
(* Load the xray functions and parameters *)
<<functionsXray';
<<pre>constructionsXray';
```

```
(*read the refl data*)
refdat = ReadList["./data/xr7.tsv", {Number,Number, Number}];
RoverRf = {#[[1]], #[[2]]/RfAbs[#[[1]], Qoffset, Qc, lambda, \[Beta]]} & /@ refdat;
RoverRfFit = DataToFit[RoverRf, 2];
weigths = WeightsErr[refdat, 2];
```

```
{
```

```
paramSet,
Part[result,1,1,2],
Part[result,1,2,2],
Part[result,1,3,2],
Part[result,1,4,2],
Part[result,1,5,2],
Part[result,1,6,2],
Part[result,1,7,2]
```

```
}];
```

```
(* 3 Layer model *)
model = RRF[x, 3];
(* Initial model parameters *)
    r1i=0.1;
               r2i=1.01;
                          r3i=0.1;
    L1i=15;
               L2i=5.0;
                            L3i=5;
    s1i=3.52;
(*walk over the 4D space of the selected model parameters *)
Do[
    For[i=0, i<30, i++,</pre>
For[j=0, j<30, j++,</pre>
For[k=0, k<30, k++,
      startingList = {
r1 -> r1i+i*0.01, r2 -> r2i, r3 -> r3i+j*0.01,
L1 -> L1i, L2 -> L2i+k*0.1, L3 -> L3i+l*0.1,
s1 -> s1i
};
starting = {#[[1]], #[[2]]} & /@ startingList;
result= fit[RoverRfFit, weigths, model, starting]
                                                       ;
SQLInsertCols[4, result]
Print[1," ", i," ", j," ", k];
      ]
  ]
      ٦
,{1,0,30,1}]
```

In order to run this from the command line execute the command.

```
$math -run <mlayer.m</pre>
```

Typically that command might take to over a day to run over all the four loops. It is a good idea to execute the command from inside a linux screen application.

Appendix A (Continued)

Exporting the subset of the solutions satisfying specific criteria into an tsv file that can be

opened with a spreadsheet application.

SELECT * FROM params WHERE r1<2 AND r2<2 AND r3<2 AND s1>0 AND L1 BETWEEN 0.1 AND 30 AND L2 BETWEEN 0.1 AND 30 AND L3 BETWEEN 0.1 AND 30

INTO OUTFILE '/tmp/params.tsv'

Another example query with the conditions

SELECT * FROM params WHERE WHERE L3*r3>18 AND L3 BETWEEN 14 and 20
A.3 Programs with Graphical User Interface

In this section, a description of several most important Mathematica notebook applications that were developed and used for visualization and processing of the data as well as for numerical fitting is presented.

A.3.1 XR Data Visualization

This GUI displays the XR data loaded from 3 column ASCI files located in a sub directory called **data** of the notebook Figure 42. Dropdown menu changes the data set to be displayed. User has control of the q range display and can tweak the q_{offset} via the slider. The checkbox **isRF** toggles the display of XR data normalized to the Fresnel. The checkbox **qrange** enforces the display of the predefined Q_z range in the fields below.



Figure 42. GUI XR data Visualization

A.3.2 M Layer fitting

This GUI loads the external XR data file, normalizes it to the Fresnel A.1 and fits the normalized data to the box Model given by A.2. By default the layers roughness values are unified across all layers. All of the input parameters can be controlled via the input boxes and/or their respective sliders. The number of layers used is set automatically based on the number of non-zero layer parameters being set. Maximum number of layers is 3 but can easily modified for use in a greater number of layers. The parameters to be fit are determined by their respective check boxes. This program is complemented by the notebook application described in the next subsection.



Figure 43. GUI Mlayer

A.3.3 Subtracting a linear background

User interactive application subtracts averaged peak from linear background. The background is determined from the linear fit of the dynamically selected points. It computes the weighted average of the selected peak points reduced by linear background.



Figure 44. GUI subtraction from linear background

The data is subtracted by the linear fit f(x) on the selection of background points. The x-axis is shifted by the quantity $x_{CM,peak}$ so that the weighted sum over the peak points is zero.

$$x_{CM,peak} = \frac{\sum w_i x_i}{\sum w_i} \tag{A.4}$$

Where the sums are taken over the selection of the peak points. The error of the slope coefficient is calculated from the following quantity

$$\sigma_a^2 = \frac{\sum w_i (x_i - x_{CM, peak})^2}{\Delta} \tag{A.5}$$

$$\Delta = \sum w_i \sum w_i (x_i - x_{CM,peak})^2 - \left(\sum w_i (x_i - x_{CM,peak})\right)^2 \tag{A.6}$$

Here the sums are taken over the background points. The peak value reported is given by

$$y_{peak} = \frac{\sum w_i(y_i - f(x_i))}{\sum w_i} \tag{A.7}$$

Since the error bars of the data are very close to one another the error of the subtracted value is calculated from

$$\sigma_{peak} = \sqrt{\frac{1}{\sum w_i} + \sigma_a^2} \tag{A.8}$$

A.4 Mathematica notebook applications

A list of applications that are used as a regular Mathematica notebook application.

A.4.1 Electron Density calculator

This application takes the dot product of the number of atoms with the respective atomic number. For example to obtain the number of electrons in the chemical composition C18H37

$$Ne = [18, 37] \cdot [Z_C, Z_H] = 18 \cdot Z_C + 37 \cdot Z_H$$
(A.9)

Which in Mathematica code this translates to

Dot[{18, 37}, ElementData[#, "AtomicNumber"] & /@ {"C", "H"}]

Note that the ordering of the elements of the two vectors matters.

A.4.2 Parratt Reflectivity calculation from ED

The Electron Density Profile is read from an external ASCI file where the non normalized values of electron densities are uniformly sampled every h [Å]. The file has two numeric columns. The first column corresponds to the interface depth and the second one corresponds to the respective absolute electron density value. The quantities k_0 $k_{z,j}$ and δ_j are given by

$$k_0 = \frac{2\pi}{\lambda} \tag{A.10}$$

$$k_{z,j} = -k_0 \sqrt{\frac{Q}{2k_0} - 2\delta_j}$$
(A.11)

$$\delta_j = \frac{\rho_j}{2\rho_{sub}} \left(\frac{Q_c}{2k_0}\right)^2 \tag{A.12}$$

```
Refraction[q_, j_] := ScalingMatrix[Kzj[q, j + 1]/Kzj[q, j], {1, -1}];
Trnslation[q_, j_] := DiagonalMatrix[{Exp[-I Kzj[q, j] h], Exp[I Kzj[q, j] h]}];
DotP[q_, j_] := Dot[Trnslation[q, j], Refraction[q, j]];
reflectance[q_] :=
Dot[
ScalingMatrix[Kzj[q, 2]/Kzj[q, 1], {1, -1}],
Fold[Dot, DotP[q, 2], Table[Dota[q, i], {i, 3, 999}]]
];
```

```
Reflect[q_] := Abs[reflectance[q][[1, 2]]/reflectance[q][[2, 2]]]^2
```

To obtain n sampled reflectivity over a q range 0.01 to 0.6 with a step 0.02 use the iteration xrParrat = Table[{q, Reflect[q]}, {q, 0.01, 0.6, 0.02}];

Appendix B

CALCULATIONS FOR THE TROUGH

B.1 Trough opening as a function of motor coordinate

Mathematica expression used for converting from motor position to trough area:

$$\mathbf{F}[\mathbf{rot}] = \left\{ 1000 \left(\text{Convert} \left[\left(9 - \frac{1}{4} - \frac{1}{4} \right) \text{Inch, Meter} \right] [[1]] - \frac{\mathbf{barGap} + \frac{10(\# + \mathbf{m1Max})}{2268} - 6.5}{10^3} \right) \right\} \& / @\mathbf{rot}$$
(B.1)

Where the quantities in B.1 are as follow:

rot Motor coordinate. Typical range [+3000: -33000]

m1Max The value of the motor when barrier completely open

barGap The distance [mm] between the inner edge of the trough when motor is at **m1Max**

 $6.5~[\mathrm{mm}]$ is the barrier width

2268/10 is the displacement in [mm] for one full rotation of the lead screw

Currently employed screw has 16 threads per inch, which amounts to $360\frac{16}{25.4}/10 = 2267.72$ On Table VIII a measured opening of the Trough as a function of motor position is shown. Linear fit to that data and compared to the values calculated with B.1 is shown on Figure 45

m1 $\times 10^3$	-12	3	0	-3	-15	-10
$d1 \ [mm]$	89	26	34	48	102	80

TABLE VIII

Trough opening as a function of motor coordinate values

B.2 Area per molecule calculation

When spreading a volume $V[\mu l]$ with concentration C [mM] of surfactant solution on the surface of the trough we use the following expression that gives us the area per molecule Å²

$$\frac{\mathrm{F}[\mathbf{rot}] \times \mathrm{Convert}\left[\left(5 - \frac{1}{4} - \frac{1}{4}\right) \mathrm{Inch}, \mathrm{Meter}\right]\left[\left[1\right]\right]}{V \times 10^{-6} C \times 10^{-3}} \tag{B.2}$$

Where F[rot] is the convertion from motor coordinate to barrier position and is described in the previous section. The factors of 10^{-6} and 10^{-3} are accounting for the volume and concentration of the spread solution.a



Figure 45. Barrier position as a function of the motor coordinate.

Appendix C

ERROR ANALYSIS

C.1 Chi-Squared Test for Goodness of Fit

C.1.1 Chi-Squared and Chi-Squared Distribution

Fitting an m-parameters function $y(a_1, a_2, ..., a_m, x)$ to a set of N experimental data points consists of minimizing the sum of squares term called χ^2 (44),(85)

$$\chi^{2} = \sum_{i=1}^{N} \left[\frac{y_{i} - y(a_{1}, a_{2}..., a_{m}, x)}{\sigma_{i}} \right]^{2}$$
(C.1)

The factor $\nu = N - m$ is the number of degrees of freedom. The quantity χ^2 has the probability distribution function called χ^2 distribution with ν degrees of freedom and is given by (44)

$$p_{\chi}(\chi^2;\nu) = \frac{1}{2^{\nu/2}\Gamma(\nu/2)} e^{-\chi^2/2} (\chi^2)^{\nu/2-1}$$
(C.2)

On Figure 46 is shown the distribution function for the number of degrees of freedom The mean value of $p_{\chi}(\chi^2; \nu)$ is equal to ν and its variance equals to 2ν .

In other words repeating the experiment should result in clustering of the χ^2 values around the median value of the distribution function $p_{\chi}(\chi^2; \nu)$.

More useful is the integral probability giving us the probability that a random set of N data points drawn from the parent distribution would yield a value of χ^2 greater than $P_{\chi}(\chi^2; \nu)$. That

Appendix C (Continued)



Figure 46. Chi-square distribution function for $\nu=3,5$ and 10

integral value for a given χ^2 is determined by the Cumulative Distribution Function (CDF) of $p_{\chi}(\chi^2;\nu)$ and equals to the Regularized Gamma Function (86),(87) ,which is the Mathematica function **GammaRegularized**[$\nu/2$, 0, $\chi^2/2$]

When dealing with confidence intervals for a system with a given number of degrees of freedom ν we need to determine the χ^2 value for a given integral value.

For this the Inverse GammaRegularized function is employed. For example the median value is given by **2** InverseGammaRegularized[$\nu/2$, 1/2] where the 1/2 in the function argument is the integral value.

In general the median value is always smaller than the mean and larger the degrees of freedom the closer the median gets to the mean. Since the expected value of χ^2 is ν it makes sense to introduce the per degree of freedom χ^2/ν also called reduced Chi-square. We will use that quantity while determining the individual goodness of fit parameters. On Figure 47 is illustrated the the probability of exceeding the χ^2 versus reduced Chi-square χ^2/ν values for a number of different degrees of freedom.



Figure 47. Probability of exceeding the χ^2 values versus the Reduced Chi-square

C.1.2 Chi-Squared Error Bar Estimation

The χ^2 is a continuous function of the m parameters model $y(a_1, a_2..., a_m, x)$ thus defining a hypersurface in the m dimensional space with the minimum value χ^2_{min} corresponding to the most adequate set of parameters of the model describing our data. On Figure 48 is shown an example of such hypersurface for 2 parameters model.



Figure 48. Chi-square hypersurface for m=2

The error on these parameters is determined by the quantity $\Delta \chi^2 = \chi^2 - \chi^2_{min}$ that corresponds to the desired confidence level. For a best fit parameter a_i we take the region between $a_i - \delta_1$ and $a_i + \delta_2$ for which $\chi^2(a \pm \delta_{1,2}) = \chi^2_{min} + \Delta \chi$ Figure 49.



Figure 49. χ^2 along a given parameter dimension a_i

We achieve that by fixing all the rest of the parameters from the given best fit parameters set and varying the a_i until a change greater than the $\Delta \chi^2$ is reached.

Appendix D

EPICS CONTROL SYSTEM IMPLEMENTATION AND USE

This guide is for installing, configuration EPICS on Linux operating system. Some of the

commands, system filenames, system locations and package names may vary across different

linux distributions.

D.1 Installation and configuration

Create in your \$HOME directory called EPICS. In there we will place the BASE,synApps

and extensions directories. The following EPICS environment variable need to be set prior the

Installation.

```
EPICS_HOST_ARCH=linux-x86_64
EPICS_BASE=$HOME/EPICS/BASE
EPICS_DISPLAY_PATH=$HOME/EPICS/synApps_5_5/support/all_adl/
LD_LIBRARY_PATH=$HOME/EPICS/BASE/lib/linux-x86_64
PATH=$PATH:$HOME/EPICS/BASE/bin/linux-x86_64:$HOME/EPICS/extensions/bin/linux-x86_64/
IOC_DIR=$HOME/EPICS/synApps/support/UIC_app/iocBoot/iocTrough/
```

```
export EPICS_HOST_ARCH
export EPICS_BASE
export EPICS_DISPLAY_PATH
export PATH
export LD_LIBRARY_PATH
export IOC_DIR
```

D.1.0.1 Installation of EPICS base

As of the writing of this documents versuib R3.14 is the stable Branch of EPICS and is the

one being used. Get the latest version from http://www.aps.anl.gov/epics/download/base/index.php

Put the contents of the archive in \$HOME/BASE directory.

Determine your EPICS_HOST_ARCH with one of the scripts in the BASEstartup directory and set the environment variable in your .bashrc file.

In the command line change the working directory where EPICS base is and execute the paralel make.

make -sj clean make -sj

D.1.0.2 Installation of synApps

Download the synApps package from from http://www.aps.anl.govbcdasynAppssynApps_5_5.html For my current task I need to read Keithley 2000 multimeter through the RS-232 port. And drive one motor from the SmartMotor series. For the multimeter I need the ip module.The ip module itself depends on asyn , ipac and scnseq. For building the EPICS application I will need xxx module. Also autosave,std bisy are modules It is good to have. Download and uncompress the archive into the \$HOME/EPICS directory.

```
$wget http://www.aps.anl.gov/bcda/synApps/tar/synApps_5_5.tar.gz
$tar xzvf synApps_5_5.tar.gz
$cd synApps/support/
$vi configure/RELEASE
$make clean
$make
```

In the configure/RELEASE leave only the needed modules. Here is the content of the RELEASE

file.

Status: working toward synApps 5.5 SUPPORT=/home/user/EPICS/synApps_5_5/support EPICS_BASE=/home/user/EPICS/BASE ASYN=\$(SUPPORT)/asyn-4-13 AUTOSAVE=\$(SUPPORT)/autosave-4-6

```
BUSY=$(SUPPORT)/busy-1-3
CALC=$(SUPPORT)/calc-2-8
IP=$(SUPPORT)/ip-2-10
IPAC=$(SUPPORT)/ipac-2-11
IPUNIDIG=$(SUPPORT)/ipUnidig-2-7
MOTOR=$(SUPPORT)/motor-6-5
SNCSEQ=$(SUPPORT)/seq-2-0-12
SSCAN=$(SUPPORT)/seq-2-0-12
SSCAN=$(SUPPORT)/sscan-2-6-6
STD=$(SUPPORT)/std-2-8
VME=$(SUPPORT)/std-2-7
XXX=$(SUPPORT)/xxx-5-5
```

Also edit the main make file ./synApps_5_5/support/Makefile and comment out the entries referring to modules that will not be compiled. If you still cannot run make without any errors comment some lines from the motors and xxx src files. Edit the motor make file ./synApps_5_5/support/motor-6-5/motorApp/Makefile For the motors initially I had some compile errors referring to Newport. Probably need some driver for that but since we are not using that type of motors at the moment I commented out lines referring to Newport as well.

For the xxx I had to comment out some lines in the files in ./synApps_5_5/support/xxx-5-5/xxxApp/ . For easy documentation I saved the original files before editing them appending the name .orig. I'm posting here partial output of the diff command showing the commented lines only. \$cd \$HOME/EPICS/synApps_5_5/support/xxx-5-5/xxxApp/src

```
$diff xxxCommonInclude.dbd xxxCommonInclude.dbd.orig
$diff xxxCommonInclude.dbd xxxCommonInclude.dbd.orig
$\exercise #include "opticsSupport.dbd"
$\exercise #include "devNewport.dbd"
$\exercise #include "stream.dbd"
$\exercise #include "streamSynApps.dbd"
$\exercise #include "ADSupport.dbd"
$\exercise #include "simDetectorSupport.dbd"
$\exercise #include "pluginSupport.dbd"$\exercise #include "streamSynApps.dbd"$\exercise #include "streamSynApps.dbd"$\exercise #include #
```

```
$ diff Makefile Makefile.orig
< #xxx_Common_LIBS += mca
< #xxx_Common_LIBS += optics
< xxx_Common_LIBS += Micos MicroMo NewFocus Oriel PI PIJena Parker SmartMotor #Newport
< #xxx_Common_LIBS += stream streamSynApps
< #xxx_Common_LIBS_Linux += usb
< #xxx_LIBS_Linux += vaPI ImageLib
< #xxx_LIBS_Linux += PvAPI ImageLib
< #xxx_LIBS_Linux += NeXus mfhdf df hdf5 mxml
< #xxx_LIBS_Linux += tiff jpeg z</pre>
```

Pretty much removing the entries referring to modules which won't be compiled. areadetectors, mca, optics,.. as well the reference to the Newport. Now I can compile all of the synApps needed for my task at once.

```
$cd ./synApps_5_5/support/
$make release
$make install
```

D.1.0.3 Installation of extensions

Extract the extensions Top into the EPICS directory. Change directory to extensions and

run make. Might need to edit the file \$HOME/EPICS/extensions/configure/RELEASE

Once we have the extensions compiled we extract the medm.tar.gz into the src folder of

extensions.

Comment all but the medm EPICS extensions in the Makefile in \$HOME/extensions/src/-

Makefile and run make.

```
#KM = km
# NOBCONFIG = knobconfig
MEDM = medm
# MOTIFBUTTON = motifButton
# EXTENSION_MSI = msi
```

D.1.0.4 Installation of Fonts

Make sure you have the fonts server xlsfonts and following fonts installed.

x11-font-sony-misc, X11-font-adobe-75dpi, X11-font-adobe-100dpi

As root update the fonts file located in /usr/share/X11/fonts/misc/fonts.alias or /usr/share/-

fonts/misc/fonts.alias

with the contents of the \$HOME/EPICS/extensions/src/medm/medm/fonts.alias.sun and

restart the font server.

```
$cd /usr/share/fonts/misc/
$cat $HOME/EPICS/extensions/src/medm/medm/fonts.alias.sun >>fonts.alias
$/etc/init.d/xfs restart
```

```
widgetDM_4 -misc-fixed-medium-r-normal--8-60-100-100-c-50-iso8859-1
widgetDM_6 -misc-fixed-medium-r-normal--8-60-100-100-c-50-iso8859-1
widgetDM_8 -misc-fixed-medium-r-normal--9-80-100-100-c-60-iso8859-1
widgetDM_10 -misc-fixed-medium-r-normal--10-100-75-75-c-60-iso8859-1
widgetDM_12 -misc-fixed-medium-r-normal--13-100-100-c-70-iso8859-1
widgetDM_14 -misc-fixed-medium-r-normal--14-110-100-100-c-70-iso8859-1
widgetDM_16 -misc-fixed-medium-r-normal--15-120-100-100-c-90-iso8859-1
widgetDM_18 -sony-fixed-medium-r-normal--16-120-100-100-c-80-iso8859-1
widgetDM_20 -misc-fixed-medium-r-normal--20-140-100-100-c-100-iso8859-1
widgetDM_22 -sony-fixed-medium-r-normal--24-170-100-100-c-120-iso8859-1
widgetDM_24 -sony-fixed-medium-r-normal--24-170-100-100-c-120-iso8859-1
widgetDM_30 -adobe-times-medium-r-normal--25-180-100-100-p-125-iso8859-1
widgetDM_36 -adobe-helvetica-medium-r-normal--34-240-100-100-p-176-iso8859-1
widgetDM_40 -adobe-helvetica-bold-r-normal--34-240-100-100-p-182-iso8859-1
widgetDM_48 -adobe-helvetica-bold-r-normal--34-240-100-100-p-182-iso8859-1
widgetDM_60 -adobe-helvetica-bold-r-normal--34-240-100-100-p-182-iso8859-1
```

then run as root again

xset fp rehash
xlsfonts | grep widgetDM

D.1.1 Building and running Software IOC (SoftIOC)

We will build our EPICS ioc app in the UIC_app directory.

- Copy the example XXX app directory from \$HOME/EPICS/synApps_5_5/support/xxx-5-5 to to UIC_app/
- Rename the folder UIC_app/xxxApp into UIC_app/uicApp
- Edit the UIC_app/configure/RELESE
- Copy the iocLinux directory to iocTrough directory which is our \$IOC_DIR
- Edit the file iocTrough/serial.cmd with the respective device names and locations
- Edit the file iocTrough/st.cmd
- Also edit the files iocTrough/auto_settings.req and iocTrough/motor.substitutions

Start your IOC from the command line executing.

\$cd \$IOC_DIR
\$../../bin/linux-x86_64/xxx st.cmd

D.1.2 Running the MEDM GUI

We already have the environment variable _DISPLAY_PATH pointing to the location where all the MEDM gui screens are located. Executing memd -x screenName.adl will launch the respective MEDM gui. The most commonly used is the composite XXX MEDM gui. It provides direct access to a common set of MEDM screens such as the motor, multimeters and calc out records. On D.1.2 is showing the generic XXX MEDM gui screen and the click-flow diagram for accessing the rest of the records. The main xxx gui is accessed via the command. **\$medm -x xxx.adl**





Appendix E

MATHEMATICA CODE

This appendix contains the complete Mathematica Code with comments and examples discussed earlier.

Parratt Procedure Calculations

This method generates the Electron Density Profile from a known solution MLayer solution

Alternatively we can read The Electron Density Profile from an external two numeric column file with format "ElDen [Nelectrons/Ang^3]"

```
\begin{split} & \text{SetDirectory}[\text{NotebookDirectory}[]];\\ & \text{Q}_c = 0.0217; \ \lambda = 1.23984; \ h = 0.14;\\ & \text{ElDen = ReadList["elden_ph7.dat", {Number, Number}];}\\ & \delta[\text{j}_{-}] := \frac{\text{EDProfile}[[\text{Jength}[\text{EDProfile}], 2]]}{\text{EDProfile}[[\text{Length}[\text{EDProfile}], 2]]} \frac{\text{Q}_c^2}{8\left(\frac{2\pi}{\lambda}\right)^2}\\ & \text{Kzj}[\text{q}_{-}, \text{j}_{-}] := \frac{2\pi}{\lambda} \sqrt{\left(\frac{q\lambda}{4\pi}\right)^2 - 2\delta[\text{j}]};\\ & \text{Refraction}[\text{q}_{-}, \text{j}_{-}] := \text{ScalingMatrix}[\text{Kzj}[\text{q}, \text{j}+1] / \text{Kzj}[\text{q}, \text{j}], \{1, -1\}];\\ & \text{Trnslation}[\text{q}_{-}, \text{j}_{-}] := \text{ScalingMatrix}[\text{Kzj}[\text{q}, \text{j}+1] / \text{Kzj}[\text{q}, \text{j}], \{1, -1\}];\\ & \text{Trnslation}[\text{q}_{-}, \text{j}_{-}] := \text{Dot}[\text{Trnslation}[\text{q}, \text{j}], \text{Refraction}[\text{q}, \text{j}]];\\ & \text{reflectance}[\text{q}_{-}] := \text{Dot}[\text{Trnslation}[\text{q}, \text{j}], \text{Refraction}[\text{q}, \text{j}]];\\ & \text{reflectance}[\text{q}_{-}] := \text{Dot}[\\ & \text{Refraction}[\text{q}, 1],\\ & \text{Fold}[\text{Dota}[\text{q}, 2], \text{Table}[\text{Dota}[\text{q}, \text{i}], \{\text{i}, 1, \text{nLayers} - 1\}]]\\ & ];\\ & \text{Reflect}[\text{q}_{-}] := \text{Which}[\\ & \text{q} < \text{Q}_c, 1,\\ & \text{q} > \text{Q}_c, \text{Abs}\Big[\frac{\text{reflectance}[\text{q}][[1, 2]]}{\text{reflectance}[\text{q}][[2, 2]]}\Big]^2 \end{split}
```

Generate and Plot the Parratt Refl Data

```
xrParratt = Table[{q, Reflect[q]}, {q, 0.01, 0.6, 0.01}];
ListLogPlot[%, Frame → True, Joined → True]
```

Compare the XR from Parratt with the experimental data

```
xrData = Import["xr7.tsv"];
Show[
ListLogPlot[xrParrat, Frame → True, Joined → True],
ListLogPlot[{#[[1]], #[[2]]} & /@xrData, PlotStyle → {PointSize[0.005], Red}]
]
```

X-Ray Functions

FunctionsXray.nb Select the cell then in the menu go Cell->Cell Properties->Initialization Cell Checkbox and save as *.m

```
(* Fresnel Refl*)
```

```
RfAbs[q_, qoff_, qc_, \lambda_{,\beta}] := Abs\left[\frac{(q-qoff) - \sqrt{(q-qoff)^2 - qc^2 + \frac{32 \pm \pi^2}{\lambda^2}\beta}}{(q-qoff) + \sqrt{(q-qoff)^2 - qc^2 + \frac{32 \pm \pi^2}{\lambda^2}\beta}}\right]^2;
(* R/Rf nlay number of layer between 1 and 3
   and Single layer roughness s1=s2=s3=s4
*)
RRF[q_, nlay_] := Module {},
   s[1] = s1; s[2] = s1; s[3] = s1; s[4] = s1;
  r[0] = r0; r[1] = r1; r[2] = r2; r[3] = r3; r[4] = r4;
  L[1] = L1; L[2] = L2; L[3] = L3;
  r[0] = 1;
    Abs
         \sum_{i=0}^{nlay} \left\{ \left( \frac{r[i] - r[i+1]}{r[0] - r[nlay+1]} \right) Exp\left[ -\frac{q^2 s[i+1]^2}{2} \right] Exp\left[ -Iq \sum_{k=1}^{i} L[k] \right] \right.
                                                                                                                }
                  ^ 2
     /. r[nlay + 1] -> 0;
(*Electron Density Profile
   single layer roughness s1=s2=s3
*)
ElDen[x_, nlay_] := Module {},
       s[1] = s1; s[2] = s1; s[3] = s1; s[4] = s1;
  r[0] = r0; r[1] = r1; r[2] = r2; r[3] = r3; r[4] = r4;
  L[1] = L1; L[2] = L2; L[3] = L3;
  r[0] = 1; r[nlay+1] = 0;
    \operatorname{Sum}\left[(r[i] - r[i+1]) \frac{1}{2} \left(1 + \operatorname{Erf}\left[\frac{(x - \operatorname{Sum}[L[k], \{k, i+1, nlay\}])}{\sqrt{2 s[i+1]}}\right]\right)
        , {i, 0, nlay} + r[nlay + 1]
   ];
(*Step function used for 0 rougness El Den profile *)
StepF[x_, loc_] := If[x > loc, 1, -1];
(* Electron Density Profile zero roughness *)
ElDenSigma0[x_, nlay_] := Module { } ,
```

```
r[0] = r0; r[1] = r1; r[2] = r2; r[3] = r3; r[4] = r4;
L[1] = L1; L[2] = L2; L[3] = L3;
r[0] = 1; r[nlay + 1] = 0;
   Sum (*Export["xr10Fits.pdf",%]*)
     (r[i] - r[i+1]) \frac{1}{2} (1 + \text{StepF}[x - \text{Sum}[L[k], \{k, i+1, nlay\}], 0])
     , {i, 0, nlay}] + r[nlay + 1]
  ];
(*We plot data with error bars*)
RoverRfEB[refdat_] := {
   {#[[1]], #[[2]] / RfAbs[#[[1]], Qoffset, Qc, lambda, β],
       #[[3]] / RfAbs[#[[1]], Qoffset, Qc, lambda, β]} & /@refdat
  };
(*THESE TWO FUNCTIONS Are using the THE RoverRf data*)
DataToFit[RRFdata_, th_] := Select[{#[[1]], #[[2]]} & /@RRFdata, #[[1]] > th * Qc &];
WeightsErr[refdata_, th_] :=
  #[[2]] & /@ Select[{#[[1]], RfAbs[#[[1]], Qoffset, Qc, lambda, β] / #[[3]]} & /@
      refdata, #[[1]] > th * Qc &];
(* Fiting the RRFdata
 Returns fit result and Chi Square *)
fit[data_, weigths_, fitmodel_, starting_] := Module[{nlm},
   Quiet[nlm = NonlinearModelFit[data, fitmodel,
       starting, x, Weights \rightarrow weigths, MaxIterations \rightarrow 500]];
   {
    nlm["BestFitParameters"],
    Total[(nlm["FitResiduals"] * weigths) ^2] / Length[weigths],
    nlm["AdjustedRSquared"]}];
ExecuteFit[data_, weigths_, modelvals_, starting_, nlayers_] :=
  Module[{model, fitmodel, res, constr},
    (*model used in the fitting*)
   model = RRF[x, nlayers];
   fitmodel = model /. modelvals;
    (*Constraints*)
   fullconstr = {0 < r1 < 2, 0 < L1 < 40, 0 < r2 < 2, 0 < L2 < 40, 0 < L3 < 40, 0 < r3 < 2};
   constr = Take[fullconstr, {1, 2 * nlayers}];
    (*EXECUTE FIRST FIT*)
   res = fit[data, weigths, fitmodel, starting];
   startingNew = {#[[1]], #[[2]]} & /@modelvals;
```

```
modelvalsNew = res[[1]];
usemodel = model /. modelvalsNew;
fitmodel = Append[usemodel, constr];
(*Second Fit*)
res = fit[data, weigths, fitmodel, startingNew];
(*Final Fit*)
startingFin = Append[res[[1]], modelvalsNew[[1]]];
startingFin = {#[[1]], #[[2]]} & /@ startingFin;
fitmodel = Append[model, constr];
fit[data, weigths, fitmodel, startingFin]
];
(*round number num to n decimal points*)
Raund[num_, n_] := N[Round[num *10^n] / 10^n];
PlotModel[resArray_, RRfwEbData_, idx_] :=
Module[{res2, a, b, qcline, Twoqcline},
```

```
res2 = Part[resArray, idx, 1];
res2 = Append[res2, "X" → Part[resArray, idx, 2]];
a = ErrorListPlot[RRfwEbData, PlotStyle → Red];
b = Plot[model /. res2, {x, 0, 0.7}];
qcline = Graphics[{Red, Line[{Qc, 0}, {Qc, 5}]}];
Twoqcline = Graphics[{Green, Line[{2 × Qc, 0}, {2 × Qc, 5}]}];
Show[a, b, qcline, Twoqcline, ImageSize → 480,
BaseStyle → {FontFamily → "Verdana"}, Frame → True,
GridLines → Automatic, GridLinesStyle → Opacity[0.35],
Epilog → Inset[Framed[Style[Column[res2], 18, Bold], Background → LightBlue],
{Right, Top}, {Right, Top}]]
```

Chi-Squared Error Bar Calculation

```
SetDirectory[NotebookDirectory[]];
Needs["ErrorBarPlots`"];
<< functionsXray';
<< parameters';
refdat = ReadList["./data/xr7.tsv", {Number, Number, Number}];
RoverRf = {#[[1]], #[[2]] / RfAbs[#[[1]], Qoffset, Qc, lambda, β]} & /@refdat;
RoverRfFit = DataToFit[RoverRf, 2];
weigths = WeightsErr[refdat, 2];
model = RRF[x, 2];
Raund [num_, n_] := N [Round [num *10^n] / 10<sup>n</sup>];
deltaChi = 1.069; (*30% Chi-square error bar 100 degree of freedom *)
allpars = {r1 \rightarrow 1.291, r2 \rightarrow 0.467, L1 \rightarrow 13.26, L2 \rightarrow 13.905, s1 \rightarrow 3.538};
step = 0.0002;
Column[
 ParallelTable[
   (*step size is set based on the model parameter values *)
  If[j < 3, step = 0.0002];</pre>
  If[j > 2, step = 0.002];
  startingList = Drop[allpars, {j, j}];
  modelval = Take[allpars, {j, j}];
  starting = {#[[1]], #[[2]]} & /@ startingList;
  modelvalIni = Part[modelval, 1, 2];
  chiIni = fit[RoverRfFit, weigths, model /. modelval, starting][[2]];
  chisq = Table[
    modelval = {Part[modelval, 1, 1] \rightarrow modelvalIni + step * j};
     {modelval[[1]][[2]],
      fit[RoverRfFit, weigths, model /. modelval, starting][[2]]}
     , \{j, -150, 200\}
   ];
  chiSqData = Select[chisq, Part[#, 2] < chiIni * deltaChi &];</pre>
  minX = Min[#[[1]] & /@chiSqData];
  maxX = Max[#[[1]] & /@chiSqData];
  ListLinePlot[{
     chiSqData,
     {{minX, chiIni * deltaChi }, {maxX, chiIni * deltaChi }},
     {{modelvalIni, chiIni}, {modelvalIni, chiIni * deltaChi}}
    }, PlotRangePadding \rightarrow {0.001 / 2, 0.01}, Frame \rightarrow True, ImageSize \rightarrow 380,
    PlotLabel → Framed[Style[
       Row[{ ToString[Part[modelval, 1, 1]] <> "=", Raund[modelvalIni, 3],
          Column[{minX - modelvalIni, "+" <> ToString[maxX - modelvalIni]}
          ]}], 16, Bold]
     1,
    Epilog \rightarrow {PointSize[Medium], Point[chiSqData], InterpolationOrder \rightarrow 2}
  ], {j, 1, allpars // Length}](*END COLUMN*)
1
```





Appendix F

TECHNICAL DRAWINGS

This appendix contains the technical drawings used for rebuilding the trough



Aluminium piece to be anodized. All units inches



SolidWorks Student Edition. For Academic Use Only.



Pressure sensor back holder for the translation stage



Miroslav Mihaylov mmihay2@uic.edu Material Al. All units inches. Make one.

SolidWorks Student Edition. For Academic Use Only. Pressure sensor part for the translation stage





SolidWorks Student License Academic Use Only


SolidWorks Student License Academic Use Only SolidWorks Student License Academic Use Only



Miroslav Mihaylov UIC Physics mmihay2@uic.edu 312 355 0225 VITA

MIROSLAV N. MIHAYLOV

CAMPUS ADDRESS

845 W. Taylor St. M/C 273 Chicago, IL 60607 (312) 355-0225

EDUCATION

Bachelor of Science in Physics, July 2004 Physics Faculty Sofia University Sofia Bulgaria

Master of Science in Physics, May 2008

University of Illinois at Chicago, Chicago Illinois

EXPERIENCE

Research Assistant UIC Physics Chicago, IL June 2007-Present
Research performed in the field of Experimental Condensed Matter Physics.

- Performed synchrotron x-ray scattering experiments for structural study of liquid interfaces at molecular length scale. Primarily using the liquid surface/interface station at ChemMatCARS at Argonne National Lab.
- Chemical preparation and treatment of experimental samples.
- Designed experimental apparatus with Solid Works and Qcad (Liquid surface sample cells, Langmuir Trough, Detector holders). The design was then implemented by working closely with an on-site machine shop and external vendors.
- Developed software for scientific data processing and analysis using Wolfram Mathematica, Python, awk.
- Implemented the EPICS control system on a custom built Langmuir Trough.
- Developed web based software for data acquisition and visualization of high density time series data generated from the EPICS soft IOC.
- Ab initio molecular dynamics computer simulations of condensed phase materials.
- Administered the computers and Beowulf cluster of our research group. Linux environment.

Teaching Assistant UIC Physics Chicago, IL Jan 2005-Present

- Taught introductory level physics laboratory classes and led discussion sections.
- Tutored students on problem solving skills during physics Tutoring sessions.
- Participated in the development of new hands-on assignments for student laboratory classes.
- Developed collaborative web based multi-user Learning Management System (LMS).

Graduate Assistant UIC Physics Electronics Shop, Chicago IL

Aug 2013 - Aug 2014

- Physics Department IT Help Desk
- Administered the website of the physics department.
- Developed web based multi-user applications for internal use.

PRESENTATIONS

Poster Presentation at APS User Meeting May 2012 Argonne National Lab "EPICS@Home"

UIC Physics Department Student Colloquium

"Mixed Charge Amphiphilic Systems"

PUBLICATIONS

"X-ray fluorescence from a model liquid/liquid solven extraction system" Wei Bu, Binyang Hou, M. Mihaylov, Ivan Kuzmenko, Binhua Lin, Mati Meron, Lin Soderholm, Guangming Luo, and Mark Schlossman Journal of Applied Physics, 110(10):, 2011.

"Tuning ion correlations at an electrified soft interface"

Nouamane Laanait, **M. Mihaylov**, Binyang Hou, Petr Vanysek, Mati Meron, Binhua Lin, Ilan Benjamin, and Mark L.Schlossman.

Proceedings of the National Academy of Sciences, 109(50):2032620331, 2012.

"X-ray Reflectivity Reveals a Nonmonotonic Ion-Density Profile Perpendicular to the Surface of ErCl3 Aqueous Solutions"

Guangming Luo, Wei Bu, M. Mihaylov, Ivan Kuzmenko, Mark Schlossman and Lin Soderholm, The Journal of Physical Chemistry C 117(37):1908219090, 2013.

"X-ray Studies of Interfacial StrontiumExtractant Complexes in a Model Solvent Extraction System" Wei Bu, M. Mihaylov, Daniel Amoanu, Binhua Lin, Mati Meron, Ivan Kuzmenko, Lin Soderholm and Mark Schlossman

The Journal of Physical Chemistry B 118(43):1248612500, 2014. PMID: 25264595.

"MLayer a Mathematica program for model depended fitting of X-ray reflectivity data" M. Mihaylov and Mark Schlossman The Journal of Applied Crystallography To be submitted.

MEMBERSHIPS

American Physical Society

TECHNICAL EXPERTISE

Programming Languages: Experienced with PHP, MySQL, JQuery, HTML, CSS. Hardware Control: EPICS, SCPI enabled instruments over IEEE-488 and RS-232. Other Languages: Proficient with Wolfram Mathematica, python, C, LATEX. Scripting with awk, Python and gnu bash. Familiar with Java, C++, SAS, R, IDL and Esri ArcGIS. Platforms: Gnu Linux, LAMP stack, Beowulf clusters. Familiarity with Hadoop and Mahout. Databases: MySQL, MongoDB, Elasticsearch, Familiar with MS SQL, Postgre SQL and Sqlite. MVC Web Frameworks: Symfony 1.4 with Propel ORM, Symfony 2 with Doctrine ORM. JavaScript MVC Frameworks: AngularJS.

Frontend Frameworks: Twitter Bootstrap, JQuery-UI, JQuery Mobile, Foundation.

Visualization libraries: d3js, Highcharts, Dygraphs.

Design: Solidworks, Qcad, GIMP, Inkscape, Blender.

Software And Project Management: git, Netbeans IDE, JetBrains IDEs, Atlassian JIRA.

LANGUAGES

- $\bullet\,$ English fluent
- Bulgarian native language
- Russian technical reading comprehension

CITED LITERATURE

- 1. Möhwald, H.: Surfactant layers at water surfaces. <u>Reports on Progress in Physics</u>, 56(5):653, 1993.
- Pocivavsek, L., Frey, S. L., Krishan, K., Gavrilov, K., Ruchala, P., Waring, A. J., Walther, F. J., Dennin, M., Witten, T. A., and Lee, K. Y. C.: Lateral stress relaxation and collapse in lipid monolayers. Soft Matter, 4:2019–2029, 2008.
- Zasadzinski, J., Ding, J., Warriner, H., Bringezu, F., and Waring, A. J.: The physics and physiology of lung surfactants. <u>Current Opinion in Colloid & Interface Science</u>, 6(5–6):506–513, 2001.
- 4. ed. J. Texter <u>Reactions And Synthesis In Surfactant Systems</u>, volume (Book 100). CRC Press, <u>1 edition</u>, June 2001.
- Bu, W., Mihaylov, M., Amoanu, D., Lin, B., Meron, M., Kuzmenko, I., Soderholm, L., and Schlossman, M. L.: X-ray Studies of Interfacial Strontium–Extractant Complexes in a Model Solvent Extraction System. <u>The Journal of Physical Chemistry</u> B, 118(43):12486–12500, 2014. PMID: 25264595.
- 6. Paiva, A. and Malik, P.: Recent advances on the chemistry of solvent extraction applied to the reprocessing of spent nuclear fuels and radioactive wastes. Journal of Radioanalytical and Nuclear Chemistry, 261(2):485–496.
- 7. Martin, F. J.: Liposomes: From biophysics to therapeutics. Edited by Marc Ostro. <u>Journal</u> of Pharmaceutical Sciences, 78(2):181–182, 1989.
- 8. Gaines., G. L.: Insoluble Monolayers at Liquid-gas Interfaces. Wiley & Sons, 1966.
- Swalen, J. D., Allara, D. L., Andrade, J. D., Chandross, E. A., Garoff, S., Israelachvili, J., McCarthy, T. J., Murray, R., Pease, R. F., and . et al.: Molecular monolayers and films. A panel report for the Materials Sciences Division of the Department of Energy. Langmuir, 3(6):932–950, 1987.
- Mohwald, H.: Phospholipid and Phospholipid-Protein Monolayers at the Air/Water Interface. Annual Review of Physical Chemistry, 41(1):441–476, 1990. PMID: 2257038.

- 11. Pockels, A.: Surface tension. Nature, 43:437–439, March 1891.
- F.R.S., L. R.: XXXVI. Investigations in Capillarity:—The size of drops.—The liberation of gas from supersaturated solutions.—Colliding jets.—The tension of contaminated water-surfaces. Philosophical Magazine Series 5, 48(293):321–337, 1899.
- Langmuir, I.: THE CONSTITUTION AND FUNDAMENTAL PROPERTIES OF SOLIDS AND LIQUIDS. II. LIQUIDS.1. Journal of the American Chemical Society, 39(9):1848–1906, 1917.
- Als-Nielsen, J. and Pershan, P.: Synchrotron X-ray diffraction study of liquid surfaces. Nuclear Instruments and Methods in Physics Research, 208(1–3):545–548, 1983.
- Pershan, P. S. and Als-Nielsen, J.: X-Ray Reflectivity from the Surface of a Liquid Crystal: Surface Structure and Absolute Value of Critical Fluctuations. <u>Phys. Rev. Lett.</u>, 52:759–762, Feb 1984.
- Braslau, A., Deutsch, M., Pershan, P. S., Weiss, A. H., Als-Nielsen, J., and Bohr, J.: Surface Roughness of Water Measured by X-Ray Reflectivity. <u>Phys. Rev. Lett.</u>, 54:114–117, Jan 1985.
- Kjaer, K., Als-Nielsen, J., Helm, C. A., Laxhuber, L. A., and Möhwald, H.: Ordering in Lipid Monolayers Studied by Synchrotron X-Ray Diffraction and Fluorescence Microscopy. Phys. Rev. Lett., 58:2224–2227, May 1987.
- Dutta, P., Peng, J. B., Lin, B., Ketterson, J. B., Prakash, M., Georgopoulos, P., and Ehrlich, S.: X-Ray Diffraction Studies of Organic Monolayers on the Surface of Water. Phys. Rev. Lett., 58:2228–2231, May 1987.
- Lösche, M. and Möhwald, H.: Fluorescence microscope to observe dynamical processes in monomolecular layers at the air/water interface. <u>Review of Scientific Instruments</u>, 55(12):1968–1972, 1984.
- Moy, V. T., Keller, D. J., Gaub, H. E., and McConnell, H. H.: Long-range molecular orientational order in monolayer solid domains of phospholipid. <u>The Journal of</u> Physical Chemistry, 90(14):3198–3202, 1986.
- Hénon, S. and Meunier, J.: Microscope at the Brewster angle: Direct observation of firstorder phase transitions in monolayers. <u>Review of Scientific Instruments</u>, 62(4):936–939, 1991.

- 22. Hönig, D. and Möbius, D.: Reflectometry at the Brewster angle and Brewster angle microscopy at the air-water interface. <u>Thin Solid Films</u>, 210–211, Part 1(0):64–68, 1992.
- Herrington, K. L., Kaler, E. W., Miller, D. D., Zasadzinski, J. A., and Chiruvolu, S.: Phase behavior of aqueous mixtures of dodecyltrimethylammonium bromide (DTAB) and sodium dodecyl sulfate (SDS). <u>The Journal of Physical Chemistry</u>, 97(51):13792– 13802, 1993.
- 24. ed. M. Abe Mixed Surfactant Systems. CRC Press, 2nd edition edition, December 2004.
- 25. Dubois Monique, Deme Bruno, Gulik-Krzywicki Thaddee, Dedieu Jean-Claude, Vautrin Claire, Desert Sylvain, Perez Emile, and Zemb Thomas: Self-assembly of regular hollow icosahedra in salt-free catanionic solutions. <u>Nature</u>, 411(6838):672–675, jun 2001. 10.1038/35079541.
- 26. Tah, B., Pal, P., Mahato, M., and Talapatra, G. B.: Aggregation Behavior of SDS/CTAB Catanionic Surfactant Mixture in Aqueous Solution and at the Air/Water Interface. The Journal of Physical Chemistry B, 115(26):8493–8499, 2011. PMID: 21675762.
- 27. Wang, Y., Pereira, C. M., Marques, E. F., Brito, R. O., Ferreira, E., and Silva, F.: Catanionic surfactant films at the air-water interface. <u>Thin Solid Films</u>, 515(4):2031– 2037, 2006.
- 28. Maiti, K., Bhattacharya, S., Moulik, S., and Panda, A.: Physicochemistry of the binary interacting mixtures of cetylpyridinium chloride (CPC) and sodium dodecylsulfate (SDS) with special reference to the catanionic ion-pair (coacervate) behavior. <u>Colloids and Surfaces A: Physicochemical and Engineering Aspects</u>, 355(1– 3):88–98, 2010.
- Vaknin, D. and Bu, W.: Neutrally Charged Gas/Liquid Interface by a Catanionic Langmuir Monolayer. The Journal of Physical Chemistry Letters, 1(13):1936–1940, 2010.
- 30. Sung, W., Seok, S., Kim, D., Tian, C. S., and Shen, Y. R.: Sum-Frequency Spectroscopic Study of Langmuir Monolayers of Lipids Having Oppositely Charged Headgroups. Langmuir, 26(23):18266–18272, 2010. PMID: 20977244.
- Stripe, B., Uysal, A., Lin, B., Meron, M., and Dutta, P.: Charge, Stereochemistry, or Epitaxy? Toward Controlled Biomimetic Nucleation at Mixed Monolayer Templates. Langmuir, 28(1):572–578, 2012. PMID: 22077377.

- 32. Greenfield, M. A., Palmer, L. C., Vernizzi, G., de la Cruz, M. O., and Stupp, S. I.: Buckled Membranes in Mixed-Valence Ionic Amphiphile Vesicles. Journal of the American Chemical Society, 131(34):12030–12031, 2009. PMID: 19705907.
- 33. Loverde, S. M., Velichko, Y. S., and Olvera de la Cruz, M.: Competing interactions in two dimensional Coulomb systems: Surface charge heterogeneities in coassembled cationic-anionic incompatible mixtures. <u>The Journal of Chemical Physics</u>, 124(14):-, 2006.
- 34. Kohlstedt, K. L., Vernizzi, G., and de la Cruz, M. O.: Electrostatics and optimal arrangement of ionic triangular lattices confined to cylindrical fibers. <u>Phys. Rev. E</u>, 80:051503, Nov 2009.
- 35. Vernizzi, G., Zhang, D., and Olvera de la Cruz, M.: Structural phase transitions and mechanical properties of binary ionic colloidal crystals at interfaces. <u>Soft Matter</u>, 7:6285–6293, 2011.
- 36. Sknepnek, R., Vernizzi, G., and Olvera de la Cruz, M.: Buckling of multicomponent elastic shells with line tension. Soft Matter, 8:636–644, 2012.
- 37. Tondre, C. and Caillet, C.: Properties of the amphiphilic films in mixed cationic/anionic vesicles: a comprehensive view from a literature analysis. <u>Advances in Colloid and Interface Science</u>, 93(1–3):115–134, 2001.
- Carriere, D., Belloni, L., Deme, B., Dubois, M., Vautrin, C., Meister, A., and Zemb, T.: In-plane distribution in mixtures of cationic and anionic surfactants. <u>Soft Matter</u>, 5:4983–4990, 2009.
- Levental, I., Christian, D. A., Wang, Y.-H., Madara, J. J., Discher, D. E., and Janmey, P. A.: Calcium-Dependent Lateral Organization in Phosphatidylinositol 4,5-Bisphosphate (PIP2)- and Cholesterol-Containing Monolayers. <u>Biochemistry</u>, 48(34):8241–8248, 2009. PMID: 19630438.
- Wang, Y.-H., Slochower, D. R., and Janmey, P. A.: Counterion-mediated cluster formation by polyphosphoinositides. <u>Chemistry and Physics of Lipids</u>, 182(0):38–51, 2014. Physical chemistry and biophysics of polyphosphoinositide mediated lipid signaling.

- Schwartz, D. K., Schlossman, M. L., and Pershan, P. S.: Reentrant appearance of phases in a relaxed Langmuir monolayer of tetracosanoic acid as determined by xray scattering. J. Chem. Phys., 96(2356), 1992.
- 42. EPICS Experimental Physics and Industrial Control System.
- 43. Fuller, W. A.: Introduction to Statistical Time Series. Wiley, December 1995.
- 44. Bevington, P. and Robinson, D. K.: Data Reduction and Error Analysis for the Physical Sciences. McGraw-Hil Science/Engineering/Math, 3rd edition, July 2002.
- 45. Millipore Corp. Bedford, MA. 01730.
- 46. Pershan, P. S. and Schlossman, M. L.: <u>Liquid Surfaces and Interfaces, Synchrotron X-ray</u> Methods. Cambridge University Press, August 2012.
- 47. Schlossman, M. L., Synal, D., Guan, Y., Meron, M., Shea-McCarthy, G., Huang, Z., Acero, A., Williams, S. M., Rice, S. A., and Viccaro, P. J.: A synchrotron x-ray liquid surface spectrometer. Review of Scientific Instruments, 68(12):4372–4384, 1997.
- 48. Lin, B., Meron, M., Gebhardt, J., Graber, T., Schlossman, M. L., and Viccaro, P.: The liquid surface/interface spectrometer at ChemMatCARS synchrotron facility at the Advanced Photon Source. <u>Physica B: Condensed Matter</u>, 336(1–2):75–80, 2003. Proceedings of the Seventh International Conference on Surface X-ray and Neutron Scattering.
- Meron, M., Gebhardt, J., Brewer, H., Viccaro, J. P., and Lin, B.: Following transient phases at the air/water interface. <u>The European Physical Journal Special Topics</u>, 167(1):137–142.
- 50. Bu, W., Hou, B., Mihaylov, M., Kuzmenko, I., Lin, B., Meron, M., Soderholm, L., Luo, G., and Schlossman, M. L.: X-ray fluorescence from a model liquid/liquid solvent extraction system. Journal of Applied Physics, 110(10):-, 2011.
- 51. Laanait, N., Mihaylov, M., Hou, B., Yu, H., Vanýsek, P., Meron, M., Lin, B., Benjamin, I., and Schlossman, M. L.: Tuning ion correlations at an electrified soft interface. Proceedings of the National Academy of Sciences, 109(50):20326–20331, 2012.

- 52. Mitrinović, D. M., Tikhonov, A. M., Li, M., Huang, Z., and Schlossman, M. L.: Noncapillary-Wave Structure at the Water-Alkane Interface. <u>Phys. Rev. Lett.</u>, 85:582–585, Jul 2000.
- 53. Tikhonov, A. M., Pingali, S. V., and Schlossman, M. L.: Molecular ordering and phase transitions in alkanol monolayers at the water-hexane interface. <u>The Journal of</u> Chemical Physics, 120(24):11822–11838, 2004.
- 54. Luo, G., Malkova, S., Pingali, S. V., Schultz, D. G., Lin, B., Meron, M., Benjamin, I., Vanysek, P., and Schlossman, M. L.: Structure of the Interface between Two Polar Liquids: Nitrobenzene and Water. <u>The Journal of Physical Chemistry B</u>, 110(10):4527–4530, 2006. PMID: 16526678.
- 55. Als-Nielsen, J. and McMorrow, D.: <u>Elements of Modern X-ray Physics</u>. Hoboken, John Wiley & Sons, Inc., 2001.
- 56. Jacquemain, D., Wolf, S. G., Leveiller, F., Lahav, M., Leiserowitz, L., Deutsch, M., Kjaer, K., and Als-Nielsen, J.: Dynamics of two-dimensional self-aggregation: pressure and pH-induced structural changes in a fluorocarbon amphiphile at liquid-air interfaces. An x-ray synchrotron study. Journal of the American Chemical Society, 112(21):7724–7736, 1990.
- 57. Jacquemain, D., Wolf, S. G., Leveiller, F., Deutsch, M., Kjaer, K., Als-Nielsen, J., Lahav, M., and Leiserowitz, L.: Two-Dimensional Crystallography of Amphiphilic Molecules at the Air–Water Interface. <u>Angewandte Chemie International Edition</u> in English, 31(2):130–152, 1992.
- 58. Leveiller, F., Jacquemain, D., Leiserowitz, L., Kjaer, K., and Als-Nielsen, J.: Toward a determination at near atomic resolution of two-dimensional crystal structures of amphiphilic molecules on the water surface: a study based on grazing incidence synchrotron x-ray diffraction and lattice energy calculations. <u>The Journal of Physical</u> Chemistry, 96(25):10380–10389, 1992.
- 59. Als-Nielsen, J., Jacquemain, D., Kjaer, K., Leveiller, F., Lahav, M., and Leiserowitz, L.: Principles and applications of grazing incidence X-ray and neutron scattering from ordered molecular monolayers at the air-water interface. <u>Physics Reports</u>, 246(5):251–313, 1994.
- 60. Daillant, J.: Recent developments and applications of grazing incidence scattering. <u>Current</u> Opinion in Colloid & Interface Science, 14(6):396–401, 2009.

- Daillant, J. and Alba, M.: High-resolution x-ray scattering measurements: I. Surfaces. Reports on Progress in Physics, 63(10):1725, 2000.
- Braslau, A., Pershan, P. S., Swislow, G., Ocko, B. M., and Als-Nielsen, J.: Capillary waves on the surface of simple liquids measured by x-ray reflectivity. <u>Phys. Rev. A</u>, 38:2457–2470, Sep 1988.
- 63. Tidswell, I. M., Ocko, B. M., Pershan, P. S., Wasserman, S. R., Whitesides, G. M., and Axe, J. D.: X-ray specular reflection studies of silicon coated by organic monolayers (alkylsiloxanes). Phys. Rev. B, 41:1111–1128, Jan 1990.
- 64. Ashcroft, N. W. and Mermin, D. N.: <u>Solid State Physics</u>. Toronto, Thomson Learning, 1 edition, January 1976.
- Daillant, J. and Gibaud, A.: <u>X-ray and Neutron Reflectivity Principles and Applications</u>. Lecture Notes in Physics. Springer, 2009.
- 66. Kiessig, H.: Interference of X-rays in thick layers. <u>Annalen der Physik</u>, 402(7):769–788, 1931.
- Parratt, L. G.: Surface Studies of Solids by Total Reflection of X-Rays. <u>Phys. Rev.</u>, 95:359–369, Jul 1954.
- 68. Born, M. and Wolf, E.: Principles of Optics. Cambridge University Press, 7 edition, 1999.
- Vidal, B. and Vincent, P.: Metallic multilayers for x rays using classical thin-film theory. Appl. Opt., 23(11):1794–1801, Jun 1984.
- 70. Tolan, M.: X-Ray Scattering from Soft-Matter Thin Films. Materials Science and Basic Research.. Springer; Softcover reprint of the original 1st ed. 1999 edition (March 26, 2013), March 2013.
- 71. Gaines., G. L.: On the use of filter paper wilhelmy plates with insoluble monolayers. Journal of Colloid and Interface Science, 62(1):191–192, 1977.
- 72. Kato Teiji, Iriyama Keiji, and Araki Toshinari: The time of observation of A isotherms III. Studies on the morphology of arachidic acid monolayers, observed by transmission electron microscopy of replica samples of one-layer Langmuir-Blodgett films using plasma-polymerization. Thin Solid Films, 210–211, Part 1(0):79–81, apr 1992.

- 73. Castillo, R., Ramos, S., Ruíz-García, J., and Varea, C.: Langmuir films of mixtures of {C70} and arachidic acid. <u>Fluid Phase Equilibria</u>, 110(1–2):129–135, 1995. 13th {IUPAC} Conference on Chemical Thermodynamics concerning Fluid Phase Equilibria.
- 74. Vaknin, D., Bu, W., Satija, S. K., and Travesset, A.: Ordering by Collapse: Formation of Bilayer and Trilayer Crystals by Folding Langmuir Monolayers. <u>Langmuir</u>, 23(4):1888–1897, 2007. PMID: 17279671.
- 75. Small, D. M.: <u>The physical chemistry of lipids : from alkanes to phospholipids</u>. New York : Plenum Press, handbook of lipid research, v. 4. edition, 1986.
- 76. Larsson, K.: Lipids : molecular organization, physical functions and technical applications. Dundee : Oily Press, oily press lipid library, 5. edition, 1994.
- 77. Kaganer, V. M., Möhwald, H., and Dutta, P.: Structure and phase transitions in Langmuir monolayers. Rev. Mod. Phys., 71:779–819, Apr 1999.
- 78. Biswas, S., Hussain, S., Deb, S., Nath, R., and Bhattacharjee, D.: Formation of complex films with water-soluble {CTAB} molecules. <u>Spectrochimica Acta Part A:</u> Molecular and Biomolecular Spectroscopy, 65(3–4):628–632, 2006.
- 79. Stine, K. J., Rauseo, S. A., Moore, B. G., Wise, J. A., and Knobler, C. M.: Evolution of foam structures in Langmuir monolayers of pentadecanoic acid. <u>Phys. Rev. A</u>, 41:6884–6892, Jun 1990.
- Stine, K. J., Knobler, C. M., and Desai, R. C.: Buckling instability in monolayer network structures. Phys. Rev. Lett., 65:1004–1007, Aug 1990.
- Levental, I., Janmey, P., and Cēbers, A.: Electrostatic Contribution to the Surface Pressure of Charged Monolayers Containing Polyphosphoinositides. <u>Biophysical Journal</u>, 95(3):1199–1205, 2008.
- Wang, W., Park, R. Y., Meyer, D. H., Travesset, A., and Vaknin, D.: Ionic Specificity in pH Regulated Charged Interfaces: Fe3+versus La3+. <u>Langmuir</u>, 27(19):11917–11924, 2011. PMID: 21863848.
- 83. Durbin, M. K., Malik, A., Richter, A. G., Ghaskadvi, R., Gog, T., and Dutta, P.: Transitions to a new chiral phase in a Langmuir monolayer. <u>The Journal of Chemical</u> Physics, 106(19):8216–8220, 1997.

- 84. ed. J. N. Israelachvili <u>Intermolecular and Surface Forces (Third Edition)</u>. San Diego, Academic Press, third edition, 2011.
- 85. Taylor, J. R.: <u>An Introduction to Error Analysis: The Study of Uncertainties in Physical</u> Measurements. University Science Books, 2nd edition edition, August 1996.
- 86. Abramowitz, M. and Stegun, I. A.: <u>Handbook of Mathematical Functions: with Formulas,</u> <u>Graphs, and Mathematical Tables</u>. Dover Books on Mathematics, 0009-revised edition edition, June 1965.
- 87. Weisstein, E. W.: "Regularized Gamma Function." From MathWorld–A Wolfram Web Resource.