



***LANGMUIR-BLODGETT
TROUGHS***

***OPERATING MANUAL
6th EDITION***

Welcome

The information contained within this manual is for guidance only in the use of the product. Since the product is continually being developed and improved, the information is subject to change without notice and though given in good faith, may contain errors or omissions.

Nima Technology welcomes any suggestions for further development or improvement of the product or this manual.

All suggestions and enquiries should be addressed to:

Nima Technology Ltd
The Science Park
Coventry CV4 7EZ
England

Tel: (+44) (247) 641 9457
Fax: (+44) (247) 669 2511
e-mail: info@nima.co.uk
Website: <http://www.nima.co.uk>

First edition 1989
Second edition 1991 (revised and updated)
Third edition 1992 (revised and updated), 2nd printing 1993
Fourth edition (revised and updated) 1995, 2nd printing 1998
Fifth edition (revised and updated) 1999
Sixth edition (revised and updated) 2001, 2nd printing 2002
3rd printing updated for WIN XP, 2004
Software Generation 5.16 for WIN95 - XP

Authors:

P. Martin and M. Szablewski
Cranfield University
Milton Keynes, England

Editor: Frank Grunfeld, Nima Technology Ltd

Copyright © 1989, 1991, 1992, 1993, 1995, 1998, 1999, 2001, 2002, 2004 Nima Technology Ltd.

MS-DOS and Windows are a registered trademark of Microsoft Corporation.

IBM is a registered trademark of International Business Machines Corporation.

PageMaker is a registered trademark of Adobe Aldus Corporation.

LabView is a registered trademark of National Instruments Corporation.

WELCOME

Thank you for buying a Langmuir trough from Nima Technology. Our troughs are very versatile, precision scientific instruments. They can accomplish a wide range of tasks - from the analysis of lipids and surfactants at the liquid-gas interface to the fabrication of ordered multilayers for applications in molecular electronics.

With proper care and attention, your trough will be running for many years; and the uses to which it is put then will be as relevant as they are today.

This manual is divided into several chapters and incorporates everything you need to know on how to get started in Langmuir-Blodgett (LB) films and using Nima troughs.

There is a '**Langmuir-Blodgettry**' chapter which gives a thorough grounding in the principles involved. Then there is a self-contained '**Tutorial**' which takes about a day to work through, designed to familiarise you with the basic commands of the trough and gain a practical grounding in LB films. Further understanding of Langmuir films can be gained by working through the series of experiments contained in the '**Experiments**' chapter. A full description of all the trough commands and functions is given in the '**Software**' chapter. Finally a full technical description of how to set up the motors and sensors is given in the '**Technical Appendix**'.

Should any questions arise, please do not hesitate to contact Nima Technology who will be delighted to help in any way - info@nima.co.uk

Licence Statement

Purchase of a Nima LB trough gives the buyer unlimited licence to copy and disseminate both information contained in this manual and the software for running the instruments, provided this is for educational purposes only.

Guarantee

Your Nima LB trough is covered by our unconditional guarantee. This means that if your trough does not work, we will repair it free of charge, no matter whatever cause, including accidental damage by students. We do however ask that you pay for the freight charges to and from our workshop in Coventry.

For legal reasons, this guarantee is limited to 3 years from date of purchase.

This guarantee does not, however, apply to peripheral equipment, such as PCs, surface potential sensors & pH meters, made by other manufacturers and consumables such as platinum plates and rings.

CONTENTS

GETTING STARTED	1
<i>Introduction</i>	2
<i>Unpacking</i>	3
<i>Hardware setup</i>	4
<i>Software installation</i>	8
<i>Operation</i>	11
<i>Surfactant check.....</i>	14
LANGMUIR-BLODGETTRY	17
<i>Langmuir films</i>	18
<i>The Langmuir-Blodgett technique.....</i>	19
<i>Langmuir films - theory</i>	23
<i>Langmuir films - practice</i>	28
<i>LB film deposition onto a substrate.....</i>	31
<i>Laboratory Requirements</i>	35
<i>Bibliography.....</i>	41
TUTORIAL	47
<i>Preparations</i>	48
<i>Producing an isotherm</i>	50
<i>Depositing a multilayer LB film</i>	56
<i>Deposition onto hydrophilic substrates</i>	61
<i>Interpreting transfer ratios</i>	63
<i>Operating the trough in 'coupled barrier' mode</i>	65
<i>Operating the trough in alternate layer mode</i>	66
<i>Further Work & Conclusion</i>	69
EXPERIMENTS	71
<i>Preparations</i>	72
<i>A typical pressure-area isotherm</i>	75
<i>Experiment 1 - Presence of a monolayer.....</i>	76
<i>Experiment 2 - Molecular flow</i>	78
<i>Experiment 3 - Area of a molecule</i>	82
<i>Experiment 4 - Collapse of a fatty acid</i>	83
<i>Experiment 5 - Structural changes</i>	85
<i>Experiment 6 - Acid to salt conversion</i>	87
<i>Experiment 7 - Cholesterol films</i>	89
<i>Experiment 8 - CMC determination</i>	91

SOFTWARE	93
<i>Introduction</i>	94
<i>Setup Menu</i>	98
<i>Monolayer Menu</i>	100
<i>Dipper Menu</i>	102
<i>Calibrations Menu</i>	106
TECHNICAL APPENDIX	117
<i>Frequently asked questions</i>	118
<i>Barrier mechanisms</i>	125
<i>Dipper mechanisms</i>	128
<i>Pressure sensor</i>	131
<i>Temperature sensor</i>	133
<i>Magnetic stirrer</i>	133
<i>Surface potential sensor</i>	134
<i>Cable connections</i>	137
<i>Synthesis of ferric stearate</i>	138
INDEX	139

GETTING STARTED

Introduction

This section describes how to unpack and set up your LB trough. Information is also given about how to install the software.

Before unpacking your trough, it is a good idea to check that you have everything that you will need to hand. The following list itemises the minimum laboratory accessories that are required for efficient operation.

Laboratory Requirements

Bench Space	At least 2m in a clean, draught and dust free environment.
Pump	Running water and a sink are required for connection of the aspirator pump provided - alternatively a vacuum pump and flask can be used.
Water	A supply of pure (deionised and organic free) water is required for troughs. Recommended manufacturers include Elga, Millipore and Barnstead.
Balance	To be capable of measuring accuracies of at least 0.1mg.
Sundries	Polythene powder-free gloves, surfactant-free, lint-free tissues (supplied), cleaning solvents (e.g. chloroform), small volumetric flasks (10ml).
PC	A Pentium PC running WIN95 or higher. The Nima software occupies less than 10MB of disc space. A serial or USB port is essential to communicate with the serial interface.

Unpacking

Before unpacking, make a visual check of the packaging. Make a note of any obvious damage. During unpacking, look at each item carefully, identify it (most items are labelled) and check that it looks undamaged.

***In the event of damage**, notify Nima Technology and the freight agent immediately. It is a good idea to take pictures of the damaged packaging and goods at this stage - this will help any insurance claims and speed replacement of damaged items.*

You should find some or all (depending on what type of trough you have) of the items below in the crate your instrument was shipped in:

- *Langmuir trough
- *Dipper mechanism (optional - conventional and/or alternate layer) for dipping troughs
- *Pressure sensor(s) (2 for alternate layer troughs, Models 1222D2)
- *Interface unit, serial cable and mains lead
- *1 CD with the operating software (or 2 diskettes)
- *Monolayer kit
 - plastic box with small compartments containing the following:
 - tweezers, pointed
 - tweezers, flat (for dipper trough only)
 - 10, 50 or 100µl syringe (depending on size of trough)
 - spatula
 - balance pan, pan carrier & 100mg calibration weight
 - bag of hooks
 - bag of paper Wilhelmy plates
 - miniature tools
 - chromed aspirator pump
 - PTFE nozzle for aspirator pump
- *Box of 'Kimtech' tissues - type 75512
- *Packet of polythene, powder-free gloves,
- *Rubber tubing for aspirator pump.
- *This manual!

Take care when unpacking your Nima LB trough - it is a precision piece of machinery made by craftsmen. Take exceptional care when unpacking the pressure sensor, as this is the most delicate part of the system.

Hardware setup

Locate a quiet, clean corner of your lab, free from air currents. You will need about 2m of bench space and a comfortable chair to sit on. These measurements need plenty of patience and an uncomfortable student is a sloppy researcher.

Access to running water (to connect the aspirator) is recommended. Alternatively, using a vacuum source and funnel is also recommended.

Please identify your trough from the diagrams below and set it up as shown:

Model 102M / 112D

Pressure sensor mounted on edge of trough (A) or on separate stand (B)

2 mechanically coupled barriers

Sapphire window (removable with locking key)

Tubing connectors for temperature control

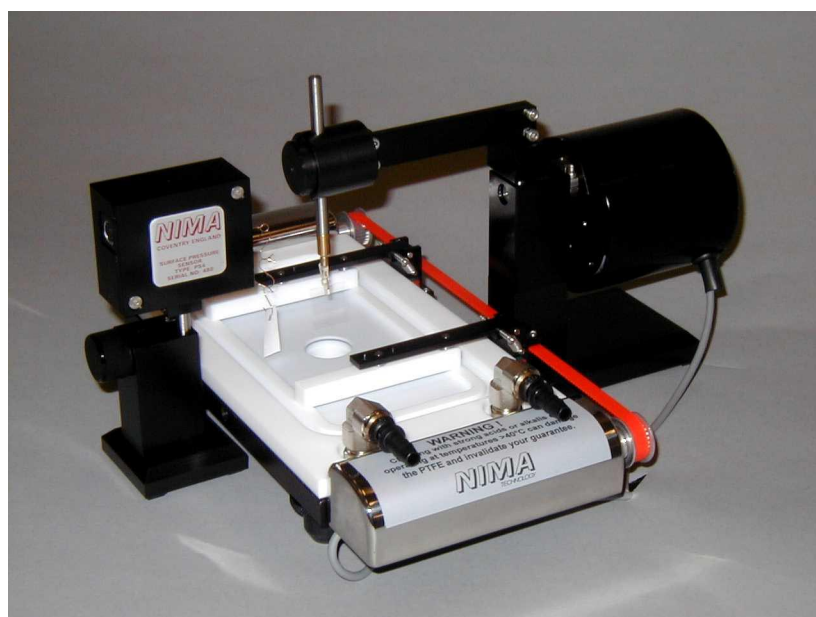
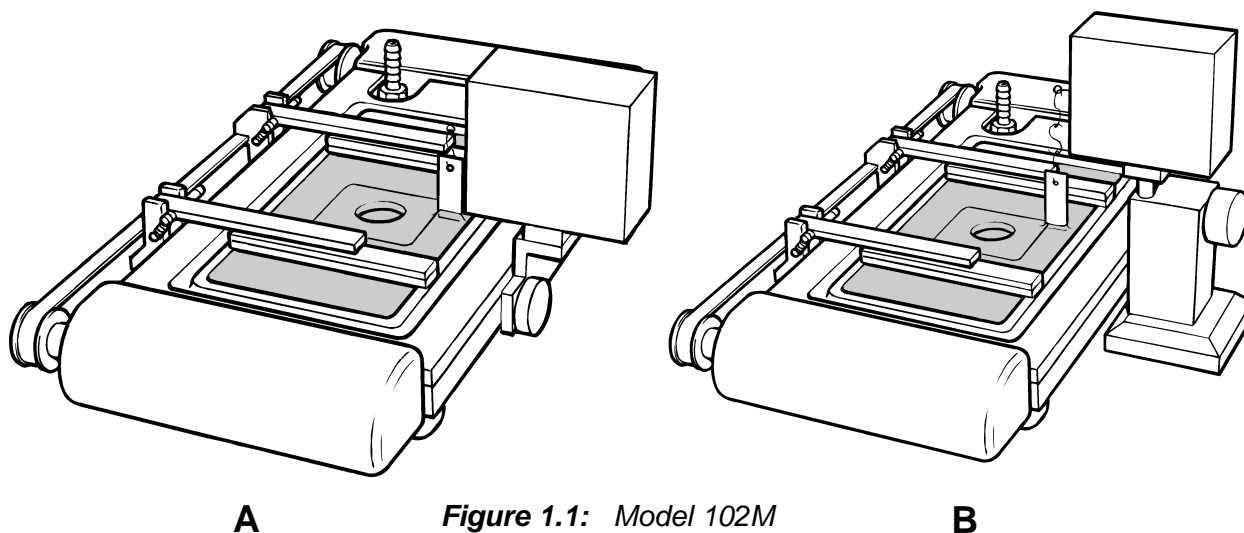


Figure 1.2: Model 112D

Model 311D / 312D

311D: Pressure sensor and dipper mounted at one end of the trough
Single barrier compressing towards one end of trough

312D: Pressure sensor and dipper mounted at centre of the trough
Two barriers compressing symmetrically towards centre of trough

With or without acrylic cover depending on application

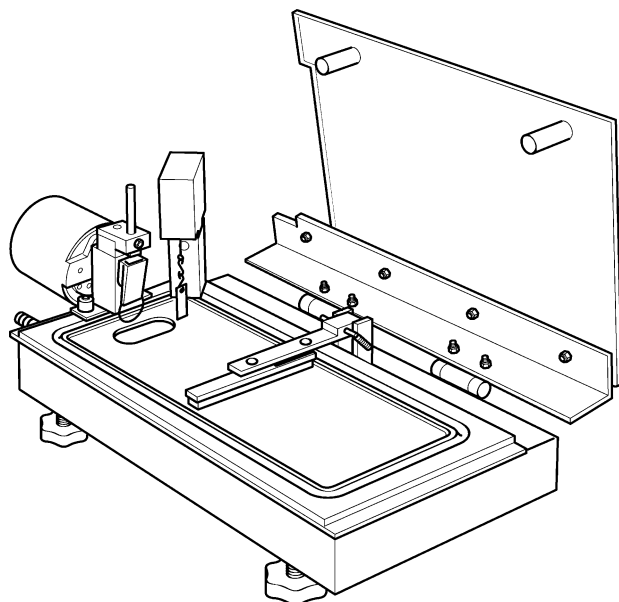


Figure 1.3: Model 311D

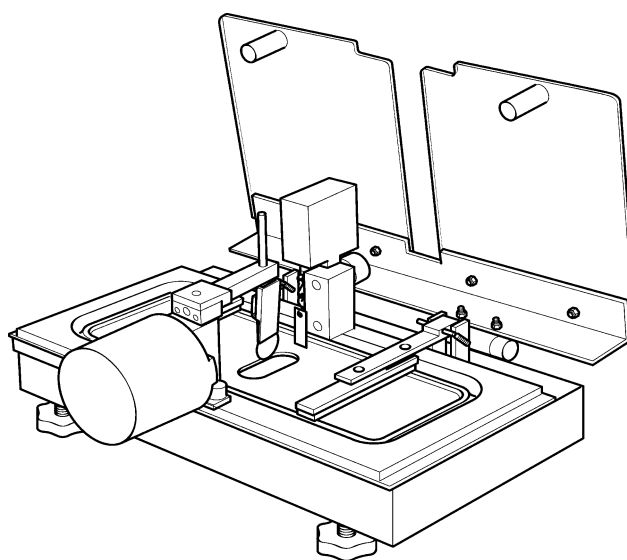


Figure 1.4: Model 312D

Most troughs have removable tops for easy cleaning.

These just lift off:

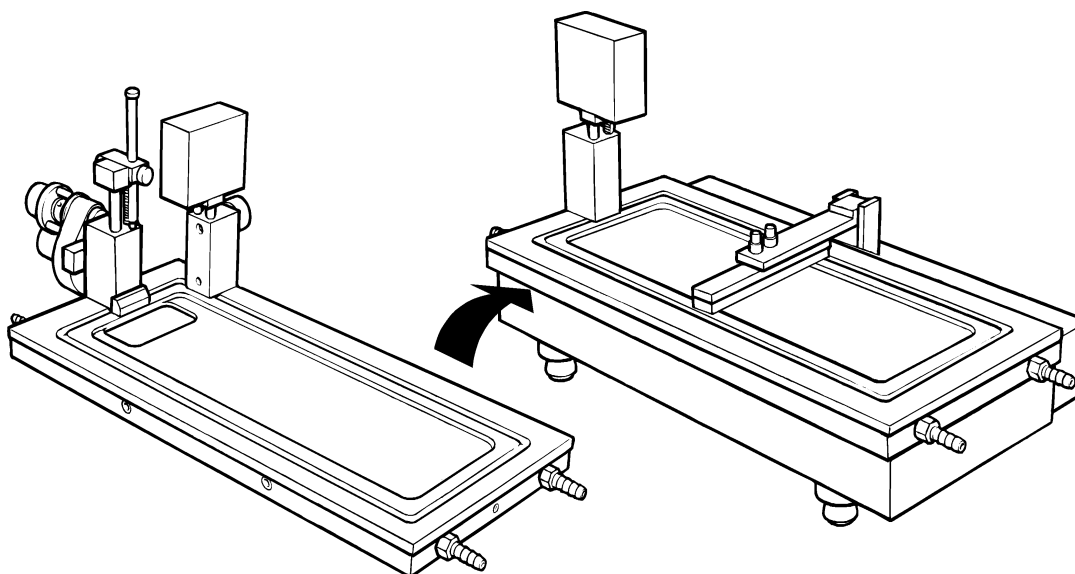


Figure 1.5: Changing / replacing removable PTFE top
Shown here: switching between Model 301S and 311D

Model 601A

- Pressure sensor at one end of the trough
- 1 barrier
- Acrylic, hinged cover
- Tubing connectors for temperature control

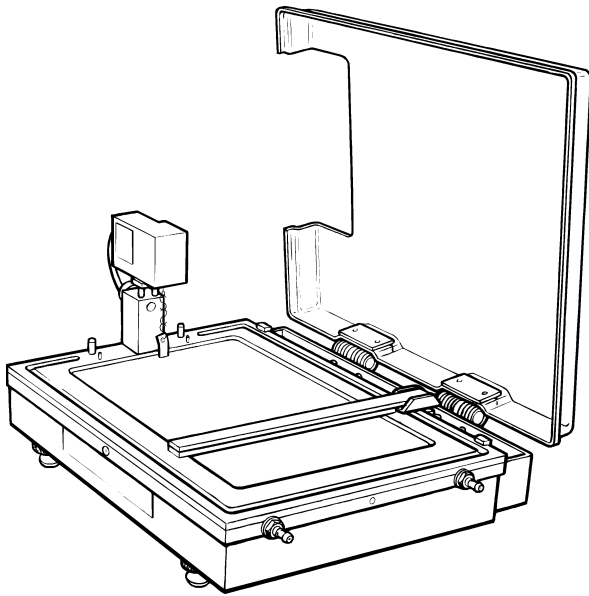


Figure 1.6 Model 601A

Model 611D

- Trough with 1 or 2 barriers
 - Pressure sensor
 - Dipper and well all at one end or in centre
-
- Hinged cover
 - Tubing connectors for temperature control

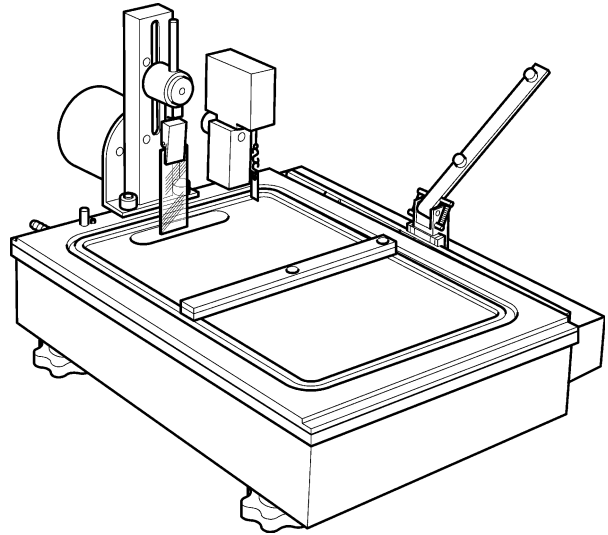


Figure 1.7: Model 611D

Model 702BAM

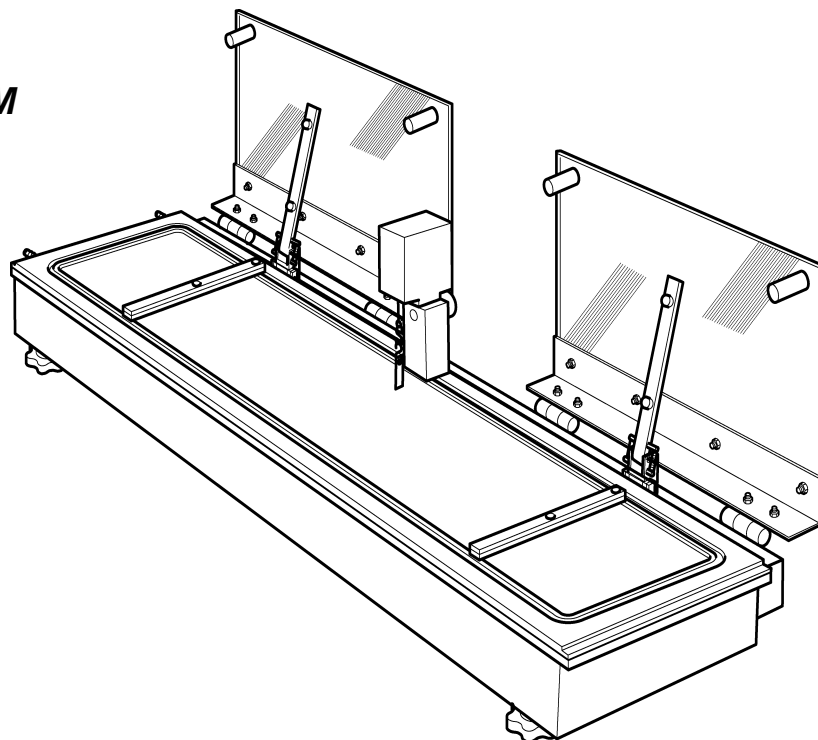
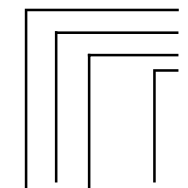


Figure 1.8: Model 702BAM

Model 1212D1 / 1222D2 / 1232D1D2

Nomenclature

1222D1



function : D1 = conventional LB
 D2 = alternate layer LB
 Number of barriers
 dipper type 0, 1 ,2 or 3
 area x 100 cm²

- 2 compartment trough with 2 pressure sensors
- Alternate layer dipper mechanism (A)
- or conventional dipper (B)
- 2 hinged covers
- 2 temperature control circuits.

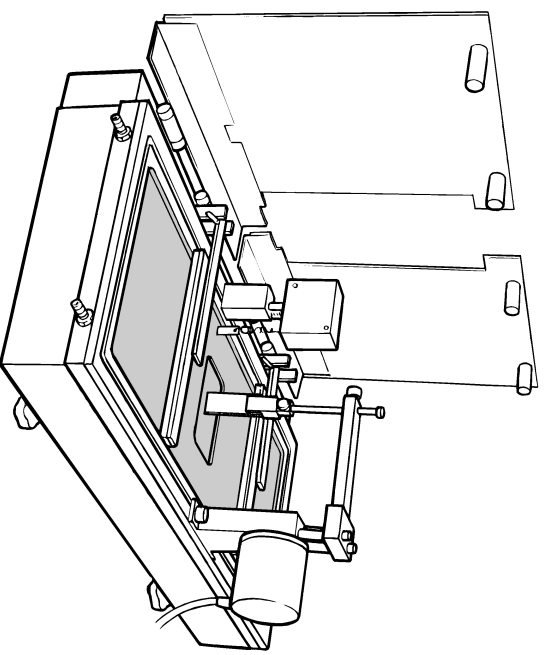


Figure 1.9: Model 1212D1

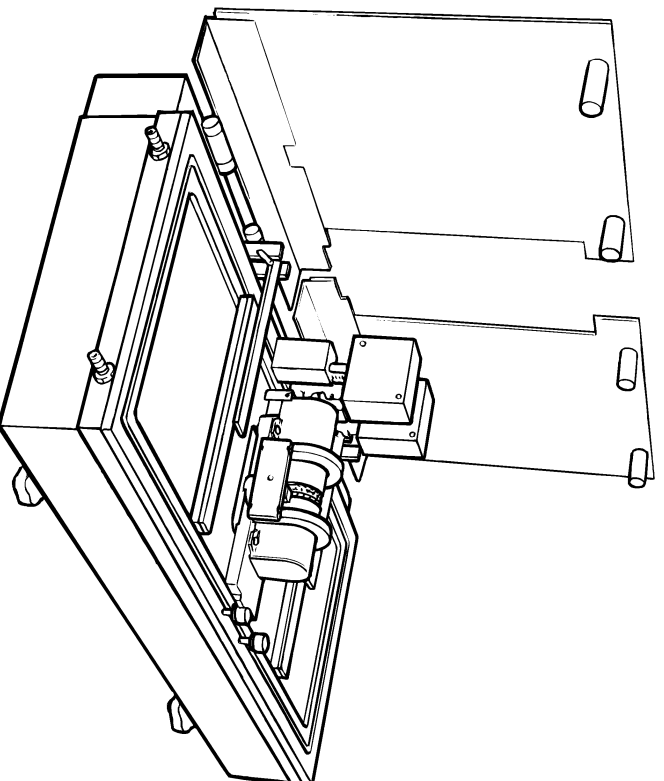


Figure 1.10: Model 1222D2

Levelling & temperature control

Nima troughs are levelled by means of the four adjustable legs which support the trough.

For temperature control, you can connect suitable tubing to the troughs now or later. The troughs come with standard fittings which can be unscrewed if you prefer your own.

Pressure sensors

The pressure sensors on troughs use a Wilhelmy plate (in this case, a small length of chromatography paper - Whatmans Chr1) to measure the surface pressure (reduction in surface tension).

For each pressure sensor, take 2 or 3 'S' shaped hooks from the monolayer kit and attach them in 'daisy chain' fashion to the small wire protruding from the pressure sensor. Take one of the pre-cut Wilhelmy plates provided, thread one of the hooks through the hole punched in it, and attach it to the lowest hook already suspended from the pressure sensor.

Interface Unit

The unit is supplied with a universal mains adaptor for 100 - 240V, 50/60Hz. Connect the three pin mains lead into the mains adaptor and the 6mm jack into the 'DC in' socket of the interface. Do not switch on yet.

Connect the round 5 pin DIN plugs to the back of the interface unit. These are marked 'BAR-A' for barrier A, 'BAR-B' for barrier B (if you have one), 'PA' for pressure sensor A, 'PB' for pressure sensor B (or tensiometer), 'LIN-DIP' for a conventional linear dipper and 'ALT-DIP' for an alternate dipper.

Attach the serial cable to the interface unit (IU4) and to the serial port of the PC - the interface end is a 9 pin 'D'. The PC end is also 9 pin D and a 25-9 way converter is also supplied.

If you are using a mouse on a serial port, you must use a different port for the interface. However, beware(!) because some mouse software drivers clash with the trough serial port driver. Check in your WIN Control Panel under:

System / Device Manager / Ports / Resources / Interrupts

Please also see our help site at:

www.nima.co.uk/help

Software Installation

Notation and computer literacy

A certain familiarity with computers and Windows is assumed. You must know the correct way to insert a CD into your personal computer (PC) and you must understand what a file is and what a directory is. You must also be able to 'Run' programs in Windows. It is also helpful if you know how to change icons.

If you are not happy with these ideas, we suggest that you consult the manuals of your computer and software vendor. There are probably also a wide range of help manuals available at your university bookshop.

PC requirements

You need to have a Pentium PC running Windows 95 or later.

Communications

Your PC has to have a serial port or USB port to communicate with the Nima interface. If you want to use a USB port, you will need a USB to serial port converter. Please make sure that you use the one compatible with your Windows version.

Display

Please set the Display to a minimum of 800 x 600 pixels. This can be changed under:

Start / Settings / Control Panel / Display / Display Modes

Fonts

The Nima software uses Microsoft Sans Serif fonts, as our software is compatible with all versions of Windows from 95 to XP you may need to load the specific MS Sans Serif font onto your PC. Copies are on the Nima CD.

Software organisation

There is one main program which controls all the functions of the instrument:

Nima516.exe where '5' is for the 5th generation and the 16 is the version number. This is the standard software for Langmuir troughs.

Then there is

Nima516.ini which contains essential data for the graphics screen and fonts

There are also files containing data which the main program needs before it will run. These initially hold standard data which you can alter as you go. These are:

install.dat	This contains all the installation data for your trough.
sensors.cal	This contains all the calibration data for your sensors.
standard.con	This contains a standard set of operating conditions.

And finally there is:

serpdrv

This is the serial port driver which allows communication between your PC and the interface unit (IU).

All these files must be located in the same directory. The default directory is C:\nima, but any other directory can be used.

Installation from CD

Insert the CD into your CD drive. Your computer may detect that a CD has been inserted and *autorun* the program. If it does not autorun then select 'Run' from Windows Start Menu. Enter 'D:\Launcher.exe' in the Open box where 'D' is the letter assigned to your CD drive. When the Launcher program loads click the top button to install the Nima software. The installation wizard will prompt you to choose a directory to install into - the default is 'c:\nima'. You can choose a different directory at this stage. Once you have chosen a directory click 'Finish' and the wizard will complete the installation.

Once the installation is complete your calibration files are copied from the CD into the directory you chose. This may leave a DOS window open, if it does you may safely close this window. The launcher software also allows you to view a copy of this manual on the CD, it also provides a link to our website. Once you have finished with the launcher program click the cross in the top right of the window to close it.

A shortcut to the Nima516.exe will be displayed in a Nima group file window. If you want to use the 'Nima' trough icon, use the right hand mouse button to click on the shortcut to change its properties and select the 'trough.ico' icon.

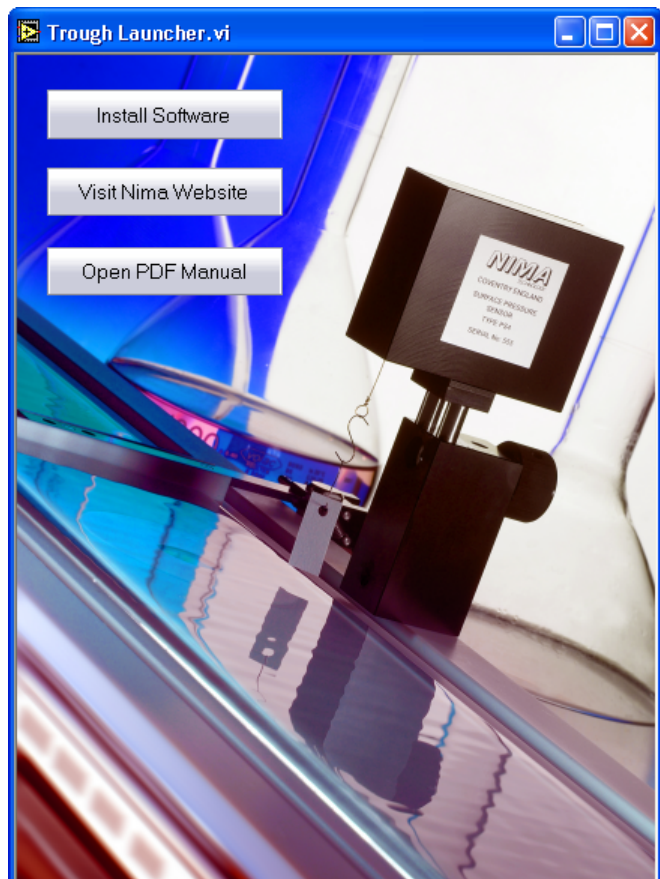


Figure 1.11: Launcher window

Installation from disk

Older models came with two floppy disks, if you have been supplied with these please follow the instructions below:

Insert disk 1 into drive a and select Run from Windows Start Panel. Enter a:\setup.exe in the Open box and the software will prompt you to load into c:\nima .You can choose a different directory at this stage. Then the Install Wizard will take over - just click on the 'finish' button to start (Microsoft Logic!).

If you have problems, such as 'unable to find disk 2', please copy the 3 files: 'setup.exe', 'data.001' and 'data.002' into the 'c:\windows\temp' directory and run 'setup.exe' from this directory, using the 'Run' command.

Installation from the website - www.nima.co.uk

Click on the 'Software' button in the margin on the left side of our home page. The instructions for downloading are given on the screen. Very briefly, these consist of:

1. Download - just click on 'download' and the 'zipped' file (2MB) is loaded onto your PC.
2. Unzip - using WinZip, unzip the file into its 3 constituents.
A link to www.winzip.com is given, if you don't have this program.
3. Setup - as above - 'Installing from disk'.

Running

Double click on Nima516.exe to run it (or on its shortcut if you have placed it on your desktop). 'OK' the introduction window and a set of pressure-area axes will be displayed with a menu bar along the top, as in the figure below. Note that an isotherm is displayed only if the interface is disabled.

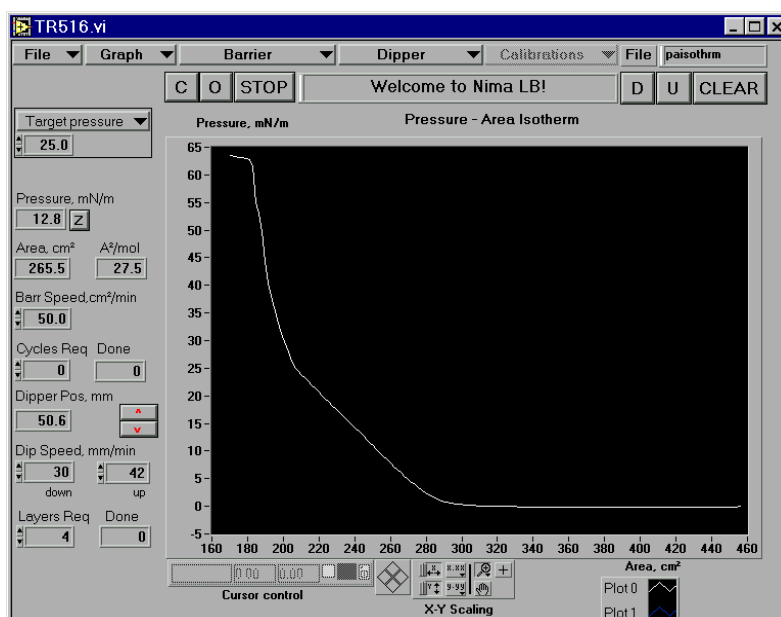


Figure 1.12: Main screen of Nima software

Setting up the Interface

Before anything else, please click on 'File' in the menu bar and 'Setup' to enter the 'Setup Menu'.

Select the port you think you are using (if in doubt, start with port 1) and enable the interface. If the V2 light on the interface illuminates, then communications have been established successfully. If nothing happens, change the port number to '2'. Usually, PCs use port 1 or 2 for the external serial port connections. If you still have trouble you can try port 3 or 4, but it is unlikely they are being used. If you are using an USB adaptor, the serial port number is often higher, say 5 or 6.

If you continue to have problems, please check that there is not a clash with other serial devices, such as mouse drivers and networks. You can look at your port settings in the WIN Control Panel under:

System/Device Manager/ Ports

Once communications have been established, click on the 'ACCEPT' button and the calibration file is updated automatically, so that the next time you launch the program, the correct serial port will be addressed immediately.

Setting up for 2 operating modes or multiple users

If you have a trough like the 632D1D2, then it is possible to run this in 2 modes - either with the conventional dipper D1L or with the alternate layer dipper D2.

The simplest way to switch between operating modes in the software is to install both versions of the software (which are supplied) into different directories. For example, you can make a directory called 'ConLB' for the conventional dipper and a directory called 'AltLB' for the alternate layer software.

If you then make shortcuts for the two different Nima516.exe files, you can run one or the other at the click of your mouse. Do not run both simultaneously, as the serial port drivers will clash - unless, of course, you have 2 serial interfaces running 2 troughs.

Software Updates

Updates are regularly made available on our website - free of charge.

The update will prompt you to install it into a different directory - 'c:\Program Files\Nima542' - but any directory will do, as long as it's not the old one!

Then copy the 3 calibration files 'install.dat', 'sensors.cal' & 'standard.con' from your existing 'Nima' directory to the new one. This will save having to re-calibrate all the motors and sensors.

Operation

There are 'one click' buttons for basic functions like 'opening' and 'closing' the barrier. These are:

O	Open barrier
C	Close barrier
D	Dipper down
U	Dipper up
STOP	Stop all motors
CLEAR	Clear data from memory
F	Dipper forwards (alternate layer troughs only)
B	Dipper backwards (alternate layer troughs only)

Other commands are embedded in the menus along the top of the screen:

File (f1) - this gives access to the **Save, Load** and **Setup Menu**. Also to **Exit** the program.

Graph (f2) - the data can be displayed as a **pressure-area isotherm, pressure & area v time, immersion depth-area** or **transfer ratios**.. Select the appropriate display from the Graph Menu. Axes are auto-scaled but may be manually re-scaled by right clicking anywhere on the graph and then typing over axes labels.

Barrier Menu (f3) Selects the barrier mode you require: Choose between **Monolayer Menu, Open, Close, Isotherm** or **Pressure (Pi) Control, Isotherm cycle, Coupled Mode** and **Area Control**.

Dipper Menu (f4) - Selects the dipper mode you require - Choose between **Dipper Menu, Up, Down (Forwards** or **Backwards** for alternate layer dipper), **Programmed Dip** and **Creep Up or Down**

Run time variables (f7 - separate box at top left of screen) - allows important values to be changed before or during a run. Choose between **Target Pressure, Feedback Gain, Immerse To, Raise To, Cycle Max Area** and **Cycle Min Area**.

The **STOP** button can also be accessed from the **'ESC'** key.

Typical operating sequences for taking a pressure-area isotherm and depositing an LB multi-layer are given overleaf.

A typical pressure-area isotherm

The following steps are recommended to take an isotherm:

1. Clean the trough thoroughly with a Kimwipe (soaked in chloroform). Ensure you are wearing the polythene gloves provided and working in a well ventilated area.
2. Make up a solution of 1mg/ml arachidic acid in chloroform.
3. Fill the trough with clean water.
4. Close the barrier(s) by clicking on 'C' - or the 'home' button of your keyboard.
- the barrier(s) will move to their 'close-to' position.
5. Aspirate the surface of the water enclosed by the barrier(s).
- keep your eye on the pressure reading - this will drop as the water level reduces and is cleared of surfactants.
6. Open the barrier(s) by clicking on 'O' - or the 'end' button of your keyboard.
-the barriers will move to their 'open-to' position.
7. Zero the pressure sensor by clicking on 'Z'
- the current surface tension (~72.8 mN/m) will be defined as zero surface pressure i.e. 0 mN/m.
8. Take an isotherm without molecules by clicking on 'Barrier' and 'Isotherm'
- the barriers will close and the isotherm will be displayed on the screen. If it the trough is clean, the curve will be horizontal along the X-axis. If there are surfactants on the surface, a small rise in pressure will be observed at smaller areas.
Please note that the axes are set to 'auto-scaling' and adapt themselves to the data recorded, so at first the data will appear greatly magnified.
9. Clean the surface again with the aspirator.
10. Zero the pressure sensor.
Whenever some water has been sucked out of the trough, it will have to be re-zeroed.
11. Open the barriers and spread the solution from the micro-litre syringe.
Wait for the pressure to return to 0mN/m - this indicates that the solvent has evaporated. If the pressure does not return to zero, you have spread too much and will have to remove some monolayer with the pump.
12. Take the pressure-area isotherm
- you should now see a good pressure area isotherm of arachidic acid on water. For an example of such an isotherm, please see the graph in Figure 1.6.
13. Stop the barrier by clicking on 'STOP' - or the 'Esc' key on your keyboard.
If you do not, the barrier will continue until it passes its 'close to' area and then a message saying 'barrier too closed' will appear. The barrier will then be stopped automatically.

A typical multi-layer deposition (conventional dipper)

1. Follow the instructions for the pressure-area isotherm first (previous page).
This will ensure that the trough is clean and ready to go.
2. Make up a solution of 10^{-4}M ZnSO_4 from the chemicals supplied with the trough.
Make enough to fill your trough about twice.
3. Prepare a glass slide by rubbing it with the ferric stearate supplied.
This will make it hydrophobic.
4. Move the dipper up by clicking on 'U' - or the 'PgUp' button of your keyboard.
The dipper will come to rest at its top position.
5. Insert the slide between the jaws of the dipper clamp.
6. Go the Dipper Menu ('Dipper' on menu bar).
7. Select the appropriate values for your deposition.

Typical values are:	Dipper Speed:	20 mm/min
	Target pressure:	25 mN/m
	Top End:	5 mm
	Bottom End:	20 mm
	Number of Layers:	10

8. Spread the monolayer and select 'Pressure Control' from the Barrier menu.
The film will be compressed to its target pressure. If pressure control is unstable, reduce the 'Feedback Gain' value (Variables menu - top left of screen). A value of 1.0 is good for almost all conditions.
9. Select 'Program Dip' from the Dipper menu
The dipper will be run down and up under the selected conditions.
10. When the required number of layers have been deposited, the dipper will stop.
11. Data can be viewed also in the (pressure & area) -time and dipper - area axes, selected from the Graph Menu.

Saving / Loading (File Menu - f1)

Saves and loads data as ASCII files with *.txt extension. These can be imported into most spreadsheets.

Copying, pasting & printing

Copy to pasteboard by hitting the 'ALT-Print Screen' keys on your PC. Paste into other applications (e.g. Word, PageMaker) - the graph will be pasted as it appears on the screen. Print out in the usual way.

Surfactant Check List

Making Langmuir-Blodgett films is easy on your Nima LB trough - provided that you know how to keep surface active agents (surfactants) at bay. The following list should help eliminate any contamination.

Water source - use a commercial de-ioniser such as those made by Vivendi (ELGA UHQII) or Millipore (Milli-Q). These units are capable of producing 18M-ohm.cm water with organic content of less than 20ppb. They have 4 stages of purification, reverse osmosis and organic removal. If you use distilled water, please be aware that conductivity won't be much better than 1M-ohm.cm. This will affect your work if you are working with, for example, fatty acids where the mineral ions in the distilled water will combine with any dissociated fatty acids.

Water storage - only store water in good quality borosilicate glass bottles with ground glass stoppers. Ideally, the water should not be stored for more than 30 minutes, as after this time significant quantities of mineral ions will leach out of the glass.

Never use plastic bottles or even 'teflon' bottles, as these can contain surfactants which will seriously contaminate your surface. Don't even use plastic stoppers on glass bottles. We recommend a 2 litre round-bottomed, long-necked pyrex glass bottle with glass stopper for your trough work.

Solvents - always buy small volumes of the best quality solvents. Free radicals can form in the solvent after 3 - 6 months (depending on temperature and light exposure), so store them in the fridge. If free radicals do form, they will cut your long chain molecules into smaller pieces and you will get some very strange isotherms.

Always dispense the solvent into an intermediate glass bottle, to prevent back-contamination of your source bottle. Keep all glassware exclusively for Langmuir film work and never use plastic bottles or stoppers. And never, ever parafilm!

Always use a balance to measure weights of solvents - and work out the volume from the solvent density. Make a note of the weight before storing your solution in the fridge and measure it again before the next time you use it - in this way you can work out the concentration despite any solvent evaporation.

Trough cleaning - always use the Kimwipe tissues (type 7105, or Kimtech type 75512 supplied with the trough - or type EX-L No 34256 in the USA) soaked in chloroform wearing polythene gloves (also supplied). Other tissues and gloves may contain surfactants which will make the trough dirtier than when you started.

Make sure you are working in a well ventilated room and ask your laboratory supervisor about safety regulations and toxic solvents. Keep a separate bottle of chloroform for cleaning, to prevent back-contamination of the source bottle.

Soak the Kimwipe with the chloroform and gently, but firmly, wipe down the trough's PTFE surface and barriers. Take extra care with the edges, as any aggregates will conglomerate there. The cleanliness of the trough can be checked visually by filling it with water and then using the aspirator pump to empty it again. Hold the pump nozzle at one corner of the trough and watch the water pull away from the PTFE. A good indication of cleanliness is if the water pulls away cleanly from the PTFE without leaving any droplets behind.

If a simple wipe with a Kimwipe does not clean it well enough, stand the trough in a fume

cupboard and fill it with chloroform. Allow it to stand for about 10mins and give all inside edges a good scrub with a 'cotton bud' (the little sticks used for cleaning out your ears). Then remove the chloroform, taking care to dispose of it safely, and rinse the trough several times with pure water. Note that the chloroform mustn't be allowed to evaporate away, otherwise the dissolved contaminant will be left in the trough.

If you are using materials that are insoluble in chloroform, use other suitable solvents to wipe the trough down. If there are no suitable solvents, then use a detergent (see below). Never use strong acids or alkalis and never experiment for the sake of it - it is very easy to contaminate a trough and very difficult to eliminate unknown contaminants.

Detergent Cleaning: If there is no suitable solvent available for your trough contamination, it will have to be washed with detergent. Commercially-available detergents include Decon-90, Helmanex and Tikopur. These need to be used sparingly and the trough has to be thoroughly rinsed (10 times with warm water) afterwards. Full details are available in the 'Langmuir-Blodgettry' section of this manual.

Remember to use the detergent sparingly and to rinse the trough thoroughly afterwards!

Conclusion

By now you should have assembled your Nima LB trough, carried out some simple checks to establish that it is operational and seen a glimpse of the cleanliness requirements.

The following chapters of this manual will give a thorough introduction to the theory and practice of Langmuir-Blodgett films.

**LANGMUIR
BLODGETTRY**

Introduction

This section deals with the theory and practice of Langmuir Blodgett. It covers the materials used - solvents, water, chemicals and substrate - and their preparation as well as cleanliness and safety. It also provides a comprehensive account of the practice of Langmuir Blodgett - its history, the subphase, spreading, isotherms and dipping.

Langmuir films

Langmuir films consist of surface active agents or 'surfactants' trapped at the interface between two dissimilar phases, either liquid-liquid or liquid-gas.

Surfactants are molecules which are amphiphilic, that is molecules which are composed of a hydrophilic part and a hydrophobic part. Hydrophilic groups consist of groups such as carboxylic acid, sulphates, amines and alcohols. These are all attracted to polar media such as water and the forces acting upon them are predominantly coulomb type ($1/r^2$). Hydrophobic (or oleophilic) groups such as a hydrocarbon chain, fats and lipids are much less (if at all) water soluble and the forces acting upon them are predominantly van der Waal's type ($1/r^{12}$ and $1/r^6$). Amphiphilic molecules are trapped at the interface because they possess these two very different types of bonding within the one molecular structure.

When surfactants, dissolved in a non-aqueous volatile solvent, are introduced onto a polar liquid surface, the solvent will evaporate leaving the surfactants oriented at the liquid-gas interface. The hydrophilic 'head' groups pull the molecule into the bulk of the water and the hydrophobic 'tail' groups point into the air. A surface monolayer will only be achieved if the amphiphatic balance of the molecule is correct; that is the balance between hydrophobic and hydrophilic parts. If the hydrophobic 'tail' group is too short (not hydrophobic enough) the molecule will be dragged into the water and will dissolve while if there is no hydrophilic part, the molecules may form thicker multilayer films on the surface or even evaporate.

Sweeping a barrier over the water surface causes the molecules to come closer together and eventually to form a compressed, ordered monolayer - much like forcing together balls on a billiard or pool table. The film produced by such a method is known as a Langmuir film.

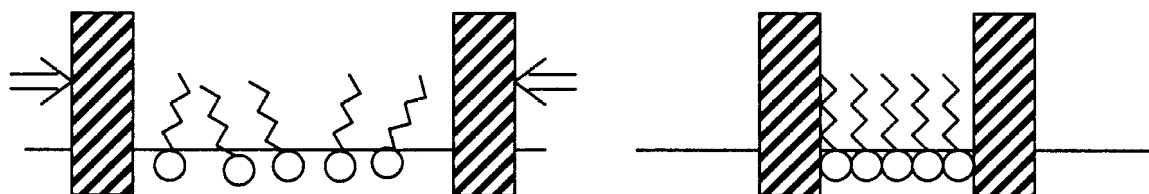


Figure 3.1: Expanded and compressed monolayers on a water surface

The Langmuir-Blodgett technique

Langmuir-Blodgett films consist of mono-molecular layers stacked sequentially onto a solid substrate. A solid substrate is lowered into the water, breaking through the Langmuir film and, provided that certain criteria have been met, the Langmuir film attaches itself to the substrate, coating it in a mono-molecular layer.

Once the first layer has been deposited, further layers will be deposited on each subsequent pass of the substrate through the air-water interface. Multilayers can therefore be deposited to produce a film, the thickness of which is the product of the individual molecular chain length and the number of times that the substrate has crossed the air-water interface.

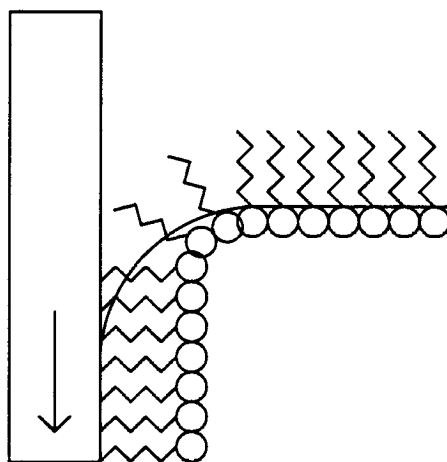


Figure 3.2: Deposition of the first monolayer onto a hydrophobic substrate.

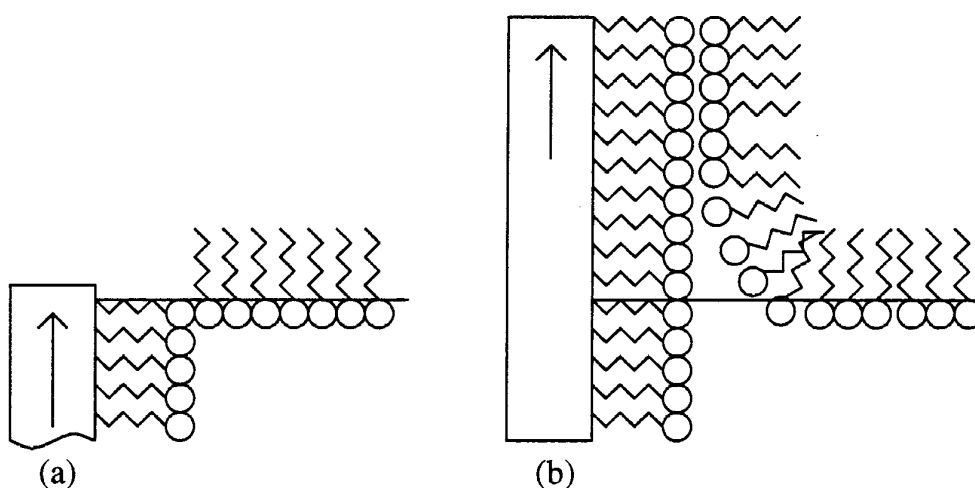


Figure 3.3: The substrate reverses (a) and the second layer is deposited (b).

History and development

The effects of oils on water surfaces have been known for many centuries. Babylonians in the eighteenth century BC have been recorded as practising divinity by observing the effects of oils spread on water. The Japanese printing art of sumi-nagashi (black-ink-let-flow) is one of the first technical applications of floating monolayers. A suspension of sub-micron carbon particles and proteins are spread on a water surface and subsequently covered with gelatin to create patterns which can then be transferred onto a sheet of paper lowered onto the surface. The traditional craft of 'marbling' also works on a similar principle - paint is dispersed on an aqueous surface and a piece of paper is drawn up out of the water to be covered by the pretty patterns created.

Scientific interest

The first scientific interest in mono-molecular layers was shown by Benjamin Franklin (during a visit to London to discuss certain colonial matters) when he spread oils onto the pond at Clapham Common and observed that the one teaspoon full of oil which he used had a calming influence over half an acre of water. Taking '1 teaspoonful' to be 5ml, this would mean that a film of thickness 2.5×10^{-7} m (about 100 layers) was covering the 'half an acre' (2,000m²). Franklin reported his findings to the Royal Society of London in 1774:

XLIV. Of the stilling of Waves by means of Oil. Extracted from sundry Letters between Benjamin Franklin, I.L. D. F. R. S. William Brownrigg, M. D. F. R. S. and the Reverend Mr. Farish.

Extract of a Letter to Doctor BROWNRIGG from
Doctor FRANKLIN.

London, Nov. 7, 1773.

DEAR SIR,

At length being at CLAPHAM where there is, on the common, a large pond, which I observed to be one day very rough with the wind, I fetched out a cruet of oil, and dropt a little of it on the water. I saw it spread itself with surprizing swiftness upon the surface; but the effect of smoothing the waves was not produced; for I had applied it first on the leeward side of the pond, where the waves were largest, and the wind drove my oil back upon the shore. I then went to the windward side, where they began to form; and there the oil, though not more than a tea spoonful, produced an instant calm over a space several yards square, which spread amazingly, and extended itself gradually till it reached the lee side, making all that quarter of the pond, perhaps half an acre, as smooth as a looking-glass.

Figure 3.4: Part of Benjamin Franklin's original paper

Modern investigations of molecular films began with Agnes Pockels experimenting with a very simple trough in her kitchen. Her ideas, expressed as letters to Lord Rayleigh, were published in 'Nature' in 1891. She realised the importance of cleanliness and developed many of the techniques which are regarded as standard today. Her experiments included the first containment of a monolayer by means of a barrier.

Further investigations carried out by Rayleigh, Devaux and Hardy confirmed the mono-molecular nature of such films. However it was Irving Langmuir who contributed the greatest advances, building on many of the ideas of Pockels and others to publish 'The Constitution and Fundamental Properties of Solids and Liquids' in 1917 which described the 'new' surface effects. Langmuir studied the pressure-area relationship of molecules on an aqueous surface. The areas occupied by molecules such as acids, alcohols and esters were found to be independent of the hydrocarbon chain length, thus showing that only the hydrophilic head groups were immersed in the subphase.

Katherine Blodgett, who worked with Langmuir on the properties of floating monolayers, developed the technique of transferring the films onto solid substrates and hence building up multilayer films. Her results were published in 1934 and 1935, culminating in a paper with Langmuir in 1937 and a paper on anti-reflection coatings in 1939 (see the 'Tutorial' chapter).

Langmuir-Blodgett films have been used in some practical devices. The first, developed by Blodgett, were the above mentioned anti-reflection coatings, and step thickness gauges.

The recent past and the future

Interest in Langmuir-Blodgett films subsided with the outbreak of the Second World War, and remained low until the 1960's when Kuhn and Möbius showed how monolayers could be used to construct precise supermolecular structures. They used the Langmuir-Blodgett technique to demonstrate the fluorescence and quenching of dye molecules attached to fully saturated fatty acids under ultraviolet light. This work and the publication of Gaines' 'Insoluble Monolayers at Liquid Gas Interfaces' in 1966 initiated a revival of interest in the field.

Many possible applications of Langmuir-Blodgett films in the fields of electronics, optics, molecular electronics and biotechnology are currently being investigated by research groups throughout world. Some examples are:

Biology: Cure for 'blue baby' syndrome. Some babies are born without the ability to breathe. This is because their lungs cannot absorb oxygen just after birth. Surfactants are being developed to be sprayed into the lungs to absorb oxygen. Once this process is stimulated, it is self regenerating. Surfactants are being designed by testing Langmuir monolayers for this oxygen absorbing ability.

Chemistry: Sensors - to have chemical sensors (such as gas detectors) it is best to have a large surface to bulk ratio. This gives higher signals for lower concentrations of gas and can improve reversibility of the detection process. LB layers are ideal candidates.

Physics: Optical waveguides and devices are being developed for computing and communications applications. The capability of fabricating dimensions to mono-molecular tolerances and their ability to incorporate different molecular architecture give LB films some unique advantages in this field.

The original troughs

Trough design has changed markedly since the early waxed troughs used by Langmuir, Schaefer and Blodgett. These were ordinary baking trays (purchased at the local hardware shop) that were waxed to make them hydrophobic. They were filled to the brim with water - this allowed for easy cleaning of the surface by simply sweeping a bar along the ridges formed by the trough walls. Films were confined by floating a length of waxed silk on the water surface thus dividing the surface into two compartments. One of the compartments was filled with piston oil of known surface pressure which compressed the monolayer, spread in the other compartment, to a pressure which would remain constant throughout the experiment. Contamination of the monolayer under study and the preparation of the waxed silk were the major problems. This prompted the development of new barrier systems which would eliminate such problems.

Gaines gives an example of a rectangular trough with a boom which moves along the top of the trough walls (the trough being filled to the very brim) by means of suspended weights attached to the barrier through a pulley system. There was no cross-contamination problem as no piston oil was involved but the gravity driven barrier did not allow easy measurement of the surface pressure-area characteristics. Although all these troughs required considerable experimental skills to operate successfully, Blodgett was able to build up thousands of layers at speeds of up to twenty layers per minute using such apparatus.

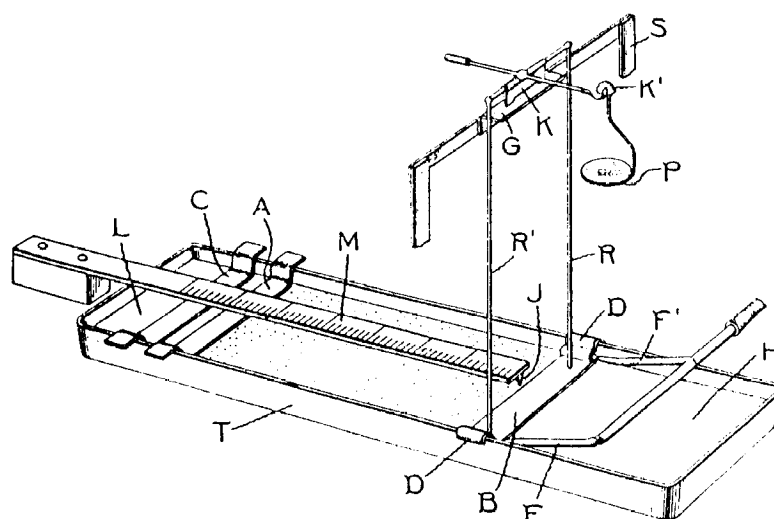


Figure 3.5: Langmuir's film balance

Reprinted with kind permission from the *Journal of the American Chemical Society*, 1917, Vol 39, pg 1869, Copyright 1917, The American Chemical Society.

Langmuir films - theory

Spreading

The monolayer is formed on the surface of the subphase by dissolving the amphiphilic substance in a suitable solvent - see also the section on 'Solvents' later in this chapter - and spreading the resulting solution dropwise on to the water surface.

The spreading solution is best applied to one point of the surface by allowing small drops to fall from the syringe while it is held a few millimetres above the sub-phase. Each drop should be allowed to evaporate before the next is applied. An alternative procedure that is used for molecules known to form more rigid films, involves distributing the drops equally over the entire surface of the sub-phase.

The process of spreading can occur in a number of ways. Usually a thin film is formed by the spreading solution while the Langmuir film forming material attains its favoured configuration at the air-water interface and the solvent evaporates, leaving behind only the monolayer. In some cases the deposited droplet does not spread over the subphase but instead a thin film of dilute solution of monolayer-forming material spreads from its edges; as solvent evaporates, more film spreads from the droplet. As most solvents used are slightly soluble in water, depletion of the spreading solvent will not be due exclusively to evaporation but also to some dissolution of it into the subphase.

Spontaneous spreading will continue until the surface pressure of the monolayer is equal to the 'equilibrium spreading pressure'. At this point, all the available surface is covered in monolayer and any further droplets of solution remain embedded in the monolayer as floating lenses, as no more spreading out can take place. Any undispersed material must be removed otherwise it may be deposited as bulk aggregates on substrates dipped into the monolayer.

Isotherms

Molecules in a solution are subject to attractive forces; in the bulk of the solution these forces are equal. However, at a surface or interface the forces are unequal and the net effect is to pull the peripheral molecules into the bulk of the solution. This effect gives rise to surface tension.

The surface tension can be defined as 'the work required to expand the surface isothermally by unit area'. The tendency of surface-active molecules to accumulate at interfaces favours expansion of the interface and hence lowers the surface tension. Such behaviour makes it possible to monitor the surface pressure as a function of the area occupied per molecule provided that the number of molecules deposited on the surface is known.

The characteristics of a monolayer on the water surface are studied by measuring the changes in surface tension upon compressing the monolayer. The reduction of surface tension is known as the surface pressure. Pressure readings are made by means of 'Wilhelmy' plates attached to a microbalance (see 'surface pressure measurement', later in this chapter). The plot of surface pressure versus area occupied per molecule is known as a 'pressure-area isotherm' - isotherm because compression takes place at constant temperature. The shape of the isotherm is characteristic of the molecules making up the film and hence provides a two-dimensional 'fingerprint'.

Forces at the subphase surface

The forces affecting the polar head groups submerged in the aqueous subphase are ionic and proportional to $1/r^2$ ('r' being the intermolecular separation) whilst the forces between the hydrocarbon chains are due to van der Waal's interactions and proportional to $1/r^6$ and $1/r^{12}$. Hence the interactions in the subphase are of longer range than those in the superphase. The isotherm can usually be seen to consist of three distinct regions:

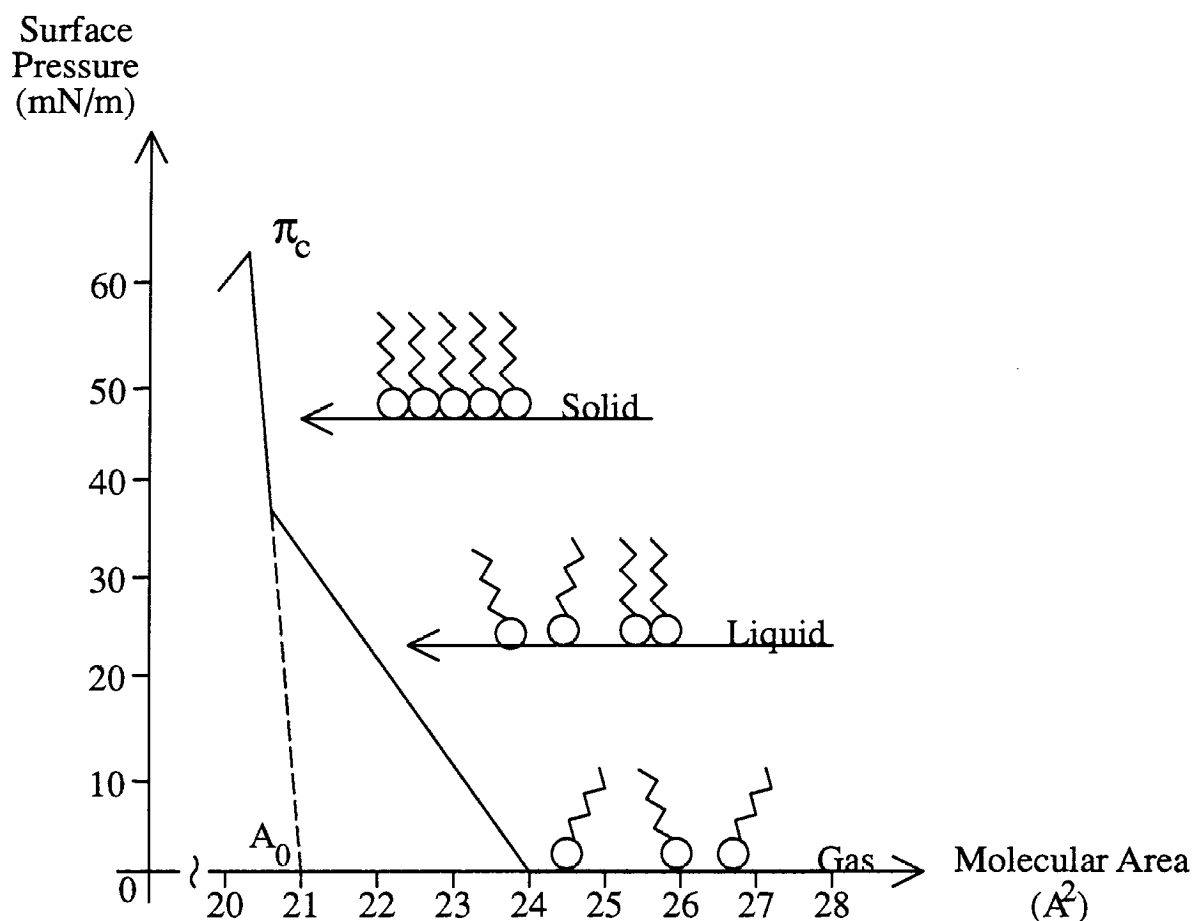


Figure 3.6: A stearic acid isotherm on pure water

After initial spreading onto the subphase, no external pressure is applied to the monolayer and the molecules behave as a two-dimensional gas, which can be described by:

$$\pi A = KT$$

where π is the surface pressure, A the molecular area, K the Boltzmann constant and T is the thermodynamic temperature. On compression of the monolayer, some ordering of the film takes place and it behaves as would be expected of a two-dimensional liquid.

With continued closing of the barrier, the increase in pressure causes additional ordering, the monolayer behaving as a quasi-solid. This solid state is characterized by a steep and usually linear relationship between surface pressure and molecular area.

Eventually the collapse pressure, π_c , is reached at which the film irretrievably loses its mono-molecular form. The forces exerted upon it become too strong for confinement in two dimensions and molecules are ejected out of the monolayer plane into either the subphase (more hydrophilic molecules) or the superphase (more hydrophobic molecules). However, collapse is not uniform across the monolayer but is usually initiated near the leading edge of the barrier or at discontinuities in the trough - such as corners or the Wilhelmy plate. Usually a 'collapsed' film will consist of large areas of uncollapsed monolayer interspersed with 'mountain ridges' where monolayers have been crushed together to form bulky aggregates. This is rather like mountain formation at the collision of the earth's tectonic plates, but on a vastly different scale.

The collapse pressure can be defined as the maximum to which a monolayer can be compressed without the detectable expulsion of molecules from the Langmuir film. It depends upon the details of the experimental procedure used, i.e. the chemical substances used, the temperature, the rate at which the film is compressed and procedures to which the film has been subjected. The value of the collapse pressure for a simple saturated fatty acid can be in excess of 50mN/m which is equivalent to about 200 atmospheres if extrapolated to three dimensions.

Quantitative information can be obtained on the molecular dimensions and shape of the molecule under study. When the monolayer is in the two-dimensional 'solid' or 'liquid condensed' phase the molecules are relatively well oriented and closely packed and the zero-pressure molecular area (A_0) can be obtained by extrapolating the slope of the 'solid' phase to zero pressure - the point at which this line crosses the x-axis is the hypothetical area occupied by one molecule in the condensed phase at zero pressure (see Figure 3.5). For a fully saturated alkanic acid such as stearic acid the molecular area determined in such a manner is 22-25 Å². Such an area corresponds to the cross-sectional area of a hydrocarbon chain, suggesting that the compressed monolayer consists of close packed vertically orientated chains. The Nima software calculates this zero-pressure molecular area (A_0) for you - as described in the 'Tutorial', later in this manual.

It is important to study the isotherm of the monolayer of the film forming material as a prerequisite to the determination of dipping characteristics. Information can be obtained as to the way in which the molecules pack at the interface and the stability of the compressed layer at high pressures. Improved quality can be obtained by 'annealing' the film, that is by compressing (never going above π_c) then expanding a number of times. Such a procedure encourages more efficient packing and usually a shift to lower molecular areas is observed. Recent work suggests that the Langmuir film exists in a number of different liquid crystal phases on the water surface, depending on the film temperature and pressure.

Measurement of surface tension

Surface pressure and surface tension

When a monolayer is compressed on the water surface, the instantaneous surface tension (ST_{inst}) of that surface is reduced - this reduction being known as the surface pressure (SP or π). ST and SP have the same units (mN/m) and magnitude, but the SP increases as the ST decreases:

Hence: $ST_{inst} + SP = \text{constant}$

- the constant being the absolute ST of the liquid - 72.8mN/m for water at STP (298K, 1 atmosphere)

	ST_{inst}	SP, π	ST_{abs} of water
clean water surface	72.8	0.0	72.8 mN/m
compressed monolayer	22.8	50.0	72.8 mN/m

Surface pressure (or surface tension) of the water surface is measured by immersing an object (typically a plate, ring or cylinder) across the air/water interface and measuring the force experienced by this object.

Consider a plate suspended across the air-water interface:

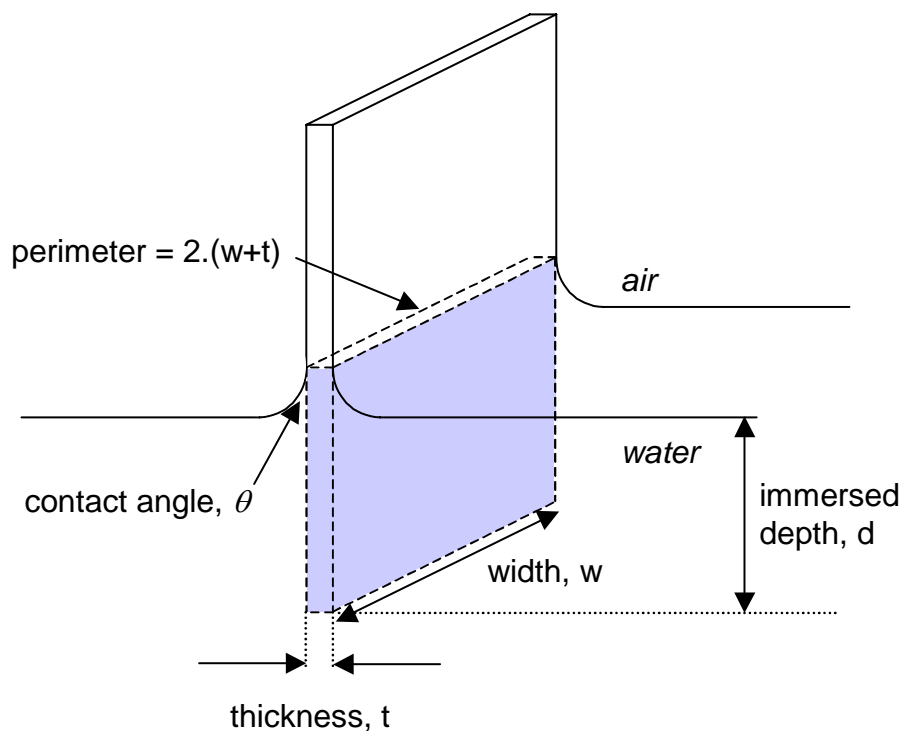


Figure 3.7: The Wilhelmy Plate

The forces upon the plate are gravity and surface tension acting downwards into the water, and buoyancy due to displaced water acting upwards.

If the plate has dimensions $l \times w \times t$ (length, width, thickness) and a density, ρ , and is immersed in water to a depth, d , then the net force downwards, F , is described by the equation:

$$\text{Force} = (\rho_p l w t).g - (\rho_L d w t).g + 2.(w+t).(ST).\cos\theta \quad \text{Eq.1}$$

(Force = weight - upthrust + surface tension)

where ρ_p is the density of the plate, ρ_L the density of the liquid, ST the surface tension of the liquid, θ the contact angle of liquid to plate and g the acceleration due to gravity.

Before making any measurements, the pressure reading is zeroed, thereby eliminating the weight term from Eq.1:

$$\text{Force} = - (\rho_L d w t).g + 2.(w+t).(ST).\cos\theta \quad \text{Eq.2}$$

(Force = - upthrust + surface tension)

The upthrust term is eliminated from Equation 2 as the plate is always kept at a constant level by the balance, no matter what the surface tension:

$$\text{Force} = 2.(w+t).(ST).\cos\theta \quad \text{Eq.3}$$

Finally, use of paper plates ensures a contact angle of liquid to plate of 0° and the expression reduces to:

$$\text{Force} = 2.(w+t).(ST) \quad \text{Eq.4}$$

Hence for a plate, the surface tension is:

$$ST_{\text{plate}} = \text{Force} / 2.(width + thickness) \quad \text{Eq.5}$$

where surface tension is in mN/m, force in mN and perimeter in metres.

Generally therefore, the surface tension is given by:

$$ST = \text{Force} / \text{perimeter} \quad \text{Eq.6}$$

Hence for a 10.25mm wide, 0.25mm thick paper plate, a 100mg weight will give a reading of 46.7mN/m. This is useful figure when you are checking your pressure sensor.

Calculation for a ring

For a ring the surface tension is given by:

$$ST_{\text{ring}} = \text{Force} / (\pi D + \pi(D-2d)) \quad \text{Eq.7}$$

where 'D' is the outer diameter of the ring and 'd' is the diameter of the wire in metres. Surface tension is in mN/m and force is in mN.

However, a correction factor is also required - this is explained in more detail in the Nima Tensiometer manual

Note that: $1 \text{ dyne/cm} = 1 \text{ mN/m}$.

Langmuir films - practice

Materials suited to the LB technique

The LB technique, by definition, requires amphiphilic molecules to be trapped at the interface of two phases (either liquid-liquid or liquid-gas). For the molecules to be trapped at the interface, the 'amphiphatic balance' i.e. the balance between the hydrophilic and hydrophobic constituents within the same molecule must be correct for the two phases concerned. For instance, the amphiphatic balance of a molecule may be correct for an air-water interface but not for a water-hexane interface. Hence, when choosing materials, this factor has to be taken into account.

In practice, monolayer and deposition criteria are not so exacting, as many researchers have produced excellent multilayer films using the LB technique with molecules that have only a very small hydrophilic component and that literally float on the water surface. Strictly speaking though, these are not LB films.

In general, materials such as long chain fatty acids and alcohols are used as film forming materials. The hydrocarbon part $-\text{CH}_2-$ of the molecule is responsible for the material's repulsion of water while the polar $-\text{COOH}$ or $-\text{OH}$ group has sufficient affinity for water to anchor the molecule in the aqueous subphase.

At an air water interface such amphiphilic molecules orient themselves with their hydrocarbon chains upwards in the air and their hydrophilic head groups downwards into the aqueous phase:

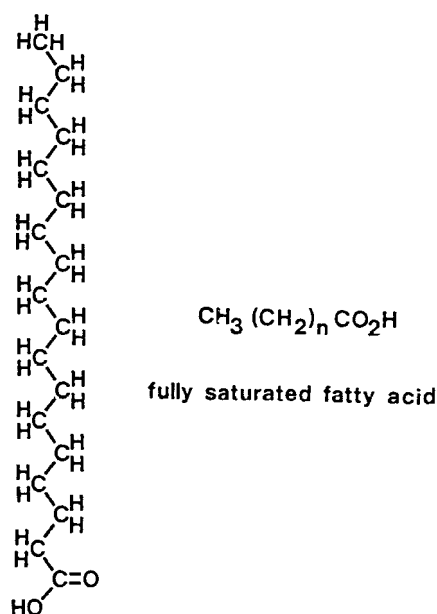


Figure 3.8: Fully saturated fatty acid (stearic acid). 'Fully saturated' signifies that all the available carbon bonds have been taken up by hydrogens

The materials which have been studied extensively as floating monolayers are the alkanolic acids and their salts and long chain alcohols. The length of the hydrocarbon chain is critical and its effect on the surface tension of the subphase is given by Traube's rule, an approximation which states that for a given homologous series of amphiphiles the concentration required for an equal lowering of surface tension in dilute solution decreases by a factor of about three for each additional CH_2 group.

The effectiveness of functional groups attached to the hydrocarbon chains in providing attraction to an aqueous subphase is summarised in the table below:

<i>No film</i>	<i>Unstable films</i>	<i>Stable film with C_{16} chain</i>	<i>C_{16} chain compounds dissolve</i>
Hydrocarbon	$-\text{C}_6\text{H}_4\text{OCH}_3$	$-\text{CH}_2\text{OH}$	$-\text{SO}_3^-$
$-\text{CH}_2\text{I}$	$-\text{COOCH}_3$	$-\text{COOH}$	$-\text{OSO}_3^-$
$-\text{CH}_2\text{Br}$		$-\text{CN}$	$-\text{C}_6\text{H}_4\text{SO}_4^-$
$-\text{CH}_2\text{Cl}$		$-\text{CONH}_2$	$-\text{NR}_3^+$
$-\text{NO}_3$		$-\text{CH}=\text{NOH}$	
		$-\text{C}_6\text{H}_4\text{OH}$	
		$-\text{NHCONH}_2$	
		$-\text{NHCOCH}_3$	

Table 3.1: Commonly used film forming materials

The types of materials listed above are those which have been extensively studied over the years and are regarded as the classic Langmuir-Blodgett film forming materials. However, current interest is primarily due to the introduction of 'active' molecules such as chromophores or biologically functional molecules into monolayer films. Although traditionally long hydrocarbon chains have been considered necessary, the incorporation of aromatic moieties and unsaturated chains into the amphiphile tends to decrease the hydrocarbon chain length necessary for deposition. For example, a substituted anthracene derivative has been successfully deposited with only a butyl chain attached to the polyaromatic system. In fact, with appropriate synthetic chemistry almost any active species can be tailored into a form which will float as a monolayer.

The subphase

The subphase most used for the study of mono-molecular films is ultra pure water. Other high surface-tension liquids which have been used as subphases include ethylene glycol, glycerol and mercury.

Usually measures are taken to exclude any contaminants from the subphase as the introduction of ions into pure water can dramatically affect the monolayer properties. For example, the repulsion between adjacent ionised acid groups can be reduced by the addition of divalent metal ions into the water. Introducing Cadmium (Cd^{2+}) into the water results in following reaction taking place:

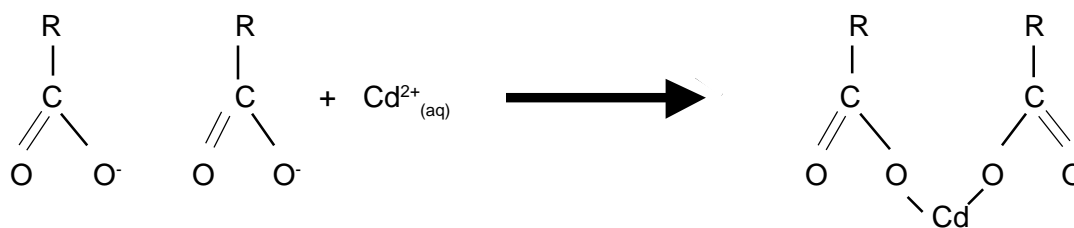


Table 3.2: Reaction of Cd^{2+} with an alkanolic acid group

Care must be taken in making up the solutions - high quality reagents and ultra-pure water must be used. Moreover, it should be remembered that the aqueous subphase consists of a number of variables, not necessarily independent of one another. A change in one ionic equilibrium will often affect several of the other equilibria within the subphase.

Changing the acidity and adding divalent ions to the subphase allows a considerable degree of control over monolayer behaviour and the successful deposition of multilayers.

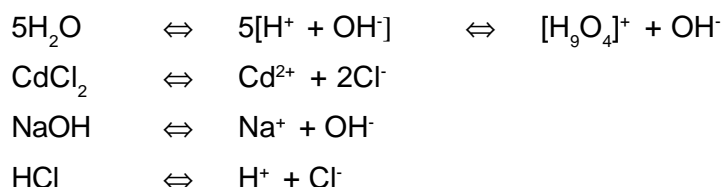


Table 3.3(a) Typical ionic equilibria in the aqueous subphase:
Primary dissociations i.e. equilibria of ionic species introduced into the subphase.

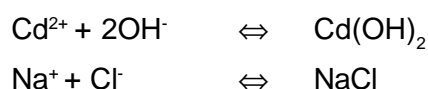


Table 3.3(b) Typical ionic equilibria in the aqueous subphase:
Secondary dissociations i.e. equilibria set up between ions introduced from differing sources. The addition of chloride ions to the subphase will reduce the pH as this results in hydroxide ions being taken out of the subphase.

Buffers should only be used in biological applications and not for making LB films, as they introduce new unknowns into the subphase.

LB film deposition onto a substrate

Two types of surfaces can be coated by the LB technique - hydrophobic (water repelling) and hydrophilic (water attracting). Deposition onto a hydrophobic surface always takes place on the down path while for a hydrophilic surface, deposition always takes place on the up path.

The surface of a substrate being coated with a LB film changes from hydrophobic to hydrophilic with every layer. Thus when a hydrophobic surface is immersed and coated with a monolayer, it will be completely hydrophilic **while it is immersed**. Then, when it is withdrawn from the subphase and a second layer is deposited, the surface will be hydrophobic again.

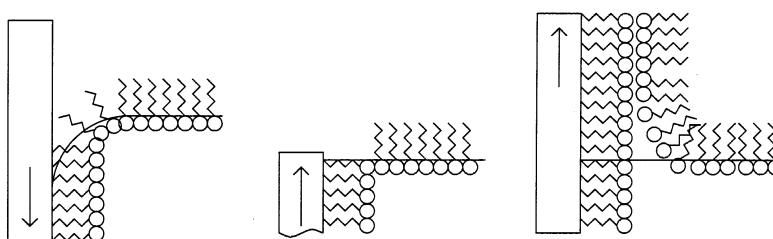


Figure 3.9: Deposition of the first 2 layers. The immersed surface of the substrate becomes hydrophilic after deposition of the first layer and becomes hydrophobic again after deposition of the 2nd layer. Note that the second layer does not start deposition until the meniscus is 'flipped' over.

Hence, for deposition to occur, the prime criterion is that the curvature of the meniscus at the liquid/substrate boundary and the direction of motion coincide.

It is easy to determine what type of surface you have - just immerse the substrate in the subphase. If the meniscus curves down, the surface is hydrophobic - if it curves up then the surface is hydrophilic.

A hydrophobic substrate will result in deposition on the first down pass, the hydrophobic hydrocarbon tails adhering to the hydrophobic substrate. With a hydrophilic substrate, no ordered deposition will occur until the first up-stroke because the hydrophobic tails are repelled by the hydrophilic substrate as it is immersed in the water.

Therefore an even (2,4,6...) number of layers is always deposited onto a hydrophobic surface and an odd (1,3,5...) number onto hydrophilic surfaces.

The surface quality and composition of the substrate controls the nature of subsequently deposited layers. The deposition of the first layer is also of importance as this predetermines the manner in which subsequent layers are laid down. For consistent film quality, the monolayer must be kept at a constant pressure, even when transfer is actually occurring.

Hydrophilic substrates

Deposition onto hydrophilic substrates proceeds in a similar manner, with the exception that the first layer is not deposited until the first 'up' path, Figure 3.10.

This is a result of the water meniscus onto a hydrophilic surface being curved upwards and, when the substrate is moved down into the subphase, the curvature of the meniscus and the direction of motion do not coincide. Hence, molecules cannot be deposited.

Thus the first monolayer on a hydrophilic substrate is deposited on the first 'up' pass through the monolayer, as the direction of the meniscus now favours the end of the molecule attracted to the surface.

It is strongly recommended that, when using hydrophilic substrates, the substrate be immersed in the subphase prior to spreading and compressing the monolayer. This will any prevent molecular film aggregates depositing onto the hydrophilic surface during the first down stroke - these have been observed to cause horizontal streaking - bands across the substrate perpendicular to the dipping direction.

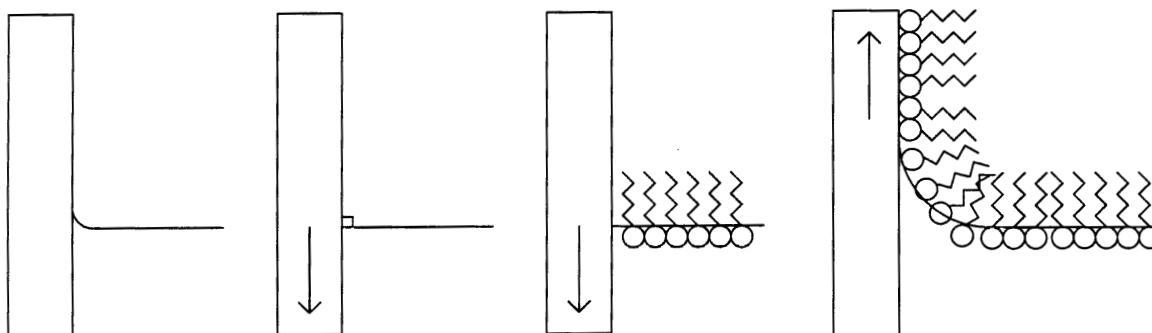


Figure 3.10: *Wetting of a hydrophilic substrate and deposition of the first monolayer onto a hydrophilic substrate*

Transfer ratios & meniscus radius

An good measure of how well a film has transferred to a substrate is the transfer ratio, given by:

$$\text{TR} = \frac{\text{area of monolayer removed from subphase at constant pressure}}{\text{area of substrate immersed in water}}$$

Such a ratio is usually measured for each substrate pass through the air-water interface. However, it must be remembered that the measured transfer ratio is an aggregate value over the entire immersed surface and often requires interpretation. It is possible, for instance, to measure a TR of 0% if 100% deposition takes place on one face of the substrate and 100% of film is peeled off the other face.

It is important to realise that for every layer after the first layer, deposition does not take place until the meniscus has 'flipped over', as shown in Figure 3.9 (previous page). This is a result of the fact that the monolayer has to turn itself 'on its head' to continue the deposition of the second layer. This gives rise to the 'head to head and tail to tail' structure of the amphiphilic

Langmuir-Blodgett film, Figure 3.11. If the meniscus radius is not taken into account, then inaccuracies will occur in the transfer ratio calculation. For instance, if the meniscus radius is 5mm and the length of the sample is 50mm, then a 10% error would occur if the area calculation were made from the point of substrate movement reversal, rather than from the point of the meniscus flipping over.

In the Nima software, the meniscus radius is taken into account in the transfer ratio calculation and can be set in the Dipper Menu.

Deposition Types

Amphiphiles deposit in this 'head to head and tail to tail' (HHTT) fashion - on both the up and down stroke of the substrate - resulting in 'Y-type' structures.

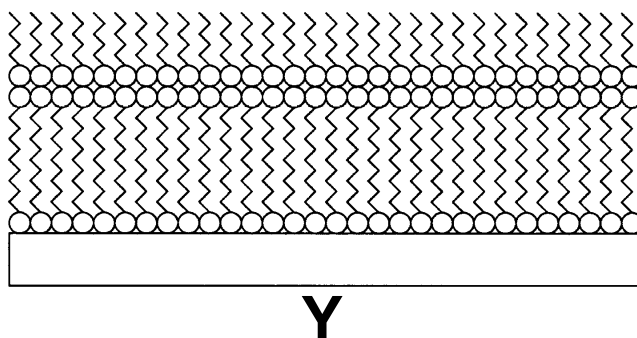


Figure 3.11: Y-type deposition onto a hydrophilic substrate

There are two other deposition modes which have been observed - 'X' and 'Z' type. At present there is no complete understanding of why some molecules dip in the X and Z manner, as this goes contrary to the whole LB principle (although such phenomena can be very desirable in the field of non-linear optics where such non-centrosymmetric structures are required). Films which apparently deposit as X or Z-type have often been found to be Y-type after X-ray analysis. Poor transfer ratios are not necessarily indicative of X or Z-type deposition but rather may simply imply patchy film adhesion, the film consisting of small areas of Y-type deposition interspersed with undefined regions where film may have been deposited and peeled off repeatedly. If 'X' or 'Z' type deposition is observed, great care must be used when interpreting results and all cleaning methods thoroughly reviewed.

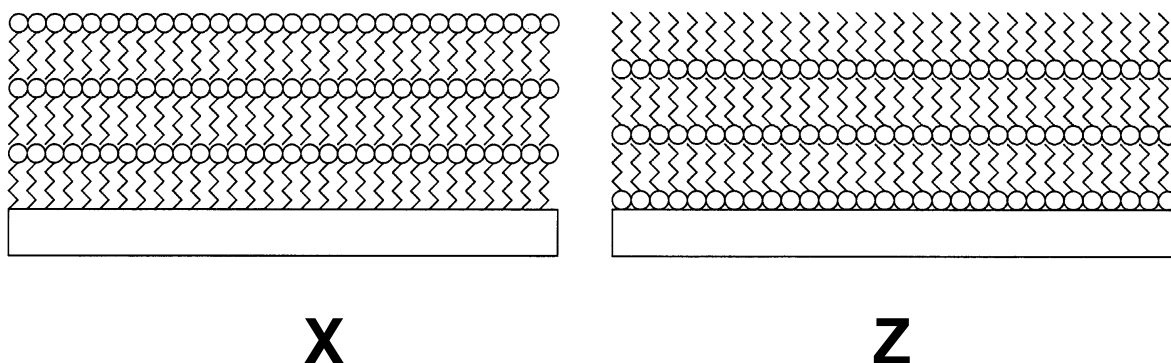


Figure 3.12: 'X' and 'Z' type deposition

Alternate layer deposition

The Nima alternate layer dipper allows the fabrication of multilayers containing 2 different film forming materials.

By depositing and compressing two different materials in compartments 'A' and 'B' and programming the dipper to pass down through monolayer A and up through monolayer B, a non-centro-symmetric multilayer structure with the sequence ABABAB... can be produced.

Such structures have been used to produce pyroelectric Langmuir-Blodgett films, using a long chain fatty acid as one material and a long chain amine as the other. Alternate monolayers have also been observed to exhibit second-order non-linear optical effects. Organic materials with large non-linear susceptibility coefficients which would normally stack in a centro-symmetric manner are incorporated into a non-centro-symmetric structure by the use of passive spacer monolayers such as fatty acids. To achieve the required structure, the spacer monolayers are alternated with the active monolayers.

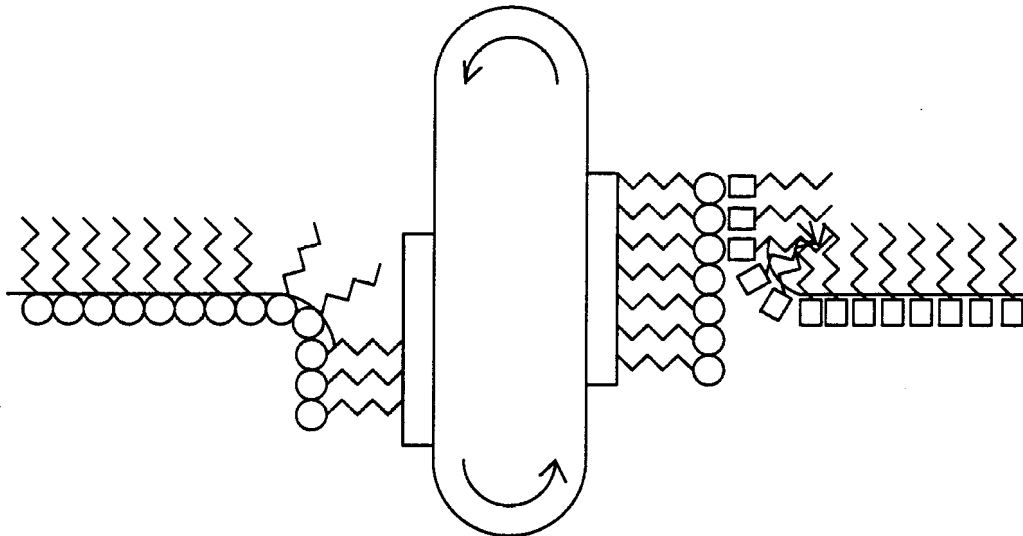


Figure 3.13: Alternate layer deposition

Laboratory Requirements

Safety

Before using any solvent, familiarise yourself with the relevant safety procedures. Solvents must never be inhaled or touch your bare skin. Work in a fume cupboard when making up the solutions. Similarly, when making up solutions of metal ions such as cadmium and potassium, always wash your hands afterwards, to prevent accidental ingestion.

Check with your laboratory supervisor on safety regulations and correct disposal after use. Remember you are responsible for your own and other's safety.

General

When studying mono-molecular layers which contain at most a few milligrams of material, even a small amount of contaminant can cause serious errors.

The trough, substrates and other apparatus must be kept as clean as possible. Extraneous greasy material concentrates at the air-water interface; the source of such contamination is usually grease from fingers or hair, this being transferred to the subphase by supposedly clean instruments which have been handled. Clean forceps or tweezers should always be used when handling substrates and for all operations it is advisable to wear disposable, powder-free polythene gloves. It is recommended that the syringes used for deposition are cleaned in between use and that they are rinsed at least once with the solution to be deposited. Clean laboratory coats should be worn, not only for protection but also to prevent the deposition of fibres from clothing onto the subphase.

When not in use the trough should be kept empty of water, covered and out of direct sunlight. If being moved, the pressure sensors and dipper mechanism should be removed from the trough to prevent accidental damage.

Lab environment

As with all aspects of Langmuir-Blodgett, cleanliness is of the utmost importance. Airborne particulates tend to accumulate at the water surface. To combat this, the water surface should be cleaned thoroughly using the water suction pump and the trough should be situated in as clean and dust-free environment as possible. When the trough is filled with water the clear covers should be in place over the water surface and dipper mechanism to protect the trough from the vagaries of the atmosphere.

Particular care must be taken with Langmuir-Blodgett films which are to be used for optical or electronic applications, as dust particles can become incorporated into the films and give rise to light scattering, pinhole defects and ambiguous results. Some troughs are housed in clean room facilities which maintain a positive pressure and filter the air intake through micropore filters. Surfaces are usually sealed and temperature and humidity are controlled. An isolated laminar flow cabinet can also be used as an alternative. However, such facilities are not essential if care is taken to operate the trough with regular cleaning in a relatively dust-free laboratory atmosphere. The room in which the trough is situated must be adequately ventilated to ensure that solvent fumes do not accumulate in dangerous quantities.

Excesses of temperature and humidity should be avoided, as should locating the trough in the close proximity to vibrating machinery as such vibrations can cause premature collapse of monolayer films. An anti-vibration table is useful if problems with obvious ripples from external disturbances can be discerned. However, small vibrations do not appear to cause serious problems and have been known to enhance film quality by annealing the surface monolayer.

Trough

The Nima troughs are fabricated from Polytetrafluoroethylene (PTFE), a material which will not contaminate the subphase. The polymer is essentially chemically inert, will not leach plasticiser and is the most hydrophobic polymer known. PTFE can be subjected to very rigorous cleaning procedures.

In general, the best way to keep the trough clean is to use it regularly and to avoid unnecessary collapse of mono-molecular films. The tissues used to wipe the trough must be surfactant-free, such as the 'Kimwipes' supplied (type 7105 or 'Kimtechs' type 75512, available from Kimberly-Clarke). Some other tissues, even if they are 'guaranteed 100% clean' may contain amphiphiles that prevent formation of pure monolayers, as 'cleanliness' has a different meaning in different environments. For example the Kimwipes would be disastrous in a semi-conductor fabrication area, as they produce clouds of dust particles, but they are ideal for LB films as they are surfactant free.

Before and after use, the trough should be thoroughly cleaned. Any leftover monolayer material should be removed from the subphase surface before the trough is emptied. To ensure that all parts of the trough are cleaned, the dipping head and barriers should be removed first. The barriers can be removed and wiped with a solvent laden tissue.

Organic solvents are the best available degreasing agents and will work over a wide range of solubilities. Hence, a thorough wipe with a chloroform laden Kimwipe cleans the PTFE well. Care must be taken to wipe off all excess chloroform, as pools of CHCl_3 will evaporate leaving surfactants behind. **Take great care not inhale any chloroform and always wear gloves. If your lab supervisor forbids the use of chloroform, use isopropyl alcohol instead.**

If you are using materials that are insoluble in chloroform, use other suitable solvents to wipe the trough down. If there are no suitable solvents, then use a detergent (see next page).

Never use strong acids or alkalis and never experiment for the sake of it - it is very easy to contaminate a trough and very difficult to eliminate unknown contaminants.

Detergent Cleaning

If there is no suitable solvent available for your trough contamination, it will have to be washed with detergent. Commercially-available detergents include Decon-90, Helmanex and Tikopur. These need to be used sparingly and the trough has to be thoroughly rinsed (10 times with warm water) afterwards.

Detergent cleaning is now recognized as the all-round best method for thorough trough cleaning. It should be performed about once a week. Use only a detergent suitable for the purpose. Do not use normal detergents. Nima recommends the use of the pure generic detergent potassium octanoate.

The contaminants which are troublesome in an LB trough are the surface-active ones. Most of them are only weakly surface active, not introduced on purpose, and present in only microgram quantities. Normal detergents will remove contaminants, but being highly surface active themselves, leave a trough useless for further work. The only detergents which you can use to clean your trough are ones which can be completely rinsed away afterwards.

The logic of detergent cleaning is that the micelles of the detergent present the contaminant with an enormous area of surface with a hydrophilic-hydrophobic gradient. By the law of mass action, any material with the slightest of tendencies to accumulate at the air-water interface will also incorporate itself into the micelles, which are then removed. The technique was first used over a decade ago in Switzerland and Germany and has proved itself, in spite of its mildness, to be extremely effective against both low-molecular-weight and polymeric contamination.

Commercially-available detergents capable of being rinsed completely from fluoropolymers include Decon-90, Helmanex and Tikopur. Look for the mention "completely rinsable" on the label. These detergents can be removed to deep sub-monolayer level with ten rinses of water at 40°C .

We recommend the generic detergent potassium octanoate as being generally superior, mainly because it can be removed to deep submonolayer level by four rinses of water at room temperature. It is obtained most easily by neutralizing the free acid with potassium hydroxide. Octanoic acid is liquid at room temperature and is obtainable from many chemical suppliers at approximately \$US 20 per liter. First dissolve the potassium hydroxide carefully in the minimum quantity of hot water, then add the stoichiometric quantity of acid and stir until thoroughly mixed. Finally, check the pH with a pH electrode or indicator paper, and if this is greater than 9 reduce it by adding a little more acid. The pH is not critical for cleaning the trough, but at a pH of 10 or greater the solution will attack the aluminium parts.

Remember to use the detergent sparingly and to rinse the trough thoroughly afterwards!

Chemicals

The materials which are deposited should be as pure as possible. Very small quantities of impurities, especially surface active contaminants, can radically alter the molecular area calculated from the isotherm and affect the material's film forming characteristics.

To avoid contamination, and so improve results, impurities should be restricted during synthesis. Care should not only be taken with the purification of materials but also with the solvents and starting materials used, which should be of the highest available purity.

Once prepared, materials should be carefully stored and handled to prevent hydrolysis, oxidation or contamination. Ideally, samples should be kept in a clean, dry, sealable, inert vessel, preferably made of glass as there can be contamination from plasticisers in plastic materials. Non-contaminating methods should be devised for the weighing out and transfer of materials. Care should be taken to ensure that spatulas are kept clean.

Water

The Nima troughs have different capacities between 40 and 1500ml. This small volume reduces the demand of deionised water and the risk of contamination, and also eases cleaning.

The water used in a Langmuir-Blodgett trough should be as pure as is possible. The quantity of particles, ions, and surface-active materials should be kept to such a low level that they will not significantly affect the surface properties of monolayer systems.

In the past, water was usually distilled a number of times, sometimes with an oxidative stage using an alkaline permanganate solution. Nowadays, reverse osmosis, ultra-filtration, and ion exchange resins are commonly used. A charcoal filter is usually located on the feed line to the still. For consistent results any of the commercially available deionisers are recommended. (Manufacturers include Barnsted, Elga, Millipore & others.)

The water should be freshly made and discarded every time the molecule type is changed. Storage should be in clean vessels which are inert; some plastic containers leach dialkyl phtalate esters which are used as plasticisers in their manufacture.

The prime criterion for establishing the cleanliness of the subphase is a high value of surface tension. The surface tension of pure, clean water at 293K is 72.8mN/m. A minimal change should be observed on aging and insignificant changes should be seen on compression of the surface. It should be noted that the value will decrease with an increase in temperature. The surface tension of the water in the trough can easily be measured by lifting the Wilhelmy plate out of the water after having zeroed the pressure sensor. To protect the water surface from air borne particulates the transparent lid should be kept on the trough whenever possible when the trough is full of water.

Solvents

Some Langmuir-film forming materials, such as vegetable oils, spread spontaneously on a water surface. However most materials must be deposited onto the subphase in a solution of a volatile solvent. The solvent which is chosen is critical and will affect the film forming properties of the solute. A number of factors must be considered:

Firstly a solvent must be chosen which has sufficient solvent power to dissolve a substantial quantity of the material under investigation. A solution with much less than 0.1 mg/ml will require too large a volume to be deposited to form a reasonable area of compressed monolayer.

The solvent must also be chemically inert with respect to the material under study and should also be relatively pure. Small amounts of contaminants such as grease can be removed by distilling the solvent in grease-free glass systems. The cleanliness of the solvent can be verified by spreading the solvent neat on the subphase, allowing it to evaporate and then running an isotherm of the remaining surface material. Any increase in surface pressure observed will be due to surface active contaminants in the solvent which need to be removed. This technique is known as 'blank spreading' and, as many commercially available solvents contain film forming contaminants, is highly recommended.

The volatility of the solvent must also be considered - it must be such that the evaporation time is short but not so short that the concentration of the solution cannot be determined due to evaporation. The boiling point of the solvent should lie in the range 40-80°C. Important factors to consider are the hazards associated with organic solvents - when allowing the solvent to evaporate the solvent vapours should not be inhaled.

Organic solvents which are very soluble in water should be avoided as they will tend to carry amphiphilic material into the subphase and precipitate it out. If a water-miscible solvent is used, a high concentration of the material to be studied must be used to counteract the effect of the material being pulled into the subphase. Care must be taken when interpreting molecular areas obtained with such solvents as they will usually be incorrect. If a material is not soluble in non-polar, volatile spreading solvents, an acetone-hydrocarbon (e.g. hexane) mixture can be used to increase the amount of solute which will dissolve without introducing serious solubility problems.

The table below shows the properties of a few solvents which have been used for depositing Langmuir film forming materials. Solubilities in water are at 25°C, in g/Kg.

<i>Solvent</i>	<i>Melting point (°C)</i>	<i>Boiling point (°C)</i>	<i>solubility in water</i>
n hexane	-94	69	0.01
Cyclohexane	6.5	81	0.07
Choloform	-64	61	8
Diethyl ether	-116	35	75
Acetone	-93.4	56	∞
Dichloromethane	-98	40	1.3

Table 3.3: Properties of solvents

Substrate

The quality of the first layer deposited onto the substrate determines the deposition behaviour of subsequent layers - defects in the first layer can be passed through to and observed in layers subsequently deposited. Because the substrate determines the nature of the first layer deposited, it must be thoroughly cleaned.

At all stages of the cleaning procedure care should be taken not to touch the slides with fingers as the skin grease contains a mixture of surface active biological lipids.

Substrates can be divided into two groups according to their surface - they can be either hydrophilic or hydrophobic. A standard glass microscope slide or a polished silicon wafer make excellent substrates for deposition of LB films. Both are normally hydrophilic, the silicon always has an oxide layer after exposure to air.

Many substrate cleaning procedures are commonly employed. One which has been found to work well is to wash the slides with detergent, then rinse in an ultrasonic bath in deionised water and then with isopropanol. Instead of using an ultrasonic bath, Soxhlet cleaning can be used. Argon plasma cleaning (100W incident power at 13.6MHz and 0.1 Torr for 2 minutes) just prior to deposition also gives an excellent surface.

Strong oxidising agents such as acidic peroxide or chromic acid are **not** recommended - as they are a health hazard and require the substrate to be thoroughly rinsed post immersion because they can introduce as many contaminants as they remove.

A hydrophilic glass surface can be prepared by soaking the clean slides overnight in a 2g/dm³ solution of sodium hydroxide. They are then rinsed with ultra-pure water and dried in a stream of dry nitrogen.

A hydrophobic surface is obtained by standing the clean glass slide overnight in a fume cupboard, in a beaker containing a few drops of hexamethyl disilazane and covered with a watchglass. On evaporation, the hexamethyl disilazane condenses onto the clean slide, rendering it hydrophobic. Evaporation of gold will also make a slide hydrophobic. Katherine Blodgett also used the technique of rubbing in molten ferric stearate (see the 'Tutorial' section) which works well and is not as hazardous to health as the other techniques.

Glass is not the only material which can be used as a substrate. Many other surfaces such as fused silica and silicon wafers can also be used. When infra-red studies of Langmuir-Blodgett multilayers are to be undertaken, calcium fluoride plates which are effectively insoluble in water and transparent to infra-red radiation can be used. All these materials can be prepared in the same manner as glass.

After preparation the slides should be stored in a clean dust-free sealable box.

Bibliography - edited & updated by Jens-Peter Krause

This section contains a review of a number of books, journals, original papers and conference proceedings as a guide to locating detailed information on the history, practicalities and current research in the field of Langmuir-Blodgetty.

The list of references from books and journals to be found in this section has been revised and expanded to some more general topics of surface science which might be important for those working in the field of Langmuir-Blodgetty. A section with original papers on polymer and protein monolayer is now available. However, the list is by no means comprehensive as the amount of available literature in the field of Langmuir-Blodgetty is constantly and rapidly growing. It is included merely as a starting point for those beginning to work with Langmuir and Langmuir-Blodgett films.

Books and review papers

General aspects on surface and colloid sciences

1. Adamson, A.W., Physical chemistry of surfaces, 5th ed., Wiley-VCH, New York, 1990.
2. Desjonqueres M.-C., Spanjaard D., Concepts in surface physics, 2nd ed., Springer Verlag, Berlin, 1996.
3. Evans D.F., Wennerström H., The colloidal domain: where physics, chemistry, biology and technology meet, 2nd ed., Wiley-VCH, New York, 1999.
4. Lyklema, J. Fundamentals of interface and colloid science, Academic Press, London, Vol. I. Fundamentals: 1991, Vol. II. Solid-liquid interfaces:1995, Vol. III. Liquid-fluid interfaces: 2000
5. Fler G.J., Cohen Stuart M.A., Scheutjens J.M.H.M., Cosgrove T., Vincent B., Polymers at interfaces, Chapman&Hall, London, 1993.
6. Jones R. A., Richards R.W., Polymers at surfaces and interfaces, Cambridge University Press, Cambridge, 1999.
7. Brezesinski G., Mögel H.-J., Grenzflächen und Kolloide: physikalisch-chemische Grundlagen, Spektrum Akad. Verlag, Heidelberg, 1993.
8. Theoretical approaches to surface structure, surface forces and monolayer rheology. Israelachvili J. N., Intermolecular and surface forces, 2nd ed., Academic Press, London, 1992.
9. Lawley K. P., Molecular surface interactions, Wiley-VCH, New York, 1989.
10. Dynarowicz P., Recent developments in the modelling of the monolayers structure at the water/air interface, Adv. Colloid Interface Sci., 45, 215, 1993.
11. Dynarowicz-Latka P., Dhanabalan A., Jr. Oliveira O.N., Modern physicochemical research on Langmuir monolayers, Adv. Colloid Interface Sci. 91, 221, 2001.
12. Davis, H. T. Statistical mechanics of phases, interfaces and thin films, Wiley-VCH, New York, 1996.
13. Ghezzi F., Earnshaw J.C., Finnis M., McCluney M., Pattern formation in colloidal monolayers at the air-water interface, J. Colloid Interface Sci. 238, 433, 2001.

Physical methods for characterising surfaces

1. O'Connor D. J., Sexton B. A., Smart R. St. C. (Eds.), Surface analysis methods in materials science, Springer Verlag, Berlin, 1992.
2. Czanderna A. W. (Ed.), Methods of surface analysis, (Methods and Phenomena: their Applications in Science and Technology ; 1), Elsevier, Amsterdam, 1989.
3. Walls J. M. (Ed.), Methods of surface analysis: techniques and applications, Cambridge Univ. Press, Cambridge, 1989.
4. Woodruff D. P. ,Delchar T. A., Modern techniques of surface science, 2nd ed., Cambridge Univ. Press, Cambridge, 1994.

Theory and practical considerations concerning the formation of LB films

1. Pethica B.A., Experimental criteria for monolayer studies in relation to the formation of Langmuir-Blodgett multilayers, *Thin Solid Films* 152, 3, 1987.
2. Mingins J. and Owens N.F., Experimental considerations in insoluble spread monolayers, *Thin Solid Films* 152, 9., 1987.
3. Peterson I.R., Veale G. and Montgomery C.M., Preparation of oleophilic surfaces for LB deposition, *J. Colloid Interface Sci.* 109, 527, 1986.
4. Roberts G.G., Molecular electronics using Langmuir-Blodgett films; *Adv. Chemistry Series* 218, 225, 1988
5. Peterson I.R., Langmuir-Blodgett films, *Journal of Physics. D. Applied Physics*, 23, 379, 1990.
6. Swalen J.D., Molecular Films, *Annual Reviews in Materials Science* 21, 373, 1991.
7. Kurihara K., Langmuir-Blodgett films in advanced molecular engineering, *Colloids Surfaces A*: 123-124, 425, 1997.
8. Ulman A., An introduction to ultrathin organic films from Langmuir-Blodgett to self-assembly, Academic Press, San Diego, 1991
9. Vandevyver M., Barraud A., Methods of characterization for Langmuir-Blodgett films, *J. Mol. Electronics* 4, 207, 1988.
10. Welzel P.B., Weis I., Schwarz G., Sources of error in Langmuir trough measurements Wilhelmy plate effects and surface curvature, *Colloids Surfaces A*: 144, 229, 1998.
11. Mingotaud A.-F., Mingotaud Ch., Patterson L.K., Handbook of monolayers, Academic Press, San Diego, 1993.

Thin films in science and industry

1. Dowson D., Priest M., Taylor C. M., Ehret P., Childs T. H. C., Dalmaz G., Berthier Y., Flamand L., Georges J.-M. and Lubrecht A.A. (Eds.), *Lubrication at the frontier: the role of the interface and surface layers in the thin film and boundary regime*, Elsevier, Amsterdam, 1999.
2. Kahovec J.(Ed.), *Surface and interfacial phenomena in macromolecular systems* Wiley-VCH, Weinheim, 1999.
3. Venables J. A., *Introduction to surface and thin film processes*, Cambridge University Press, Cambridge, 2000.
4. Volkov, A.G. (Ed.), *Liquid interfaces in chemical, biological, and pharmaceutical applications*, Marcel Dekker, New York, 2001.

Biological Systems

1. Baszkin A., Norde W. (Eds.), *Physical chemistry of biological interfaces*, Marcel Dekker, New York, 2000.
2. Magdassi S. (Ed.), *Surface activity of proteins: chemical and physicochemical modifications*, Marcel Dekker, New York, 1996..
3. MacRitchie F., *Chemistry at interfaces*, Academic Press, San Diego, 1990.
4. Lvov Y. and Möhwald G. (Eds.), *Protein Architecture: Interfacing Molecular Assemblies and Immobilization Biotechnology*, Marcel Dekker, New York, 2000.
5. Malmsten, M. (Ed.), *Biopolymers at interfaces*, Marcel Dekker, New York 1998.
6. Bos M.A., van Vliet T., *Interfacial rheological properties of adsorbed protein layers and surfactants: a review*, *Adv. Colloid Interface Sci.* 91, 437, 2001.

Original papers

Polymer monolayers and LB-films

1. Allain M., Benattar J.J., Rieutord F., Robin P., *Surface study of langmuir-blodgett films by electron microscopy and X-ray reflectivity*, *Europhys. Lett.* 3, 309, 1987.
2. Cárdenas-Valera A.E., Bailey A.I., *The interfacial rheological behaviour of monolayers of PEO/PMMA graft copolymers spread at the air/water and oil/water interfaces*, *Colloids Surfaces A*: 79, 115, 1993.
3. Fleer G.J., Scheutjens J.M.H.M., *Interaction between adsorbed layers of macromolecules*, *J. Colloid Interface Sci.*, 111, 504, 1986.
4. Maruyama T., Fuller G., Frank C., Robertson C., *Flow-induced molecular orientation of a Langmuir film*, *Science* 274, 233, 1996.
5. Oliveira O.N., Bonardi C., *The surface potential of langmuir monolayers revisited*, *Langmuir* 13, 5920, 1997.

Protein monolayers and LB-films

1. Picard G., *Dynamic thin laminar flow method for making protein monolayers*, *Langmuir* 13, 264, 1997.
2. Balla A., Razafindralambo H., Blecker Ch., Paqout M., *Interfacial properties of gluten monolayers spread on various chloride salt solutions: Effects of electrolytes, salt concentrations, and temperature*, *J. Agric. Food Chem.* 46, 3535, 1998.

3. Douillard R., Aguié-Beghin V., Surface pressure of protein adsorption layers: application to molecular mass and molecular area measurements, *Colloids Surfaces A*: 149, 285, 1999.
4. Dubreuil N., Alexandre S., Lair D., Sommer F., Duc T.-M., Valleton J.-M., Scanning force microscopy of mixed fatty acid/protein Langmuir-Blodgett films transferred on muscovite, a model of their organization, *Colloids Surfaces B*: 11, 95, 1998.
5. Innocente N., Blecker C., Deroanne C., Paquot M., Langmuir film balance study of the surface properties of a soluble fraction of milk fat-globule membrane, *J. Agric. Food Chem.* 45, 1559, 1997.
6. Löscher F., Ruckstuhl T., Jaworek T., Wegner G., Seeger S., Immobilization of biomolecules on Langmuir-Blodgett films of regenerative cellulose derivatives, *Langmuir* 14, 2786, 1998.
7. Murray B.S., Dynamics of proteins at air-water and oil-water interfaces using novel Langmuir trough methods, *Progr. Colloid Polym. Sci.* 103, 41, 1997.
8. Krause J.-P., Schwenke K.D., Behaviour of a protein isolate from rapeseed (*Brassica Napus*) and its main protein components - globulin and albumin - at air/solution and solid interfaces, and in emulsions, *Colloids Surfaces B*: 21, 29, 2001.

Special LB editions & conference proceedings

- Barlow W.A. (Ed.), 1980, Vol 68.
- LB1: Roberts G.G. (Ed.), First international conference on LB, Durham, England; *Thin Solid Films*, 1983, Vol 99.
- LB2: Gaines G.L. Jr. (Ed.), Second international conference on LB, Schenectady, USA; 1985, *Thin Solid Films*, Vols 132, 133 and 134.
- Stroeve, P. and Franses (Eds.), Molecular engineering workshop, Davis, USA; 1987, *Thin Solid Films*, Vol 152.
- LB3: Möbius D., Barraud A. and Roberts G.G. (Eds.), Third international conference on LB, Göttingen, Germany; 1988, *Thin Solid Films*, Vols 159 and 160.
- LB4: Fukuda K. and Sugi M. (Ed.), 4th international conference on LB, Tsukuba, Japan; 1989, *Thin Solid Films*, Vol 180.
- LB5: Barraud A. (Ed), Fifth international conference on LB, Paris, France; 1991, *Thin Solid Films*, Vols 210 and 211
- LB6 *Thin Solid Films* vols 243 (1994) (1993: TroisRivieres)
- LB7 *Thin Solid Films* vols 284/285 (1996) (1995: Ancona)
- ECOF6 *J. Supramolecular Science* vol 4 (1997) (1996 Sheffield)
- LB8 *Thin Solid Films* vols 327-329 (1998) (1997: Asilomar)
- ECOF7 *Materials Science and Engineering C* vols C8-C9 (1999 Potsdam)
- LB9 *Colloids and Surfaces A* * (in press 2001) (2000: Potsdam)
- ECOF 8 Lecce (2002)
- LB10 Beijing 2003 (in press)
- ECOF9 Valladolid (2004)

Journals

Thin Solid Films - this journal publishes original research on thin-film synthesis, characterization, and applications. Contents and abstracts are available online: <http://www.elsevier.nl/inca/publications/store/5/0/4/1/0/6/>

Journal of Colloid and Interface Science - this journal publishes original research on fundamental principles of colloid and interface science and application of these principles. Contents and abstracts are available online: <http://www.academic.press.com/jcis>

Langmuir - this journal publishes original research on surface and colloid chemistry. Coverage includes such topics as micelles, vesicles, emulsions, gels, surfacants, colloids, crystal growth, nucleation, liquid crystals, imaging spectroscopy, electro-chemistry, biological colloids & interfaces, biopolymers, nanostructures, multicomponent systems, and materials. Contents and abstracts are available online: <http://pubs.acs.org/journals/langd5>

Colloids and Surfaces A: Physicochemical and Engineering Aspects - this journal publishes original research and review articles on the science of the fundamentals, engineering fundamentals, and applications of colloidal and interfacial phenomena and processes. Contents and abstracts are available online: <http://www.elsevier.nl/locate/colsurfa>.

Colloids Surfaces B: Biointerfaces - this journal publishes original research and review articles on fundamental and applied research on colloid and interfacial phenomena in relation to systems of biological origin. Contents and abstracts are available online: <http://www.elsevier.nl/locate/colsurfb>.

Other journals

In addition to the above journals, the Journal of the Agricultural and Food Chemistry, Advances in Colloid and Interface Science, the Journal of Molecular Electronics (up to Dec 1991 Vol 7, No 3.), Advanced Materials for Optics and Electronics (from Jan 1992) provide good background reading.

The Journal de Chimie Physique published a special issue relating to Langmuir-Blodgett films in 1988. This issue includes Langmuir-Blodgett film work in the fields of biology, non-linear optics and molecular electronics amongst others.

Barraud A. (Director), 'The NATO Advanced Workshop on Langmuir-Blodgett films and related structures', Journal de Chimie Physique 85, 1988.

Historical

Benjamin Franklin's initial communication to the Royal Society of London in 1774 contains details of his original monolayer experiments on the pond at Clapham and also describes the interesting effects of monolayer films on supposedly dead flies!

Franklin B., Of the stilling of waves by means of oil, *Philosophical Transactions of the Royal Society* 64, 445, 1774.

Wilhelmy first described the measurement of surface tension in:
L.Wilhelmy, *Angew. Physik* 119, 177, 1863.

Agnes Pockels' original letter to Lord Rayleigh was published in:
A.Pockels, Letter to the Editor, *Nature* 43, 437, 1891.

Langmuir's landmark paper was published in 1917:
'The Constitution and Fundamental Properties of Solids and Liquids'
Irving Langmuir, *J.Am.Chem.Soc* 39, 1848, (1917).

A paper by Katherine Blodgett describes one of the first suggested practical and commercial applications of Langmuir-Blodgett films, as anti-reflection coatings on glass (part of the work from which is repeated in the 'Tutorial' section):
Blodgett K.B., Use of interference to extinguish reflection of light from glass; *Physical Review* 55, 391, 1939.

A brief history of Langmuir-Blodgett films, containing many of the references to the original work on Langmuir and Langmuir-Blodgett films can be found in the preface to Volume 99 of *Thin Solid Films*:
Gaines G.L. Jr., 'On the history of Langmuir-Blodgett films'; *Thin Solid Films* 99, pg ix, 198.

Interest was rekindled in Langmuir films by the elegant work of Kuhn & Möbius:
Kuhn,H. and Möbius,D., Systems of mono-molecular layers - assembling and physico-chemical behaviour, *Angewandte Chemie (Int'l Ed)* 10, 629, 1971.

Throughout this manual, data is quoted from:

Tennent R.M (Ed.), *Science Data Book*, Oliver & Boyd, 1971.

TUTORIAL

Introduction

This tutorial is designed to teach you the basic commands of the Nima trough and the essentials of Langmuir-Blodgettry by leading you through a series of examples. It is a good idea to read the 'Langmuir-Blodgettry' chapter first. You will repeat work done originally by Katharine Blodgett in 1938* and prepare a multilayer film of Cadmium arachidate which is then skeletonised to display a series of interference colours. This technique was originally used to prepare anti-reflection coatings for glass.

Follow the instructions given. **The buttons to click are shown in the left hand column; additional comments are shown in italics.** If you get stuck, stop whatever is going on by clicking on the **STOP** button. To see a short description, right hand click on an item. For more detailed explanations of the functioning of the trough software, please refer to the 'Software' chapter of this manual.

Requirements

Before you begin, you will need:

- . 1mg of arachidic acid to make into a monolayer
- . About 100g of ferric stearate to make the substrate surface hydrophobic
- . Glass slide (substrate) to deposit monolayers onto
- . About 100mg of Cadmium chloride for the subphase
- . Ethanol for skeletonising the LB film
- . Chloroform for trough cleaning
- . Ultra-pure deionised (DI) water for trough
- . Kimwipe / Kimtech tissues (or similar surfactant free) for cleaning

Preparations

Solutions

You will deposit a mixture of arachidic acid and Cadmium arachidate onto your substrate. The Cadmium arachidate is formed on the water when the arachidic acid is spread on a Cadmium chloride subphase. The Cadmium ions bind to the (partly dissociated) arachidic acid and form Cadmium arachidate. By chance, dissolved atmospheric carbon dioxide gives rise to the required pH 5.5, at which about 50% of the fatty acid is dissociated. The water used must be free from other contaminating metal ions.

* 'Use of interference to extinguish reflection of light from glass',
K.B.Blodgett, Physical Review, volume 55, (1939) page 391.

-
- Make up a solution of approximately 1 mg/ml of arachidic acid in chloroform and note down the exact concentration. A total volume of about 100 μ l of solution will be needed, but it is recommended to make up 10 ml for future use. Store this below 10°C to reduce evaporation. Use the glass bottle provided in the Monolayer Kit to minimise contamination from surfactants.
 - Make up a solution of about 10^{-4} M Cadmium chloride in deionised water in a clean container - this can be made of borosilicate glass, as long as solution is not stored in it overnight, as detectable quantities of mineral ions leach out of the glass after about half an hour. Make up about 2 litres of solution so that the subphase can be topped up from time to time. The molecular weight of Cadmium chloride (anhydrous) is 183.3; 36 mg will be needed to make up 2 litres of 10^{-4} M solution.

Trough

- Wipe over the trough surface, with a 'Kimwipe' (type 7105 or Kimtech type 75512, supplied with the trough - or type EX-L No 34256 in the USA) soaked in chloroform wearing the polythene gloves (also supplied). Make sure you are working in a well ventilated room and ask your laboratory supervisor about safety regulations and toxic solvents.
- Wipe the other trough components (dipper mechanism, pressure sensor, acrylic trough cover) with a Kimwipe soaked in alcohol to remove loose dust. Do NOT use chloroform on plastics other than PTFE as it will dissolve them!
- Clean the syringe by sucking up and expelling a little solvent several times.
- Fill the trough with deionised water until it just brims over the top - about 2 mm over the rim of the trough.

Substrate

- Acquire a standard microscope glass slide.
- Clean the substrate initially by rubbing it vigorously with a cloth soaked in alcohol. Rinse thoroughly with deionised water. Ultrasonic in deionised water.
- If a plasma etch unit is available expose the substrate to 2 minutes of Argon ion plasma at about 0.1 Torr and 100 W incident radiated power.
- Make the substrate surface hydrophobic by rubbing it with ferric stearate on a piece of Kimwipe tissue until no visible trace of the chemical remains. Ensure that no part of the surface is missed.

A small quantity of ferric stearate is provided in your Monolayer Kit - more can be synthesised or acquired commercially - please see the Technical Appendix.

Producing an isotherm

It is now time to run the software and turn the interface ON. Therefore, click on your trough icon, or, if it is not your desktop, click on the Nima516.exe file in c:\Nima (or whichever directory you have installed it into). The main screen of the software is illustrated below.

In order to produce an isotherm, the water subphase must first be clean. The molecules have to be spread on the surface and the solvent is left to evaporate. They are then slowly compressed and the resulting pressure-area isotherm displayed.

The following sections will lead you through this operation one step at a time. The software commands are printed in **bold** down the left margin with an adjacent explanatory paragraph.

Additional comments are printed in italics.

In case of emergencies, click on the STOP button or hit the Esc key!

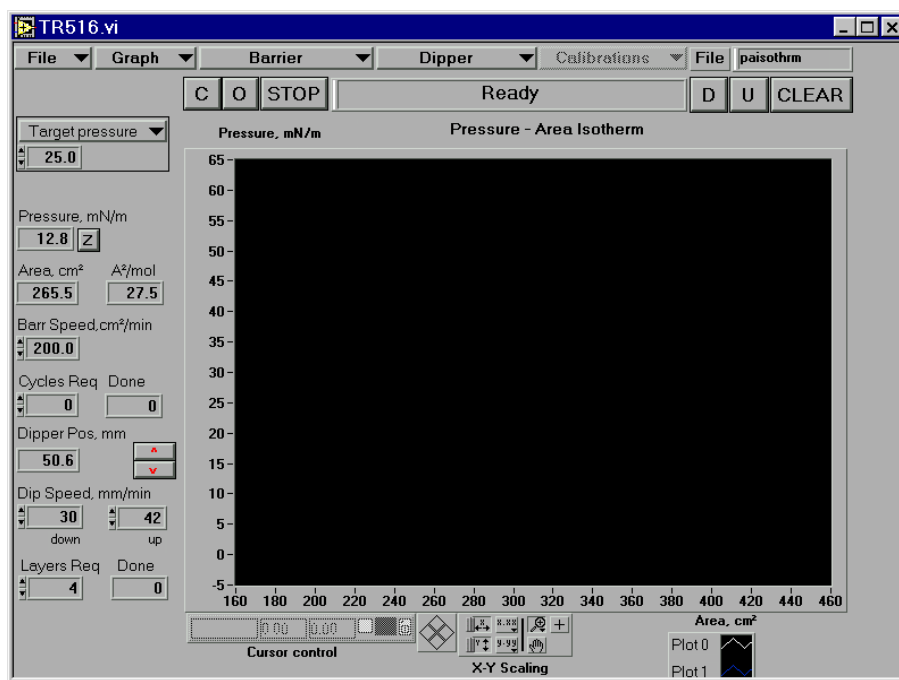


Figure 3.1: Main Screen of Nima Software

Subphase cleaning

Ensure that the trough has been cleaned and filled with pure DI water. Attach a paper Wilhelmy plate to the pressure sensor with the 'S' shaped hooks provided and lower it into the water, so that about 2mm of it is immersed.

O Open the barrier(s) by clicking on the 'O' button.

Z Zero the pressure sensor.
Check that a reading of about 70 mN/m is obtained when the Wilhelmy plate is lifted out of the water. If it does not, check the change in surface pressure for the 100mg calibration weight by adding the calibration pan and then the weight. This change should be 46.7mN/m. If it does not, recalibrate the pressure sensor as described in the 'Software' section. The reading may drift initially, this is because the paper plate is still absorbing water.

Barrier Speed 100 Set the barrier speed to 100 cm²/min by entering '100' in the 'Barrier Speed' box. *To save time, you can set it to larger values, say 250, or even 500 for larger troughs.*

Barrier Isotherm Select 'Isotherm' from the 'Barrier' dialog box to start the isotherm. The barrier will move at the given speed until either the space bar is pressed or the barrier travels outside its 'allowed' position (this is set in the Monolayer Menu and prevents accidental damage to the trough.)
Examine the isotherm produced. It should be almost flat except for a slight 'tail' at small areas due to the presence of dirt on the water surface.
Turn on the aspirator pump and touch the pipette to the water surface to suck off any floating material, such as dust and amphiphilic contaminants. If the pipette end is positioned correctly, there will be a louder sucking noise as air is sucked up with water. Move the head of the pipette around to collect all the material and clean for about 30 seconds.

O Open the barrier(s) by clicking on 'O' .

Z Re-zero the pressure sensor.
This is necessary because the water level in the trough has now changed. Make sure that the lower edge of the Wilhelmy plate is still touching the water surface.

Keep cleaning until the isotherm produced is completely flat. The change in surface pressure on compression should be less than 0.5mN/m. For a quicker check on cleanliness, simply close the barriers ('C') and watch the change in pressure sensor reading.

If you have sucked off too much water, please refill the trough until the level is again about 2mm above the rim of the PTFE. When refilling, always add the water behind the barrier i.e. the other side from where the monolayer is to be spread. This will ensure that any surfactants present in the water will rise to the surface in the unused compartment behind the barrier. Of course, the water should be clean, but you can't be too careful in LB films!

Monolayer Menu

The screenshot shows the 'NIMA Monolayer Menu' software interface. The window title is 'MonoMenu.vi'. At the top left is a 'FILE' dropdown menu. To its right is the title 'NIMA Monolayer Menu' and a 'Current File' field containing 'pairothrm'. The interface is organized into four main sections, each with a red header:

- TROUGH FUNCTIONS:** Target Pressure, mN/m (25.0); Barrier Speed, cm²/min (50.0); 'Open to' Area, cm²/min (265); 'Close to' Area, cm²/min (80).
- MOLECULAR PROPERTIES:** Molecular Weight (312.0); Concentration, mg/ml (1.004); Volume, μl (50).
- ISOTHERM CYCLE FUNCTIONS:** Cycles Required (0); Cycle Max Area, cm² (264); Cycle Min Area, cm² (81); Cycle Max Pressure, mN/m (30); Cycle Min Pressure, mN/m (-5); Wait Interval at Closed, s (0); Wait Interval at Open, s (0).
- QUASI-STATIC COMPRESSION:** Area increment, cm² (0.0); Wait interval, secs (0.0).

An 'ACCEPT' button is located in the bottom right corner of the window.

Figure 3.2: Monolayer Menu

To ensure that the area axis (in A² / molecule) is calibrated correctly, go to the Monolayer Menu and enter the correct molecular weight, concentration and volume of your solution.

Barrier Mono Menu Select 'Monolayer Menu' from the 'Barrier' menu.

MW Enter the molecular weight of your molecule.

Conc Enter the concentration of your solution.

Vol Enter the volume of your solution in μl.

The other variables can be left for now. They are fully explained in the 'Software' chapter.

Spreading

Now that the conditions have been set, the molecules can be spread on the subphase.

- Rinse out the syringe by drawing up and expelling a little chloroform. Make sure that you always expell excess chloroform into a designated 'chlorinated waste' bottle.
- Draw up 50 μ l of the arachidic acid solution into the syringe and deposit it drop by drop onto the water from just above the surface.

There is no need to deposit on different places on the trough when using arachidic acid - the molecules will spread out to cover the complete area available. With other molecules, particularly those with large dipole moments, this may not be the case and 'islands' can form.

- Leave the solvent to evaporate.

All the solvent must evaporate but Katherine Blodgett found that if it was given too long, the deposited films were 'streaky'. The evaporation time does appear to have some bearing on film quality - you may wish to devote your PhD to investigate this unexplained observation! However, just wait until the pressure reading returns to zero - that will do for now.

Compression

- Barrier Speed 100** Set the barrier speed to 100 cm²/min by entering '100' in the 'Barrier Speed' box. This is a reasonable compromise between a good isotherm (i.e. undistorted by dynamic effects) and time available. At this speed, the barrier takes about 5 minutes to close for a standard size trough.
- CLEAR** Clear the memory and the graphs by clicking on 'CLEAR'. You will be asked to confirm this clear, as once cleared, all the data is irretrievably lost!
This will clear the data stored when the subphase was being cleaned. It is good practice to clear the data before taking an isotherm, to prevent the graph getting cluttered up with unnecessary data from previous runs.
- Graph cm²<->A²** Switch the area axis between absolute area (cm²) and area per-molecule (Å²) as calculated from the data in the Monolayer Menu.
- Barrier Isotherm** Start the compression by clicking on 'Isotherm' in the 'Barrier' menu.
Watch the isotherm on the screen and compare it to Figure 3.3. It should show three distinct regions - an initial flat region, corresponding to a 'gaseous' phase of the molecules on the water, a gently rising liquid-expanded or 'liquid' phase and a steeply rising, liquid-condensed or 'solid' phase.
- STOP** When the isotherm begins to collapse, click on STOP to stop the compression.
At this point, the steep upward rise of pressure will begin level off. Physically, the monolayer can no longer support the force applied and the molecules move over each other to form aggregates on the surface, or are dissolved in the subphase. With highly coloured films, this is clearly visible. Remember that a surface pressure of 50mN/m is equivalent to 200 atmospheres pressure over the molecular length of 25Å !

Barrier Speed -100 Change the barrier speed to -100 cm²/min. A negative speed corresponds to the barrier moving backwards.

Barrier Isotherm Expand the floating monolayer by clicking on 'Isotherm' again. *The isotherm should have exactly the same shape as when the film was compressed but will be shifted towards smaller areas (i.e. to the left of the graph) by an amount equal to the area of collapsed film.*

Barrier Pi control Clean off the surface. Use the suction pump with its teflon tip to clean the molecules off the surface as previously described.

Target Pressure 25 Select 'Target Pressure' from the 'Variables' menu and adjust it to 25mN/m. *This will compress the barriers, keeping the pressure at 25mN/m as you remove the molecules, ensuring that the monolayer is not collapsed. Cleaning shouldn't take more than a minute or so.*

Well done - you have now taken your first pressure-area isotherm!

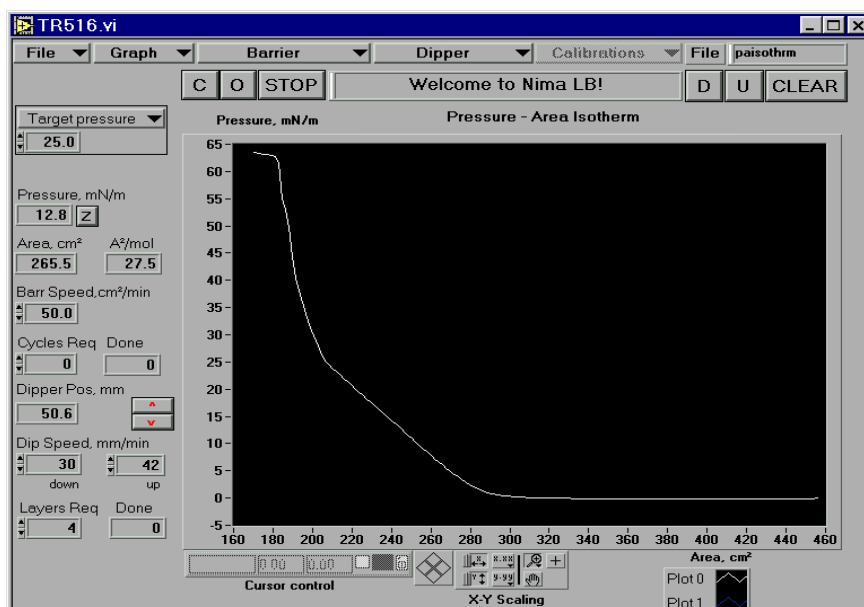


Figure 3.3: Typical isotherm of fatty acid

Saving and further analysis

File Save Save the isotherm, by clicking on 'Save' in the 'File' dialog box. *Enter a name (such as 'test1') and the data will be saved as a *.txt file (i.e. test1.txt) along with its operating conditions which are saved as a *.con file. The data file can be loaded into Excel (or other spreadsheets) and the data will be displayed in columns, each headed by a label to signify what it is. It can be charted and pasted into your reports or papers.*

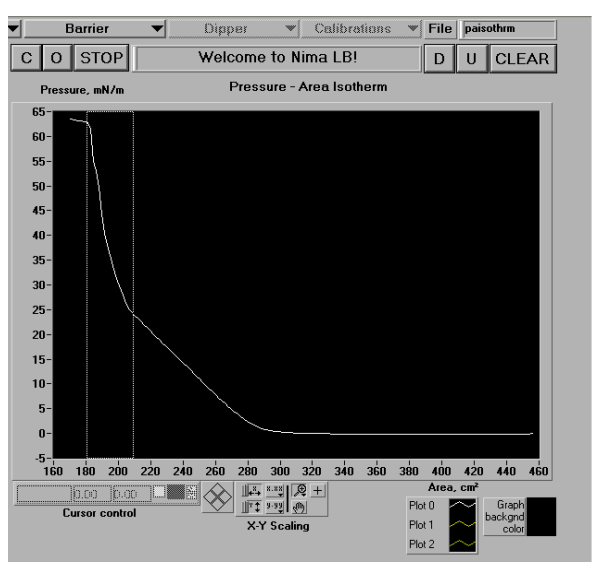
Graph P&A-T Click on 'P&A-Time' on the 'Graph' menu to view two separate plots of pressure-time and area-time.

Graph $A^2 \leftrightarrow cm^2$ Click on 'Graph' and 'Change Axes $A^2 \leftrightarrow cm^2$ ' to convert the area scale to \AA^2 . The conversion will use the data supplied by you in the Monolayer Menu.

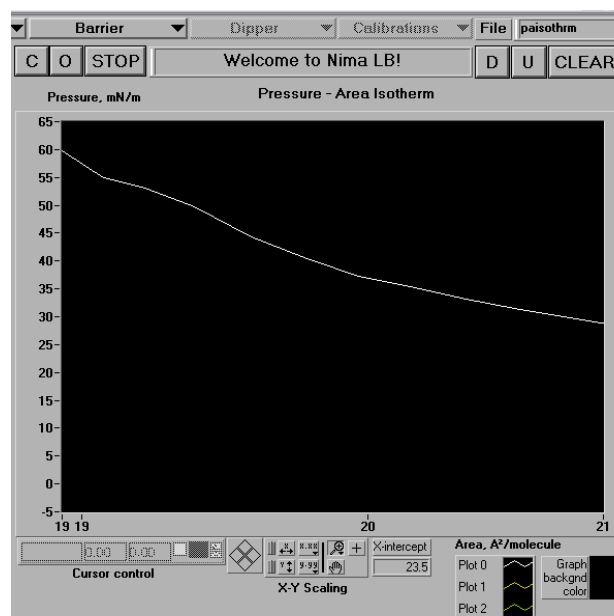
Right click over the graph and de-select 'AutoScale X' - then use the pointer to mark off an area of the isotherm such as the 'liquid condensed phase'. The selected area will expand to fill the screen and the Area/molecule / \AA^2 will be displayed in the box below the graph, Figure 3.4.

If you disable auto-scaling for both X and Y axes, then you can set the scaling of the axes by writing over the minimum and maximum abscissa values. Or you can select different areas of the graph with the 'X-Y scaling palette'. Feel free to experiment.

Cursor control Click on the cursor control palette (bottom left of the graph).
There is a white square which activates the cursor controls when clicked. You can move the cursor anywhere on the screen and read off the X and Y co-ordinates. Click on the little padlock icon and select 'lock on plot' to move the cursor along the actual curve.



a) x-axis now in $\text{\AA}^2/\text{molecule}$
 - liquid condensed phase selected



b) expanded to read off
 'zero pressure molecular area'

Figure 3.4: Isotherm of fatty acid

Further investigations

Repeat the isotherm procedure two or three times, varying the amount of material used, solvent evaporation time, compression speed etc. to try to improve upon your first isotherm and get a feel for the technique.

You might like also to change the concentration of Cadmium chloride in the subphase. This will alter the pressure at which the liquid-expanded changes to the liquid-condensed phase. The greater the concentration of CdCl_2 , the lower the pressure of the phase change. The liquid expanded phase disappearing altogether at about 10^{-3}M concentration.

Depositing a multilayer LB film

Now that you have an isotherm of the material to be studied, it can be deposited with some confidence. Arachidic acid / Cadmium arachidate forms good, optical quality Langmuir films on the subphase and deposits easily at surface pressures of about 25mN/m (in the liquid condensed phase).

For simplicity, the following sequence is for a conventional LB dipper:

- Prepare a subphase of about 10^{-4} M CdCl_2 .
- Clean and check the water surface as before.
- Have the glass slide coated with ferric stearate ready.

U Move the dipper to its topmost position by clicking on 'U'.
Attach the glass slide to the clamp.

D Move the dipper down by clicking on 'D' until the lower edge of the slide is about 5mm above the water surface.

STOP Stop it by clicking on STOP

h Read off the dipper position reading - let's call this h mm.
Select 'Dip Top End' from the 'Variables' Menu (top right of screen) and enter h into the box (top left of the screen).
The 'Variables' Menu contains a number of useful parameters that may be changed in the main screen of the program before or during a run. Hence, it is not necessary to stop the process and go to the Monolayer or Dipper Menu in the middle of a run.

h+d Now decide how far you want to dip the substrate into the water - i.e. what length of substrate you want to coat. Typically this may be 30mm for a standard dipper or maybe 10mm if you are using a mini dipper with a small slide.
If we call the immersion depth 'd', then enter 'h+d' into the 'Dip Bottom End' variable box (again selected from the 'Variables' Menu).

Z Zero the pressure sensor by clicking on 'Z' .
Then spread the solution of molecules onto the subphase.
To avoid having to replenish the molecules on the subphase too often, it is useful to put the maximum possible number on each time. Spread the solution with the syringe until the surface pressure displayed in the data margin to the left of the axes just begins to rise. At this point, the surface is completely covered with molecules.

Target pressure 25 Select 'Target Pressure' from the 'Variables' Menu (top left of screen)
Enter a target pressure of about 25mN/m in the 'Target Pressure' box.
The exact value will depend on the phase change between 'liquid expanded' and 'liquid condensed' phases. It is best to deposit just 2 or 3 mN/m above the phase change, as the molecules will be tightly compressed, but small excursions in pressure (caused by the action of the slide entering the water) will not give rise to local collapse of the monolayer.

Barrier Pi Control Enable the pressure control by clicking on 'Pressure Control' in the 'Barrier' menu.

The barrier(s) will compress the monolayer to the target pressure according to the relationship:

$$\text{barrier speed} = \delta\pi * (\text{feedback gain})$$

where $\delta\pi$ is the difference between current pressure and target pressure and feedback gain is a numerical value (also set in the 'Variables' Menu). Larger values of gain increase the barrier speed and so reach the target pressure more quickly, but may then overshoot. Too low a value means that target pressure is never achieved. A critical value of 1.0 is recommended.

The barriers will slow down as the target pressure is reached. Wait until surface pressure is within 1mN/m of its target.

Note that the maximum barrier speed under pressure control is limited by the value given in the 'barrier speed' display box (at the centre left of the screen). This is useful if you are using delicate molecules and don't want to compress them too fast.

Dipper Begin dipping.

Progrm Dip The dipper will move down through the water surface.

As the slide moves through the interface, the monolayer is transferred onto the solid surface. The barriers will move inwards to maintain the target pressure automatically.

Graph Select the 'Dipper-Area' graph from the 'Graph' dialog box.

Dip-Area A series of straight 'V' shaped lines will appear as the dipper is moved up and down and the barrier moves in to compensate for removal of molecules from the water surface.

Layers Req 40 Adjust the 'Layer Required' box to 40, so that 40 layers (equivalent to a thickness of $\lambda/2$ are built up, as explained later under 'skeletonisation').

The dipper will continue to deposit layers on to the substrate until either all 40 layers have been deposited or the area of monolayer is reduced to below the following:

$$\text{area} < [('\text{close-to}' \text{ area} + 2 * \text{substrate area})]$$

You are then requested by the software to reopen the barriers and respread the molecules. Spread the material, as before. If you have not collapsed the film, there is no need to clean the surface. Then re-compress and restart the dipper.

Continue until all 40 layers have been deposited.

Points to consider during dipping

* **Do not** stop the dipping whilst a layer is in the process of being transferred - it will reduce the quality of your LB film.

* **Do not** clear the memory whilst dipping as this will clear the record of the number of layers. You can, of course, keep a separate tally, if you want to work with a clear screen after every re-spreading.

- * Watch the meniscus of the subphase as deposition is occurring. If the meniscus is uniform, the deposition likely to be is good; if it 'dances around', the deposition is unlikely to be as good. This 'dancing' indicates imperfections on the substrate surface.
- * The dipping speed, target pressure, feedback gain and 'end' positions can all be varied as the dipping is taking place, without stopping the program. The 'Variables' Menu allows selection of the appropriate variable and the preset values are altered using the 'up' and 'down' arrows next to the box.

Completion

Once all the layers have been deposited, the substrate can be removed and the data can be saved and plotted out. A typical deposition isotherm is displayed below.

- * Save the data ('File' dialog box and 'Save' with a user defined file name).
- * Remove the substrate with its deposited Langmuir-Blodgett film. Be careful not to touch the surface.
- * Store it in a cool, dry place.
- * Clean the remaining monolayer off the subphase surface.
- * Empty the trough.
- * Clean the syringe.
- * It is recommended to always empty the trough overnight. If you prefer to leave the trough full of water to prevent dirt falling on the PTFE surface, please remove dipper and pressure sensor(s) to prevent corrosion of electronic components.

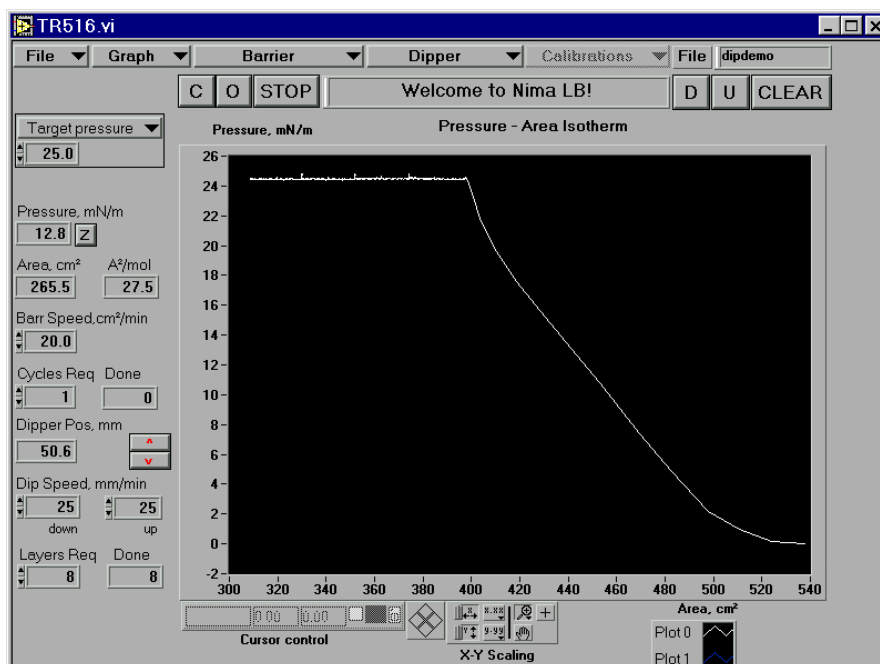


Figure 3.5: Typical deposition pressure-area isotherm

Further analysis

Graph P&A-T Click on 'P&A-Time' on the 'Graph' menu to view two separate plots of pressure-time and area-time. This will show the 'steps' in area as the barrier is moved in to compensate for the removal of monolayer onto the substrate, Figure 3.6 below.

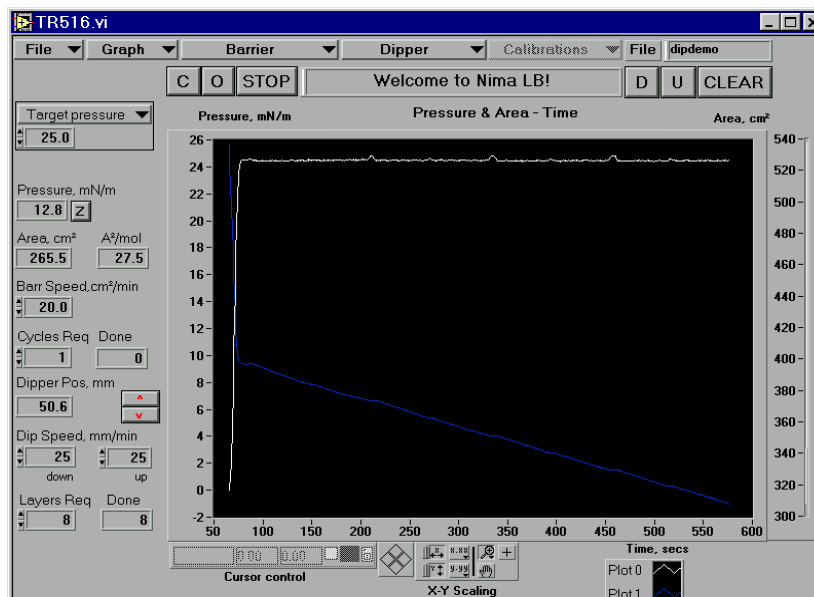


Figure 3.6: Typical deposition (pressure & area) - time isotherm

Graph Dipper -Area Click on 'Dipper-Area' on the 'Graph' menu to view the plot of area against dipper position. If there was good deposition, this plot will be in a series of regular 'V' s. As the dipper is oscillated up and down regularly, the barrier moves in linearly to compensate for the removal of monolayer, Figure 3.7 below.
Note that it takes a few mm worth of dipper travel at the start of every layer before deposition recommences - this is caused by the reversal of the meniscus radius, as explained previously in the 'Langmuir-Blodgettry' chapter of this manual.

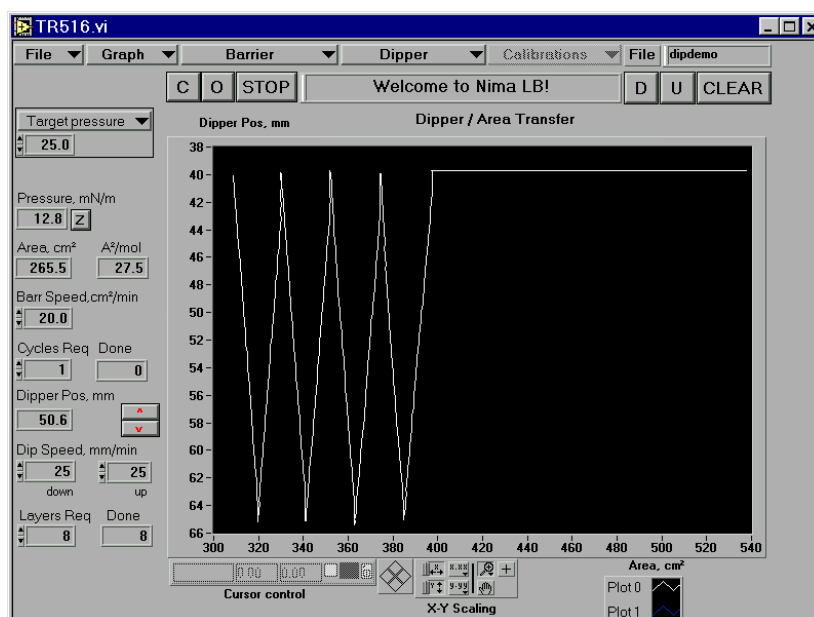


Figure 3.7: Typical dipper position-area isotherm

Transfer Ratio Click on 'Transfer ratio' on the 'Graph' menu to view the plot of transfer ratios (TRs). Ideally, TR is always 100%, but rarely in practice! There are many reasons for this, as explained in 'interpreting transfer ratios' overleaf.



Figure 3.8: Typical transfer ratio plot

Skeletonisation to produce an anti-reflective (AR) coating

It is now time to 'skeletonise' the multilayer you have produced. Before skeletonisation, the films refractive index is very similar to that of the substrate (about 1.50) making it almost invisible. The film is skeletonised by dissolving away the arachidic acid, leaving only the Cadmium arachidate. This reduces its refractive index and brings the film's optical thickness close to one quarter wavelength for blue light.

- Pour enough ethanol to cover the LB film into a beaker.
- Immerse the film in the ethanol for a number of seconds. The exact time required varies between ten seconds and two minutes. When the film is first immersed, it loses arachidic acid fairly quickly but the rate then slows. Remove the film slowly to allow time for the surface to shed the alcohol.
- The colour becomes more vivid and shifts towards the red with longer soaking as the film's refractive decreases towards the extinction value, $n = \sqrt{n_{\text{glass}}}$.
- Hold the dried slide in the reflection of a lamp. You will be amazed by the quality of the AR coating!

Deposition onto hydrophilic substrates

The previous section dealt with deposition onto an hydrophobic substrate - that is to say the first layer was deposited on the 'down' path. Deposition can just as easily take place onto an hydrophilic substrate. The only difference is that the first layer is on the first 'up' path. Hence the substrate must first be lowered into the water.

It is recommended that the substrate is lowered into the water prior to spreading and compressing the monolayer, as otherwise some irregular deposition may take place onto the hydrophilic substrate as it is immersed through a compressed monolayer.

The software can be used to start the deposition below the water surface. This is done by 'fooling' the computer that the first layer has already been completed. Hence the number of layers set will actually be $(n + 1)$ where n is the actual number of layers to be deposited. Thus even if only one layer is required, 2 layers must still be entered in the 'Layers Required' box.

The following sequence should be followed for deposition onto an hydrophilic substrate:

Dipper Menu	Enter the Dipper Menu and set the dipping routine but remember that your first layer will be the second layer as far as the computer is concerned. Thus enter $(n+1)$ layers. Set the 'top' and 'bottom' positions for the substrate, as explained in 'Setting the Dipping Conditions' earlier in this chapter.
C	Close the barrier(s) and clean the surface.
O	Open the barrier(s).
	Then attach the substrate to the dipper and, still with the barrier(s) open, move the dipper so that the substrate is immersed:
D	Move the dipper down.
STOP	Click on STOP to stop the dipper at the correct position.
	Then spread and compress the monolayer in the usual way:
Barrier Pi Control	Start the compression under pressure control.
Dipper Progrm Dip	When the film has reached its target pressure, click on 'Program Dip' to start the dipper. As the dipper is already below the surface of the water, it will assume that the first layer has already been deposited and move to deposit the 2nd layer.

The dipping will then proceed in the usual way until the number of layers required have been deposited.

Interpreting transfer ratios

Ideally, each time the substrate crosses the air-water interface, the surface of the substrate is covered completely in monolayer, giving a transfer ratio of 100%.

In practice, though, this is rarely achieved. There are several reasons for this:

1. Collapsing monolayer - unstable film

The monolayer may be unable to support the dipping ('target') pressure and may be collapsing away happily to itself. If such a film is deposited, the transfer ratio will be more than 100% as the collapse rate will be superimposed on the dip rate.

The term 'collapse' is used generally to describe a film that is unable to support a given surface pressure. The reasons for the collapse may be that:

a) the molecules are too hydrophilic and are being dissolved in the subphase. This can happen at pressure as low as 8mN/m. Molecules can dissolve in the subphase ahead of the barrier and reappear behind the barrier, i.e. they can exist in an equilibrium state between surfaces at different pressures and the subphase.

b) the molecules may simply be leaking under the barrier. Check that all PTFE surfaces are clean and that the barriers are resting firmly on the trough.

c) the film pressure is simply too high for the material and it is forming 'mountain ranges' on a molecular scale on the surface. Remember that, for a 25Å long molecule, a pressure of 25mN/m is equivalent to 100 atmospheres in the plane of the film! These molecular mountain ranges can be observed by the naked eye just ahead of the barrier.

To check for film stability, hold the film at the target pressure while under pressure control and watch the area v time plot. If the area value is decreasing linearly, this indicates that the film is unable to support the pressure or that the film is leaking under the barrier. If the area value is decreasing asymptotically to a constant area value, this indicates that the molecules are rearranging themselves (annealing) into a more energetically favourable and stable order.

A stable film can be formed from arachidic acid on a 10^{-4} M CdCl₂ subphase. The area decrease for such a film has been measured at less than 0.01cm²/min at 30mN/m.*

2. Film depositing and peeling off again

Suppose that the film is stable and that the first layer has been successfully deposited onto the substrate with a transfer ratio of 100%. If the substrate now crosses the air-water interface for the 2nd layer and the film peels off because it has not sufficient attraction to the first layer, a transfer ratio of -100% will be recorded! If this sequence is continued for 10 layers, the inexperienced observer may believe that 5 layers had been deposited when actually none have.

Watch the meniscus between subphase and substrate carefully. If it is curved the opposite direction to the direction, then the previously deposited monolayer is peeling off.

* 'A modular, multi-functional LB trough', F. Grunfeld, Rev of Scientific Instruments, vol 64 (2) Feb 1993

3. Partial peeling off of monolayer

Extending on case (2) above where 100% of the film peeled off again, consider the case where only 50% peels off. If on 50% of the area, the film peels off and on the other 50% there is deposition, then to the outside observer it appears that the transfer ratio is 0%. This can easily happen on substrates that have not been cleaned properly.

Great care must be taken to avoid such a situation. A good indicator is always the meniscus of the subphase on the moving substrate. If the curvature of the meniscus is uniform and follows the direction of dipping, this indicates good deposition. If the meniscus 'dances' around i.e. its radius of curvature is constantly changing, the substrate and/or subphase is probably very dirty.

Ensure that you do not report X or Z type deposition when you really have poor quality Y type!

Hence it always imperative that other evidence for the existence of the multilayer is obtained. Note that some of the original X and Z type deposition observed was found to have Y type structure, when checked for head group separation with X-ray diffraction (Gaines - 'Insoluble monolayers'). The editor of this manual suspects that the some X and Z type layers that have been reported in the literature are just plain bad Y type LB films!

4. Dip start and dip end positions

The setting of the dip start and dip end positions will also greatly influence the transfer ratio.

For conventional dippers (simple up and down motion), remember that even for ideal deposition, the 2nd layer will not start being deposited until the meniscus has flipped over, which can be up to 5mm worth of actual substrate movement. The 'meniscus radius' setting in the Dipper Menu helps overcome this. If a radius of 5mm is chosen, then the TR calculation is performed from 5mm after the 'dip start' position, thus eliminating this effect.

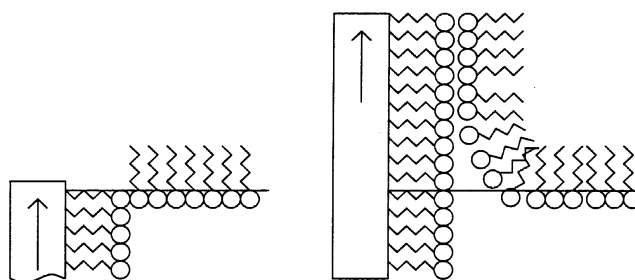


Figure 3.9: Substrate has to travel considerable distance, before meniscus flips over and 2nd layer starts being deposited. This can introduce large errors into transfer ratio calculation.

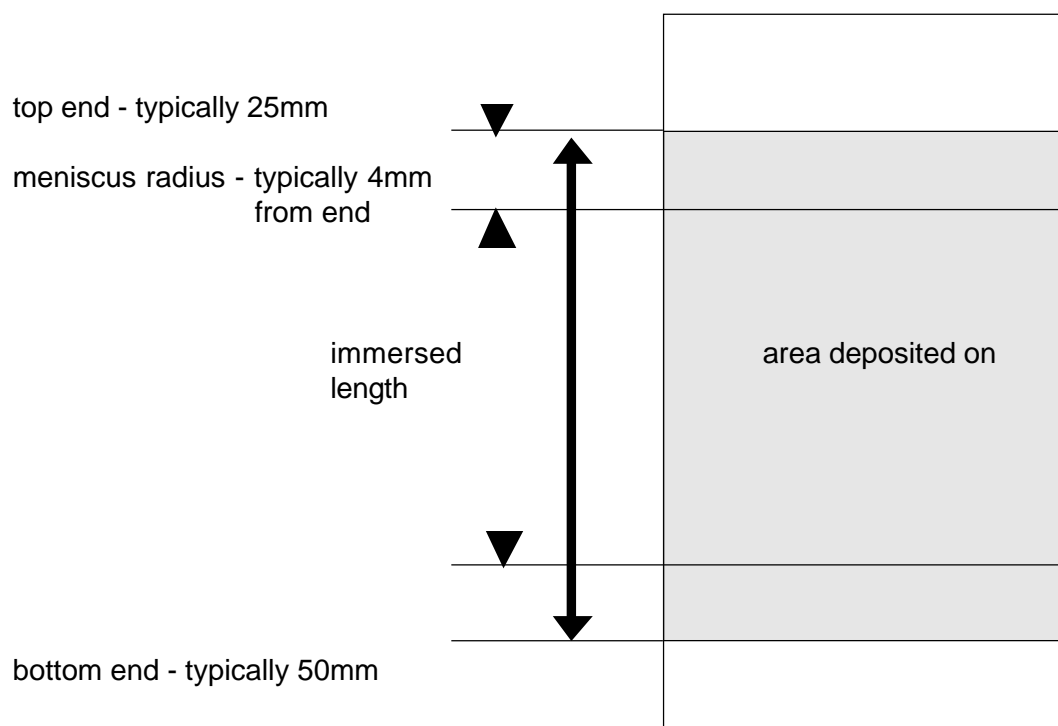
Hence, the transfer ratios will differ considerably if the dip start position is set above the subphase surface or below it.

Similarly for alternate layer dipper mechanisms, the transfer ratios are critically affected by the dip start and dip end of both sides A and B.

6. Meniscus radius and transfer ratio calculations

The transfer ratio calculation is improved by including the 'meniscus radius'. This takes into account the fact that the meniscus 'flips' over at the end of every layer before deposition re-commences on the next layer.

A sketch of the important dimension is given below:



In the example above, the slide is set to oscillate between an immersion depth of 25 and 50mm, as measured from the top of the dipper.

If the meniscus radius is 4mm, then the actual area immersed is:

$$\begin{aligned} \text{area immersed} &= 2 [\text{width} + \text{thickness}] \times [(50 - 25) - 4] \text{ mm}^2 \\ &= 2 [\text{width} + \text{thickness}] \times [(50 - 25) - 4] / 100 \text{ cm}^2 \end{aligned}$$

Hence for a standard 76 x 26 x 1 mm microscope glass slide, the (area immersed and deposited on) is actually 11.34cm², rather than 13.5cm² - a reduction of over 10%.

Please note that the top end can be above the water surface. This is perfectly ok, as long as only the immersed area of slide is given for 'substrate area' in the Dipper Menu.

Good realistic plots for area/pressure v time and transfer ratios are given below:

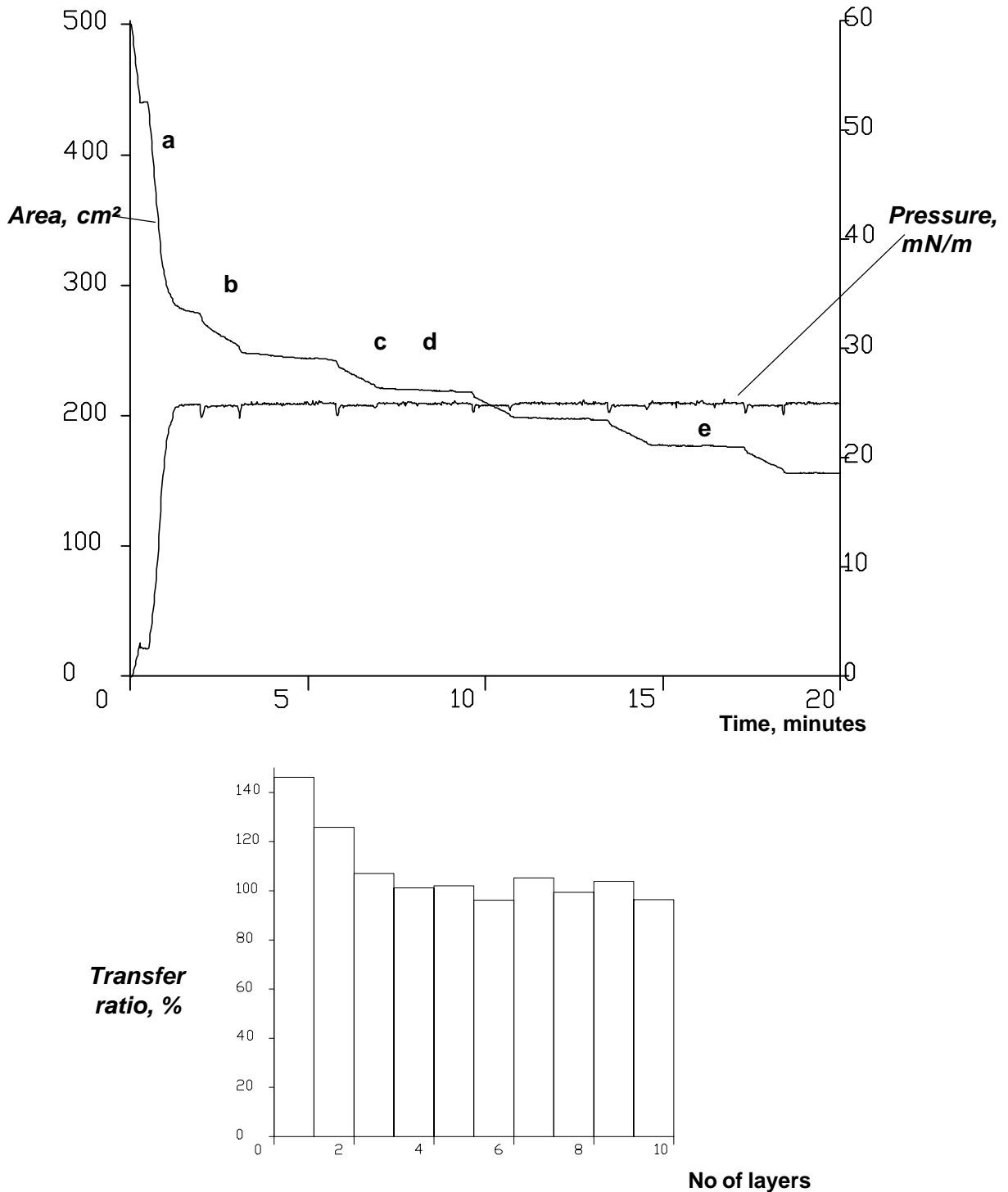


Figure 3.10: Area/pressure time plot and TRs of deposition with alternate layer dipper
 a) compressing before dipping
 b) first layer being deposited - a little too soon, as film is still annealing and TR looks too high
 c) 2nd layer better
 d) film still collapsing a little in between dips
 e) film now appears stable

Operating a trough in 'coupled barrier' mode - option 'MC'

If you have 2 independent barriers, then the software may be used to move the monolayer across the length of the trough using the 'coupled' mode. This is useful for scanning the monolayer under a microscope or for the multi-compartment troughs, where the monolayer can be moved over different subphases.

Typically, in this mode of operation, there are 2 compartments in the one trough which are filled with differing subphases. The monolayer is spread and compressed in one compartment and then transported into the second compartment, where some chemistry can be done over a different subphase. If your trough also has a dipper, then the monolayer can also be transferred to a solid substrate in the second compartment.

There are some extra function switches in this mode:

1. An 'A/B' switch to select between barrier 'A' and 'B'.
2. A 'SYM' button to switch between symmetrical compression (about the centre line of the whole trough) and asymmetrical compression (within one compartment).
3. A 'coupled' mode in the 'Barrier' dialog box for moving the barriers in unison.

A typical run consists of:

1. Open barrier A by clicking on 'O' and making sure that the 'A/B' switch is set to 'A'.
2. Close barrier 'B' by switching over to 'B' and clicking on 'C'.
3. Click on 'STOP' when barrier B is over the compartment divider.
4. Spread the molecules in compartment A.
5. With the 'SYM' button set to 'NON SYM', select 'Isotherm' from the 'Barrier' dialog box.
An isotherm will be made over compartment A.
6. 'STOP' before the monolayer collapses.
7. Select 'Coupled' from the Barrier dialog box.
The monolayer will be moved towards compartment B. Its speed is set as usual in the 'Barr Speed' box and barrier B will be controlled so as to always keep the area between the 2 barriers constant.
8. Click on STOP when the monolayer is over compartment B.
9. If you wish to dip, set up the dipper in the usual way and select 'Pi Control' from the Barrier dialog box, making sure that the SYM button is still set to 'NON SYM'.
10. When the film is at target pressure, select Program Dip form the Dipper dialog box.
The monolayer will be deposited in the usual way.

Operating a trough in alternate layer mode

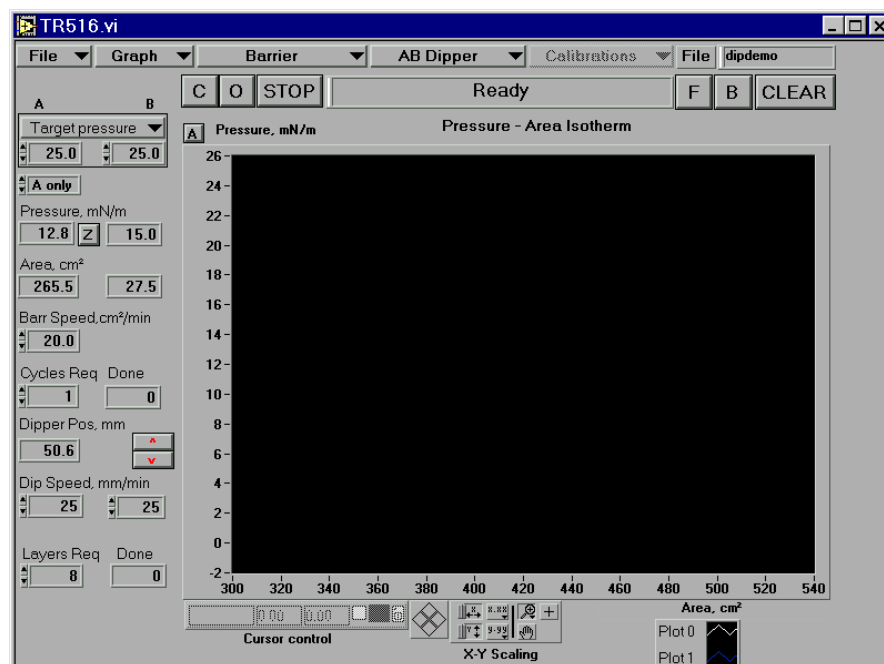


Figure 3.11: Main Screen in Alternate Layer (AB) Mode

The main screen in the AB mode differs from the standard screen because there are, in effect, 2 separate troughs. So there are 2 independent barriers and 2 separate pressure sensors.

All the data and functions are available for both compartments. They are accessed by clicking on the 'AB' switch (top left of the screen) to the compartment required. For instance, if you want to zero pressure sensor A, switch to 'A' and click on 'Z'. If you want to open barrier B, switch to 'B' and click on 'O'.

All the displayed values such as area, pressure and dipper position are grouped in 2 columns 'A' and 'B' and are displayed continuously.

A typical deposition run (alternate layer dipper)

1. Follow the instructions for the pressure-area isotherm first for compartment A. Repeat for compartment B.
This will ensure that the trough is clean and ready to go.
2. Prepare a glass slide by rubbing it with the ferric stearate supplied.
This will make it hydrophobic.
3. Move the dipper to the top by clicking on 'F' (forwards) or 'B' (backwards).
The dipper will rotate continuously.
4. Click on 'STOP' when the dipper substrate carrier is at the top position (and the carrier is horizontal).
5. Lay the slide on the substrate carrier, making sure it is held in place by the clips.
6. Go the Dipper Menu ('Dipper' in the menu bar).
7. Select the appropriate values for your deposition from the Dipper Menu below.
Typical values are displayed below.
8. Please see overleaf for an explanation of the dipper 'top end' & 'bottom end' positions. These have to set to match the size of the substrate being coated.
9. Enter the sequence of 'A' and 'B' layers in the box and don't forget to enter the corresponding 'Layers Required'.
The number counter allows you to check exactly which layer is which type.

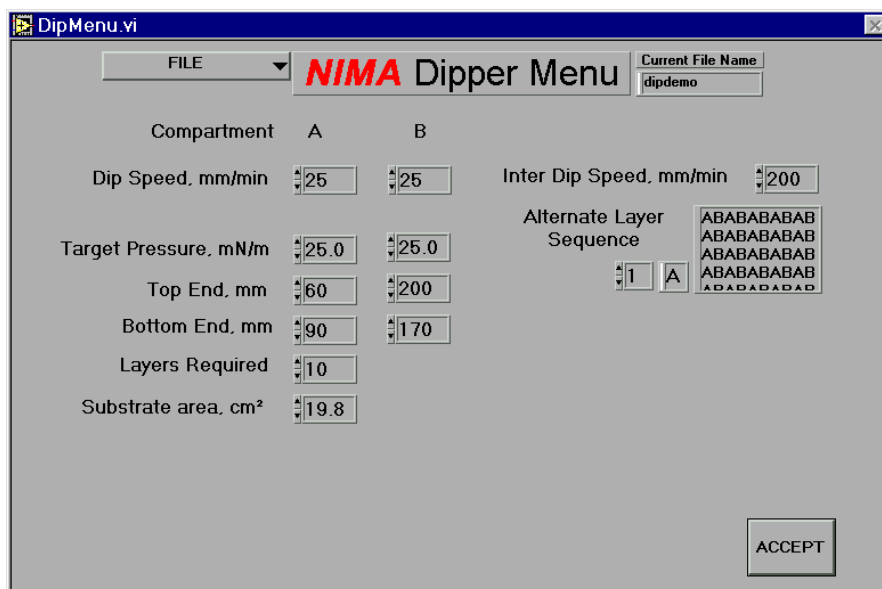


Figure 3.12: Dipper Menu for Alternating Layer Dipper

Alternate layer dipper 'top end' & 'bottom end' positions

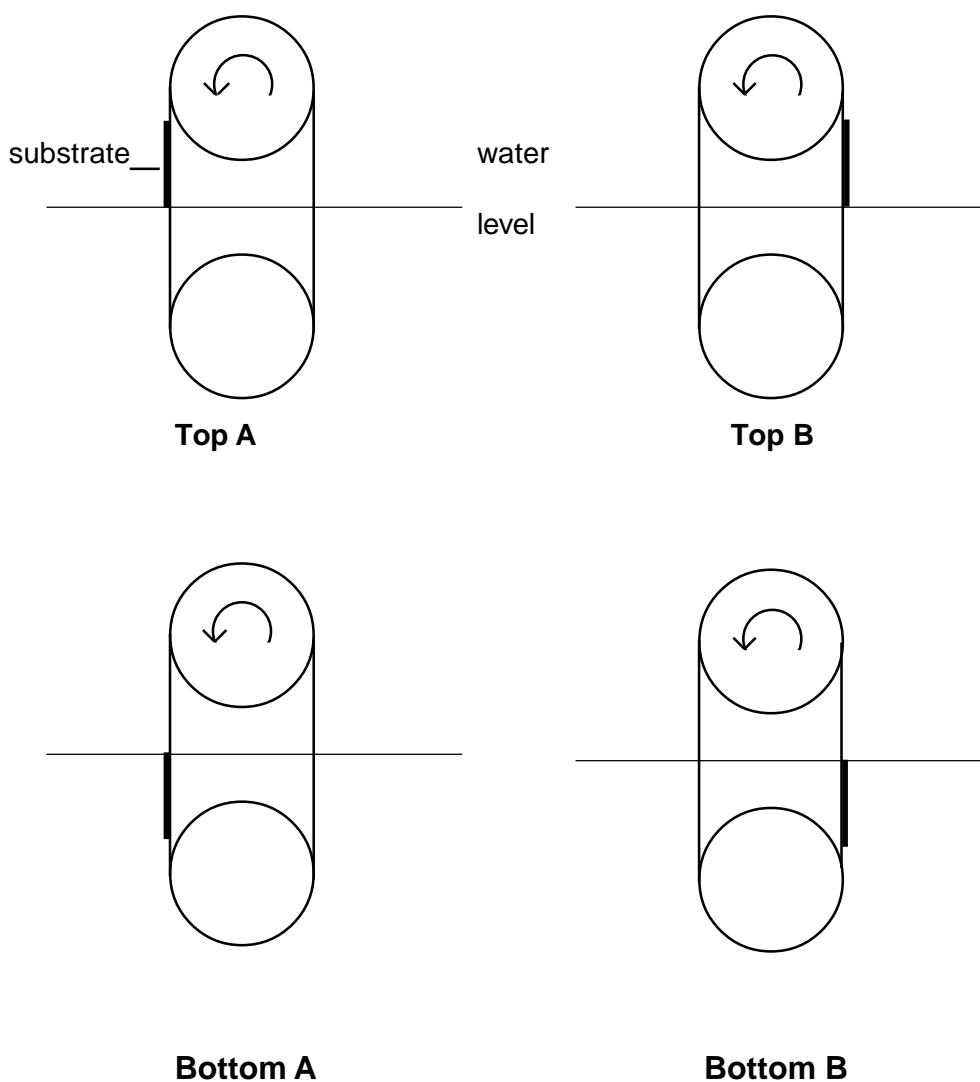


Figure 3.13: Alternate Layer Dipper 'Top' and 'Bottom' End Positions

The substrate is carried around the dipper - the arrows indicate the 'forwards' direction. The critical positions are illustrated above.

'Top A' is just as the substrate is about to be immersed in side A - typically 75mm.

'Bottom A' is when it is just fully immersed in side A - typically 100mm.

'Bottom B' is just before it emerges on side B - typically 190mm

'Top B' is immediately after it has completely emerged on side B - typically 210mm

Typical values are for a standard 76 x 25mm glass microscope slide. Other size substrates have different values, which are set before deposition commences.

10. Make sure that the dipper position is between '0mm' and 'top end A'.
If it is not, the layer counter may not start from zero.
11. Spread the monolayer in both compartments (as in the section 'taking an isotherm').
12. Select 'Pi Control' from the Barrier dialog box.
Both barriers will compress their respective monolayers.
13. Use the AB switch to view the compression in either compartment.
14. When both films are compressed to their target pressure, click on 'Program Dip' (Dipper in the menu bar) to start the dipper in its pre-programmed sequence.
The dipper will move at the 'Inter Dip Speed' between immersions and at 'Dip Speed A' when depositing monolayer A and 'Dip Speed B' at side B.

The dipper will continue until the layers have been deposited or there are not enough molecules remaining on the surface in which case a warning message 'barrier too closed!' will appear. If this happens, please open the barrier(s) and spread more molecules.

View the data also in the area & pressure - time axes and the dipper - area axes.

Save in the usual way.

Further Work

Try depositing on both glass slides and silicon wafers. LB films on silicon wafers give vivid interference colours. Try different numbers of layers and making 'stepped' layers. Vary the thickness and skeletonisation time of films on glass to improve the anti-reflection coating.

Conclusion

The tutorial is now over. You have followed in the footsteps of one of the founders of the Langmuir-Blodgett technique and replicated one of the first attempts at a commercial application for a Langmuir-Blodgett film. You should have gained at least a basic knowledge of Langmuir-Blodgett and some of the features and commands available on the Nima trough.

Many more details are given in the 'Software', 'Langmuir-Blodgett' and 'Experiments' chapters. We hope that you found this taste of the science of Langmuir-Blodgett enjoyable. If you have any problems or questions do not hesitate to get in touch with us at the address below- we will be glad to help:

info@nima.co.uk

or visit our help site at:

www.nima.co.uk/help

EXPERIMENTS

Introduction

This chapter takes you through several experiments aimed at giving you a good working familiarity with amphiphilic, mono-molecular films or 'Langmuir' films. It also gives advice on how to prepare and operate the Langmuir trough.

The theory behind mono-molecular films can be found in the 'Langmuir-Blodgetty' chapter of this manual.

It is assumed that your laboratory supervisor will have already set up your trough, so that you won't have to set it up on the PC or calibrate anything. If it has not been set up, please see the 'Getting Started' chapter of this manual.

This chapter (and indeed the whole manual) may be copied and distributed to students - provided this is for educational purposes only.

Preparations

Before each experiment is carried out the film balance and materials which are to be used must be prepared. Before any of the experiments are carried out, the film balance must have been cleaned and calibrated as per the instructions below.

Safety

Before using any solvent, familiarise yourself with the relevant safety procedures. Solvents must never be inhaled or touch your bare skin. Work in a fume cupboard when making up the solutions. When making up solutions of metal ions such as cadmium, always wash your hands afterwards to prevent accidental ingestion.

Check with your laboratory supervisor on safety regulations and correct disposal after use. Remember you are responsible for your own and other's safety.

Materials

Solvents used to disperse surface active species should be as clean and pure as possible as should all volumetric flasks and glassware which come into contact with them. Non-contaminating methods should be devised for the weighing out and transfer of materials. Care should be taken to ensure that all metal- and glass-ware are kept clean and kept only for use with the trough.

The water used in the film balance should be as pure as is possible. The quantity of particles, ions and surface-active materials should be kept to such a low level that they will not significantly affect the surface properties of monolayer systems.

General cleanliness

When studying mono-molecular layers which contain at most a few milligrams of material, even a small amount of contaminant can cause serious errors. The trough, Wilhelmy plates and other apparatus involved with the operation of the film balance must be kept as clean as possible. Extraneous greasy material concentrates at the air-water interface; the source of such contamination is usually grease from fingers or hair, this being transferred to the subphase by supposedly clean instruments which have been handled.

Clean tweezers should always be used and for all operations it is advisable to wear disposable, powder-free polythene gloves. It is recommended that the syringes used for deposition are cleaned in between use and that they are rinsed at least once with the solution to be deposited. Clean laboratory coats should be worn, not only for protection but also to prevent the deposition of fibres from clothing onto the subphase.

When not in use the trough should be kept empty of water, covered and out of direct sunlight. If being moved, the pressure sensor should be removed from the trough to prevent accidental damage.

The materials to be spread should be as pure as possible. Very small quantities of impurities, especially surface active contaminants, can radically alter the molecular areas and can affect the material's film forming characteristics.

Cleaning the trough

The trough is fabricated from Polytetrafluoroethylene (PTFE), a material which will not contaminate the subphase. This polymer is essentially chemically inert, will not leach plasticiser and is the most hydrophobic polymer known. PTFE can be subjected to very rigorous cleaning procedures.

Wipe the trough surface and barrier to remove loose dust and any contaminants present from previous experiments. The barrier arm can be raised and the barrier lifted up for easy cleaning. Wear powder free gloves and use a surfactant free 'Kimwipe' tissue soaked in chloroform for best results. If you are not working in a fume cupboard (and/or safety regulations do not permit use of chloroform), use a light alcohol such as ethanol or isopropyl alcohol.

In general the best way of keeping the trough clean is to use it regularly and to avoid unnecessary collapse of mono-molecular films. The tissues used to wipe the surfaces must be surfactant free, for example, 'Kimwipes' type 7105, available from Kimberly-Clarke. Other tissues, even if they are 'guaranteed 100% clean' may contain amphiphiles that prevent formation of pure monolayers.

Fill the trough with the cleanest available deionised water until it brims just over the top by about 2mm - giving plenty of leeway for water removal during surface cleaning. If the material to be studied as a monolayer is changed, the trough should be emptied of water and thoroughly cleaned in between each experiment.

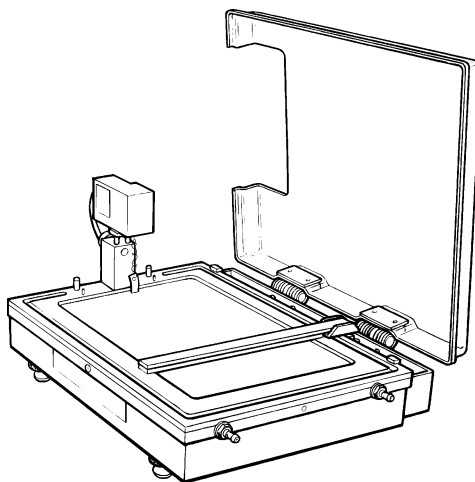


Figure 4.1: Nima Student Film Balance - pressure sensor is mounted at far end.

Pressure sensor

Check the calibration of the pressure sensor:

1. Attach the empty weighing pan and zero the pressure reading.
2. Add the 100mg calibration weight.
3. The reading should now be -46.7 ± 0.5 mN/m.
4. If it is not, follow the instructions in the 'Calibrate Pressure Sensor' Menu.

Once the pressure sensor has been calibrated, a clean 'Wilhelmy plate' has to be suspended from the meter arm. If the pre-cut plates have run out, cut out a 22mm long and 10mm wide plate, from a piece of filter paper.

Lower the Wilhelmy plate into the subphase so that it is just submerged and allow it to stand for a couple of minutes. Ensure that the barrier is fully open (furthest away from the pressure sensor). Zero the pressure sensor, first making sure that the filter paper is freely suspended at the air-water interface. Check that raising the plate out of the water produces a pressure change of about 70 mN/m (the exact value for pure water in an atmosphere of saturated water vapour at 293K is 72.8 mN/m). If the change is within 5 or 6 mN/m, do not worry at this stage as the surface is probably not yet clean. If the change is very much more or less, check the pressure sensor once more and if necessary, repeat the calibration procedure.

Cleaning the subphase

Once the pressure sensor has been calibrated and set up with its Wilhelmy plate, begin to close the barrier. The barrier should not be closed too quickly: for monitoring the cleanliness of the subphase a speed of about 250cm²/min is recommended. As the barrier is being closed, watch the pressure reading increase. Any pressure increase is due to contaminants on the subphase surface. Once the barrier is closed to its minimum area, clean the subphase surface by means of the PTFE nozzle (provided in the Monolayer Kit) connected to the suction pump. If the water level drops below the bottom of the Wilhelmy plate, lower the plate until it is once more submerged. Once the surface appears to be clean, open the barrier fully, re-zero the pressure sensor and close the barrier. If no increase in surface pressure is observed on compression the surface can be regarded as clean - if not repeat the cleaning and compressing processes.

Once the subphase is clean, open the barrier fully and cover the trough with its clear acrylic cover to prevent contamination from the atmosphere.

A typical pressure-area isotherm

The following steps are recommended to take an isotherm:

1. Clean the trough thoroughly with a Kimwipe (soaked in chloroform) and the plastic gloves provided.
2. Make up a solution of 1mg/ml arachidic acid in chloroform.
3. Fill the trough with clean water.
4. Close the barrier(s) by clicking on 'C'.
- the barrier(s) will move to their 'close-to' position.
5. Aspirate the surface of the water enclosed by the barrier(s).
- keep your eye on the pressure reading.
6. Open the barrier(s) by clicking on 'O'.
-the barriers will move to their 'open-to' position.
7. Zero the pressure sensor by clicking on 'Z'
- the current surface tension will be defined as zero surface pressure i.e. 0mN/m.
8. Take an isotherm without molecules by clicking on 'Barrier' and 'Isotherm'
- the barriers will close and the isotherm will be displayed on the screen. If the trough is clean, the curve will be horizontal on the X-axis. If there are surfactants on the surface, a small rise in pressure will be observed at smaller areas. Please note that the axes are set to 'auto-scaling' and adapt themselves to the data recorded.
9. Clean the surface again with the aspirator.
10. Zero the pressure sensor.
Whenever some water has been sucked out of the trough, it will have to be re-zeroed.
11. Open the barriers and spread the solution from the micro-litre syringe.
Wait for the pressure to return to 0.0mN/m - this indicates that the solvent has evaporated. If the pressure does not return to zero, you have spread too much and will have to remove some monolayer with the pump.
12. Take the pressure-area isotherm
- you should now see a good pressure area isotherm of arachidic acid on water.
13. Stop the barrier by clicking on 'STOP'
If you do not, the barrier will continue until it passes its 'close to' area and then a message saying 'barrier too closed' will appear. The barrier will then be stopped automatically.

Experiment 1

The spreading of a monolayer & the visual observation of its physical presence

Introduction

When a drop of oil is placed on a clean water surface it may behave in one of three ways:

1. It may not spread at all but remain as a 'lens' floating on the water surface.
2. It may form a thin film (sometimes called a duplex film) which spontaneously spreads and may show interference colours - implying a thickness of hundreds of layers.
3. It may spread to form invisible monolayers, leaving excess oil in lenses on the monolayer surface in equilibrium with the monolayer.

The spreading behaviour for any given material is determined by the difference between the cohesion that its constituent molecules have for each other and the cohesion which they have for the water molecules in the bulk of the subphase.

Stable monolayers are obtained with substances possessing both hydrophilic and hydrophobic characteristics. Such molecules have an affinity for water at one end and a repulsion for water at the other.

In studies of floating monolayers, such amphiphilic materials are often deposited onto the water surface in solution. The solvents used are such that they are not miscible with water and yet are volatile enough to evaporate completely at room temperatures leaving behind oriented amphiphilic molecules.

The amphiphatic balance of the molecules under study is critical if they are to form floating monolayers; hydrophilic head groups such as; $-\text{COOH}$, $-\text{OH}$, NH_2 or $-\text{CN}$, when attached to hydrophobic hydrocarbon chains of at least 14-16 carbon atoms in length will form oriented layers.

Requirements

Trough cleaned and calibrated, stearic acid (octadecanoic acid), chloroform.

Experimental

Make up approximately 5ml of 1mg/ml stearic acid in chloroform - the exact concentration is not important.

Fill the trough with deionised water. It is interesting at this stage to observe just how high the water meniscus can be above the (well cleaned) PTFE trough. Try filling it until it brims over. You should be able to observe that the water level is up to 4mm above the level of the PTFE. (For an explanation of this, go to the library and look up M.Lösche & H.Möhwald, Review of Scientific Instruments, vol. 55 (1984) page 1968.)

Remove the water from the trough by means of the suction pump until it is level with the PTFE. (It is a good idea to 'vacuum clean' the water surface while you're doing this - try to suck off all the little bits of dust that invariably settle on the water surface.)

Close the barrier to 100cm² and start spreading the stearic acid solution dropwise from the syringe in the 'active' part of the trough i.e. the end with the pressure sensor.

Initially, each drop will expand outwards, leaving the chloroform to evaporate and the stearic acid molecules anchored on the water surface. After several drops however, the rate of drop expansion will decrease dramatically until one drop will not expand at all and just float as a lens on the surface. Spread just two or three more drops at different places at this point.

You should now see several droplets on the water surface 'locked' in place by the invisible monolayer. Try gently blowing on the water surface. The droplets will move and return to their original position - showing how elastic the monolayer is.

Now open the barrier to about 200cm² - the droplets will now expand and disappear from view. The area has now increased, allowing more molecules to occupy the surface.

Repeat the experiment to check that the first result was no accident - add drops until lenses appear and then increase the area once more.

Now slowly decrease the area to about 30cm². You will be compressing the monolayer all the way to its 'collapse' - that is where it no longer is a monolayer. If you look at the surface carefully, you will see a slight clouding of the surface and then some white streaks running parallel to the barrier - these are agglomerations of collapsed stearic acid - rather like mountain ridges created when the earth's tectonic plates collide.

Remove all the collapsed film from the trough.

Discussion

You should now have some appreciation of the physical idea of a monolayer. Think of its effect on the water surface - what does it do to the surface tension? Repeat the above experiment with the water level 4mm above the PTFE. Can you predict what will happen?

Finally, imagine life in two dimensions. How would you describe the effect of the suction pump if you did not know of the existence of a third dimension?

Experiment 2

The observation of molecular flow during compression

Aims of the experiment

The motion of a mono-molecular film on water surface can be difficult to visualise if the amphiphilic material which has been spread onto the subphase is colourless. The movement of the mono-molecular layer can be visualised by placing a powder such as talc onto the water surface and observing the effect the floating monolayer has upon it as it spreads and as it is compressed.

Such observations, originally carried out by Henri Devaux, were reported by Irving Langmuir in his paper '*Fundamental properties of solids and liquids II*' *J. Am. Chem. Soc* **39**, 1848, (1917). It is also worth looking up B.R. Malcolm, *Thin Solid Films*, 178 (1989) 17 and H. Kumehara, T. Kasuga, T. Watanabe & S. Miyata, *Thin Solid Films*, 178 (1989) 175.

This experiment uses the same techniques to aid observation of the behaviour of monolayers as they are spread from solution, and as they are compressed and expanded by means of the barrier on the film balance. The similarity of the mono-molecular film to a flexible membrane is demonstrated.

Requirements

Trough cleaned and calibrated, 4 clean 10ml volumetric flasks, chloroform, stearic acid (octadecanoic acid), octadecanol, octadecylamide, octadecylamine, talc.

Experimental

Make up a 10 ml solution of approximately 1mg/ml of stearic (octadecanoic) acid in chloroform.

Ensure that the barrier of the trough is fully open and that the surface of the trough is free of contaminants. Gently blow dust powdered talc onto the surface of the trough so that the entire surface is covered by a thin talc layer.

Deposit one drop of the stearic acid solution into the centre of the trough. The solution should be deposited from a very small height above the surface by means of a syringe which has previously been rinsed with the spreading solution.

When the drop touches the subphase surface the talc will be immediately pushed back, forming an area of apparently clear water. What effect does the gradually evaporating spreading solution have on the apparently clean area?

Add a further drop of solution to another talc covered area of the trough. Does the second drop behave in a similar manner? Does its addition cause any distortions to the first circle? If drops are continuously added to an area where there is already a mono-molecular film present, the area of the mono-molecular film will continue to expand until all the talc has been pushed to the sides of the trough. What is the effect of adding further drops of stearic acid solution?

If the barrier is closed the mono-molecular layer will be seen to push the talc covered water surface in front of it towards the pressure sensor, the motion will be observed in the particles almost the instant that the barrier begins to move. If no film was present the particles of powder would not move until the barrier was very close enough to them.

Clean the surface of the trough thoroughly of all the talc and all the stearic acid monolayer by means of the aspirator pump. Top up the water level and check that the surface is clean by running a 'blank' isotherm without any molecules.

Once the surface is clean and the barrier fully open, deposit 4 drops of stearic acid solution in the centre of the trough and allow it to spread until it covers a large area of the subphase, sprinkle talc onto the **monolayer** covered surface only. Gently blow the dust covered film towards the pressure sensor end of the trough. Slowly begin to close the barrier. The talc free area adjacent to the barrier will become smaller until all the area between the barrier and the pressure sensor end of the trough is talc covered. Once such a situation has been achieved stop closing the barrier and make a note of the area 'A' to which the barrier has been closed.

If the barrier is closed further than 'A' the film will continue to be compressed for a while and unless it is compressed too far, it will behave as a stretched membrane would. The monolayer can also be expanded by opening the barrier, but only as far as area 'A'. If the barrier is opened further than point 'A' the monolayer will cease to expand and will no longer follow the motion of the barrier.

Not all monolayer forming materials behave in the same manner as does stearic acid. Some materials form much more viscous monolayer films which do not 'flow' as easily.

Interactions between the molecules themselves and between the molecules of the film and the subphase are primarily responsible for the different flow behaviour which can be observed by repeating the above experiment with different film forming materials.

Make up a solutions of similar concentrations to that of the stearic acid solution made up previously, of octadecylamine, octadecanol and octadecylamide. With each material repeat the second experiment - observing the manner in which the floating monolayer pushes the powder particles while the barrier is being closed.

Discussion

Were any significant differences observed between the behaviour of the different amphiphiles deposited? How can they be accounted for with regard to the properties of the hydrophilic end groups? Could you suggest any modification which could be made to the trough in order to use it to measure the viscosities of floating monolayers?

Experiment 3

Determination of the area occupied on the water surface by a fatty acid molecule

Aim of the experiment

By monitoring the changes in surface pressure observed while compressing a stearic acid monolayer a surface pressure-molecular area isotherm is constructed and the molecular area of stearic acid is calculated.

Requirements

Trough cleaned and calibrated, stearic acid (octadecanoic acid), chloroform.

Experimental

Make up a solution of stearic acid in chloroform; the concentration should be approximately 1mg/ml. Make up 10mls of solution and note the exact concentration.

Draw up 50 micro litres of the solution into the syringe (which should have been rinsed several times with the solution to be deposited) deposit the solution 'drop by drop' onto the water from just above the surface. Leave the solvent to evaporate until the pressure returns to 0.0mN/m.

To prevent contamination during the course of the experiment make sure that the transparent cover is on the trough.

Begin closing the barrier at a speed of about 250 cm²/min. As pressure begins to increase, slow down the compression rate - to say 50cm².

As the barrier is closed further and the surface pressure begins to increase quickly, decrease the speed further. Do not allow the surface pressure to increase much over 45 mN/m as the film may collapse. Film collapse will be dealt with in more detail in another experiment.

Slowly open the barrier fully and repeat the compression process, once more taking care not to compress the monolayer too much, again taking note of the surface pressure and area.

Discussion

A floating monolayer will lower the surface tension of the subphase, The decrease in surface tension is termed the surface pressure and this is the quantity which is being measured by the pressure sensor. The surface pressure varies with the area and as the molecules on the surface are behaving as a two-dimensional gas they can be described by the following relationship (under ideal conditions):

$$PA = KT$$

Where 'P' is the surface pressure, 'A' the area, 'K' Boltzmann's constant and 'T' the thermodynamic temperature. A surface pressure-area plot such as the one you are producing is known as an isotherm as the compression is taking place under constant temperature. The shape of the isotherm is characteristic of the surface-active substance being compressed. Every isotherm shows a variety of different gradients and phases - each describing a part of the compression process as the film becomes more and more ordered due to the pressure being applied to it by the barrier.

Stearic acid is a fairly 'classical' surface active material and its isotherm is not difficult to interpret. Initially very little increase will be observed in the surface pressure as the molecules are randomly distributed on the subphase surface with no ordering and are behaving as would be expected of a two-dimensional gaseous phase. The above equation holds well in this phase.

Further reduction of the surface area leads to increases in the surface pressure as the inter-molecular spacing in the subphase enter the range of the $1/r^2$ coulomb forces. Also, the hydrophobic chains which were originally oriented randomly near the surface of the subphase begin to be lifted away from the bulk of the subphase. This state is usually called the 'liquid expanded' phase.

When the surface area of the monolayer film is further reduced, the rate of increase of surface pressure is even greater. An almost vertical linear relationship between surface pressure and area characterizes the onset of the closely packed and highly ordered 'liquid-condensed' phase. In this phase the stearic acid molecules are almost standing upright with the hydrophobic tail group nearly perpendicular to the subphase.

The liquid-expanded and liquid condensed phases have been shown* to be just two of several liquid crystal phases that a monolayer can exist in.

Plot the readings on a graph of surface pressure against area.

Knowing the volume of solution initially deposited on the subphase surface and the concentration of the original solution, calculate the number of molecules which were deposited on the surface of the subphase.

Calculate the area per molecule in Ångstroms (1 Ångstrom = 10^{-10} m) when the barrier is fully opened, and the area per molecule when the barrier is fully closed.

Rescale the y-axis in terms of area per molecule.**

* I.R. Peterson, *J Phys D*, vol23, 1990, p379 'Langmuir-Blodgett films'

** Your Nima software on the PC can of course do all this, but it is instructive to have done it yourself.

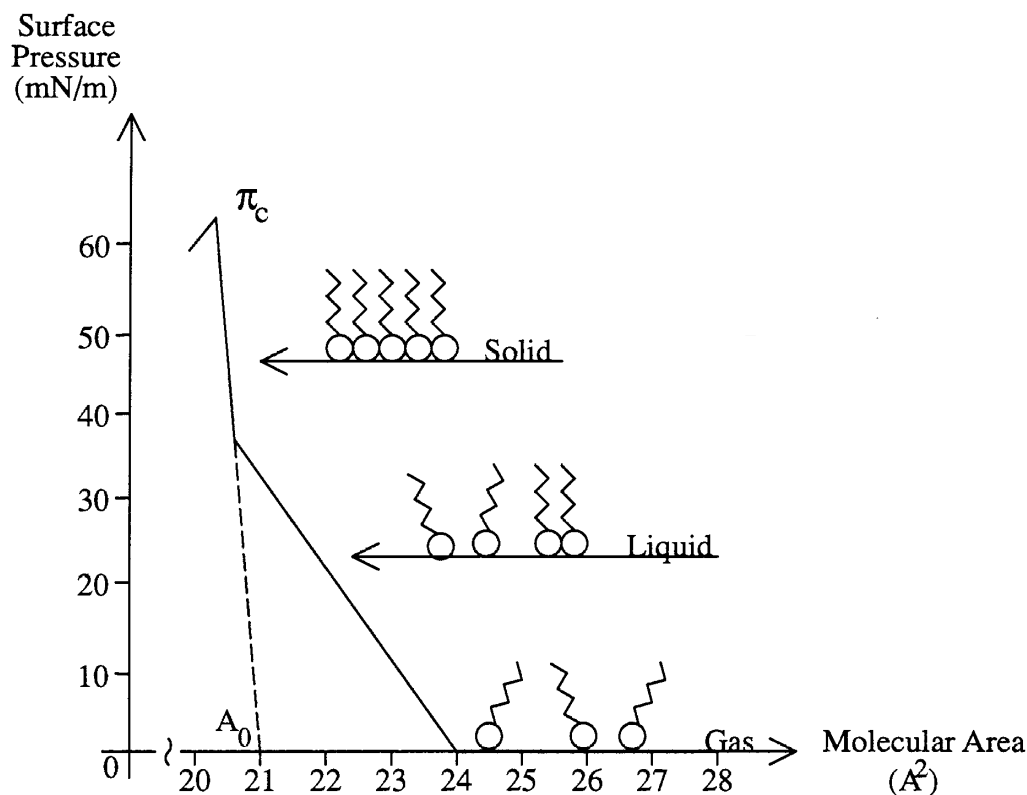


Figure 4.2: An idealised stearic acid isotherm showing molecular orientations

From the solid phase of the isotherm, when the molecules are closely packed it is possible to obtain quantitative information on the molecular dimensions and shape of the molecule under study. The molecular area (A_0) can be obtained by extrapolating the slope of the 'solid' phase to zero pressure (Fig 4.2) - the point at which this line crosses the x-axis is the hypothetical area occupied by one molecule in the condensed phase at zero pressure.

For a fully saturated alkanic acid the molecular area determined in such a manner is 22-25 Å². Does the area which you calculated for stearic acid fall into this range? Such an area corresponds to the cross sectional area of a hydrocarbon chain. This information first led Langmuir and others to suggest that the compressed monolayer consists of closely packed vertically oriented chains.

How does the isotherm for the second compression differ from that of the first? If there are differences how can they be accounted for?

Experiment 4

Determination of the collapse pressure of a fatty acid.

Aim of the experiment

This experiment looks at what happens to a mono-molecular film when it is compressed past the point when it behaves in an elastic manner. The collapse pressure (π_c) of stearic acid is determined.

Requirements

Trough cleaned and calibrated, stearic acid (octadecanoic acid), chloroform.

Experimental

Repeat Experiment 3, but this time continue to compress the stearic acid until the surface pressure has climbed to a value over 40mN/m. Compress the film very slowly at this stage. Eventually the surface pressure increase will stop, begin to level off and eventually fall sharply.

Look at the surface of the monolayer, it may be possible to see striations on the film surface, these are areas of collapse. Open the barrier slowly and note the shape and position of the isotherm on the x-axis. Compress the film again and note the area at which the film collapses and compress an extra 50 cm². Relax and recompress the film.

Discussion

Plot a graph of surface pressure against area, the maximum of the isotherm is known as the collapse pressure (π_c) and for a saturated alkanolic acid such as stearic can have a value in excess of 50mN/m.

At the collapse pressure some of the monolayer irretrievably loses its mono-molecular form. The forces exerted upon it become too strong for confinement in two-dimensions and molecules are ejected out of the monolayer plane to form a new phase. Molecular layers are piled on top of one other resulting in disordered multilayers.

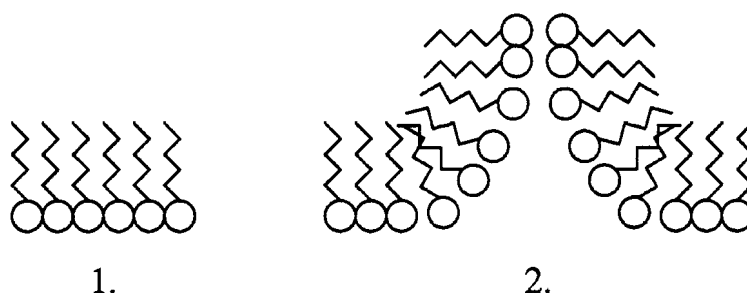


Figure 4.3: Illustration of monolayer collapse

The compressive forces which some monolayers can withstand are very high. If a molecule 25 Ångstroms in length is subjected to a force of 1 mN/m in a compressed monomolecular film, calculate the three-dimensional equivalent force which would be acting on it.

What will be the three dimensional equivalent pressure acting on your molecule at the collapse pressure determined in this experiment?

What effect did collapsing the film have on successive isotherms? Devise a model to validate your experimental observations. How would you test that this model was any good?

Experiment 5

Effects of structural changes in the hydrophobic tail group on the isotherm.

Aim of the experiment

Changes within the structure of the amphiphilic material have a marked effect upon the monolayer properties and hence on the shape of the isotherm. This experiment compares the pressure-area isotherms of three fatty acids with hydrocarbon chains of different lengths, and two acids which have the same number of carbon atoms in their hydrocarbon chains as stearic acid but have a carbon - carbon double bond as part of their structure.

Requirements

Trough cleaned and calibrated, 5 clean 10ml volumetric flasks, chloroform, stearic acid (octadecanoic acid), arachidic acid (eicosanoic acid), behenic acid (docosanoic acid), Oleic acid (Z-octadeca-9-enoic acid) and elaidic acid (E-octadeca-9enoic acid).

Experimental

Prepare solutions of stearic (octadecanoic, 17+1 C-units long) acid, arachidic (eicosanoic, 19+1 C-units long) acid, behenic (docosanoic, 21+1 C-units long) acid, oleic acid (Z-octadeca-9-enoic acid) and elaidic acid (E-octadeca-9enoic acid). Each solution should be made up in chloroform to an approximate concentration of 1mg/ml. The exact concentrations should be noted. It is recommended that 10mls of solution are made up in each case.

Following the procedure outlined in Experiment 3, produce an isotherm for each species, determine also the collapse pressure for each acid. In between each determination ensure that the trough is thoroughly cleaned, small areas of collapsed film which are left by accident on the trough can induce premature collapse in floating monolayers if they come into contact with them.

Discussion

The most used materials in Langmuir-Blodgett studies have been the long chain saturated carboxylic acids which form very stable films and have therefore been very well characterised. In order for an acid of this type to be capable of orienting itself at an air-water interface a hydrophobic carbon chain of at least 13 carbon units long is required. Acids with hydrocarbon chains of lengths less than that tend to be water soluble. Changes in hydrocarbon chain length down homologous series are known to change the surface tension of a clean water surface to different extents. (An approximation known as Traube's rule states that for a given homologous series of amphiphiles the concentration required for an equal lowering of surface tension decreases by a factor of about three for each additional CH₂ group in the alkyl chain.).

What difference would you expect the different chain lengths to have on the molecular areas determined from isotherms, such as that determined for stearic acid in Experiment 3?

Experiments

For each saturated acid calculate graphically an absolute molecular area. (Molecular area at zero pressure). How do the molecular areas differ? Is this a surprising result?

The presence of a double bond within the structure of the hydrocarbon chain can have a marked effect on the packing within a compressed monolayer.

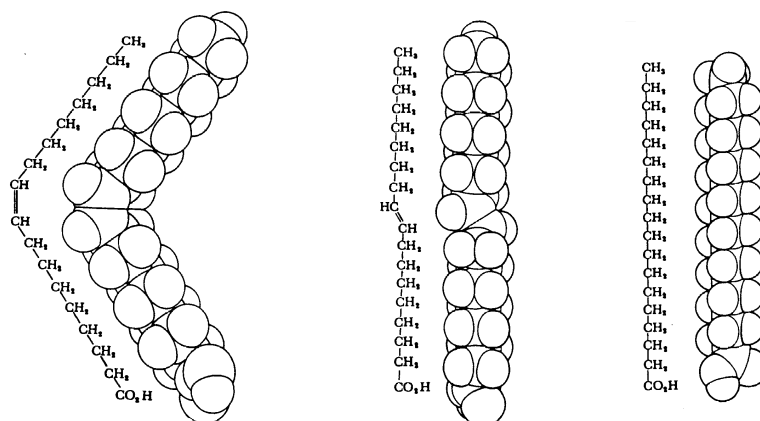


Figure 4.4: Skeleton and space filling formulas of oleic, elaidic and stearic acids. (Reprinted from 'Molecules for Langmuir-Blodgett film formation' *Phil. Trans. R.Soc. Lond A330*, by R.Hann)

Oleic acid (Z-octadeca-9-enoic acid) and elaidic acid (E-octadeca-9-enoic acid) differ only in the geometry of their unsaturated bond, both are related to stearic acid in that they all have 17 carbon atoms in their hydrophobic chains. The unsaturation has a great effect on their structures as can be seen above and hence will have a large effect on the manner in which they will pack at the air-water interface when compressed.

Plot an isotherm for each unsaturated acid and determine the absolute molecular areas. Are the molecular areas of each acid of the expected magnitude? What can you deduce about the orientation of each acid in the compressed film? What effect would a triple bond have upon the packing within a monolayer if it were located in a similar position in a similar acid?

Experiment 6

Observation of acid to salt conversion of an acid monolayer in the subphase.

Aims of the experiment

The effect of adding divalent metal ions into the subphase on the isotherm of stearic acid is investigated. The reaction between the monolayer and the metal ion containing subphase is carried out at different Cadmium chloride concentrations. The nature of the reaction and its effect on the monolayers behaviour is discussed.

Requirements

Trough cleaned and calibrated, stearic acid (octadecanoic acid), six 250ml volumetric flasks, cadmium chloride, aluminium chloride.

Experimental

Make up a series of solutions of cadmium chloride, using the same deionised water which is normally used to fill the trough. Then make up solutions of the following concentrations; 10^{-3}M , $5 \times 10^{-4}\text{M}$ and 10^{-4}M . In each case make up 250 ml of solution. **Take great care when handling cadmium chloride and the solutions, salts are irritants, the dust should not be inhaled; prolonged exposure can lead to damage of eyes, lungs and kidneys.**

Make up 10ml of a solution of stearic acid in chloroform of a concentration of approximately 1mg/ml. Note the exact concentration.

Following the procedure outlined in Experiment 3 produce isotherms of stearic acid on a clean water subphase and then, using in turn each of the CdCl_2 solutions prepared earlier as a subphase. The trough should be completely emptied in between experiments and cleaned. The cleanliness of the subphase surface should be checked just as it was when the subphase was pure water. **Check with your laboratory technician for the correct procedure for disposal of the metal ion solution.**

Discussion

The alkanolic acids are weak acids (the pKa of stearic acid is approximately 4.7) and are therefore very susceptible to ions in the subphase. Changing the pH of the subphase will have a marked effect on the hydrophilic acid head groups. If the subphase is very acidic i.e. pH 4, the acid will not be ionized and will therefore behave as an effectively neutral molecule. Due to dissolved atmospheric carbon dioxide pure water quickly attains a slightly acidic pH of about 5.5. At such a pH ionization will occur and carboxylate ions will be found in the film while hydrogen ions will be located in the subphase.

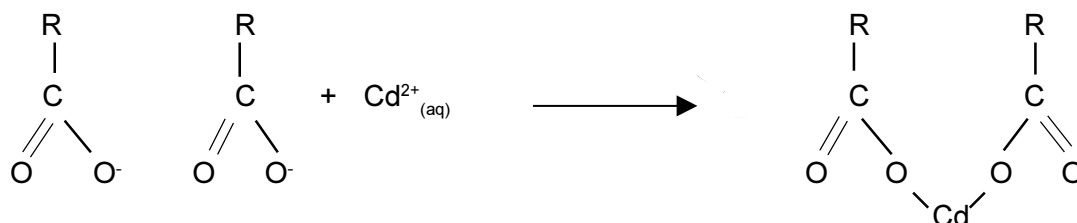


Figure 4.5: Reaction of Cd^{2+} with an alkanolic acid group

As would be expected, metal ions in the subphase will have a marked effect on the carboxylate anions, and will therefore affect the monolayer properties. Singly charged cations of group 1 metals such as Na^+ and K^+ , are particularly undesired, as the sodium and potassium salts of long chain fatty acids can be fairly water soluble and these 'soaps' may even form micelles in the subphase.

Divalent metal ions such as Zn^{2+} , Ca^{2+} , Cd^{2+} and Ba^{2+} have a marked effect on the monolayer properties.

How do the isotherms differ from those produced on a water subphase? Can any trend be observed due to the increasing Cd^{2+} concentration? Try 3 or 4 different concentrations ranging from 10^{-3}M to 10^{-4}M . Are the molecular areas calculated in each case different, and if so, why?

With increasing divalent metal ion concentration, the 'gaseous' part of the isotherm will be extended towards lower molecular areas and the 'liquid expanded' phase will shrink. This is a result of the reaction between the carboxylate ions and the Cadmium ions. Once each Cadmium ion has taken up 2 COO^- , all the dissociated fatty acid will have been converted to its salt.

Repeat the experiment but this time using similar concentrations of AlCl_3 in the subphase. How does the presence of a trivalent metal ion affect the shape of the isotherm? How does the size of the ion affect the calculated molecular area for the stearic acid? Does the way in which the film flows on the water surface change with the addition of divalent and trivalent ions into the subphase?

Experiment 7

A study of cholesterol films on water.

Aim of the experiment

The experiment determines the thickness of a floating monolayer of cholesterol. The molecular area of the molecule in a compressed film is also calculated. From these results and knowledge of the dimensions of the cholesterol molecule the approximate orientation of the molecule at the air-water interface can be calculated.

Requirements

Trough cleaned and calibrated, cholesterol, toluene.

Experimental

Make up a solution of cholesterol in toluene. Weigh out as accurately as possible 1mg of cholesterol into a 10 ml flask and make up to the mark with toluene.

Once the trough has been cleaned, the pressure sensor zeroed, and the barrier opened fully, follow the procedure described in Experiment 3 to record an isotherm of cholesterol. Deposit 50 microlitres of the cholesterol solution onto the water surface. Before closing the barrier allow the toluene to evaporate for 10 mins as the toluene is far less volatile than the chloroform which had been used to deposit the fatty acids and requires a longer time to evaporate.

Discussion

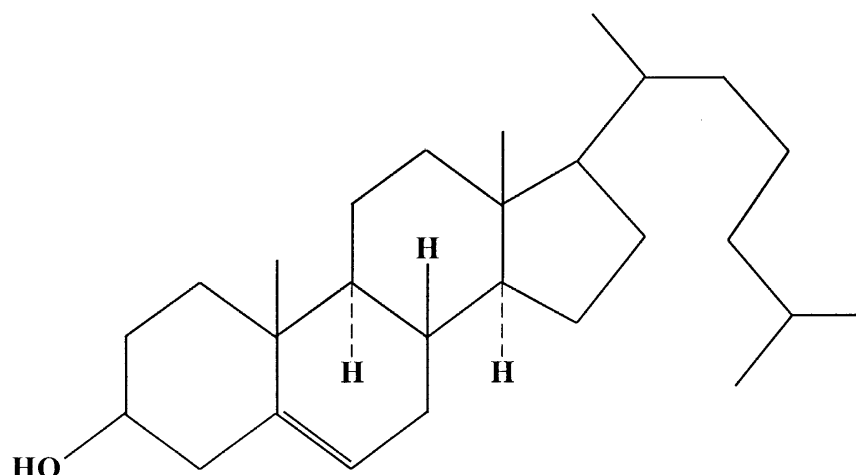


Figure 4.6: *The structure of cholesterol*

Experiments

Although cholesterol may not immediately appear to be a material which can be studied as a floating monolayer closer inspection reveals the presence of structural units vital for surface activity: a hydrophilic head group, the -OH group, and a large quantity of hydrophobic unsaturated hydrocarbon structure terminating in a six carbon unit long hydrocarbon chain.

Cholesterol's amphiphilic nature should not be surprising since, in common with other sterols, it is commonly found in membranes in many higher organisms. Many studies have been carried out on floating monolayers to elucidate the relationships between monolayers, bilayers and natural membranes,

From the isotherm obtained determine the absolute molecular area of cholesterol. Assuming that the cholesterol monolayer has the same density as a cholesterol crystal calculate the approximate thickness of the compressed layer. Calculate the approximate dimensions of a cholesterol molecule. (You will need to look up the lengths of bonds found in the molecule and the atomic radii of various atoms; these can be found in most organic chemistry text books.)

From the very approximate calculations of film thickness and molecular area experimentally determined, is it possible to deduce the orientation of the cholesterol molecules within the compressed film?

Finally, try to relate what you have learnt about cholesterol and its popular (or not-so popular) image. Do you think this image is justified? What would you do to control cholesterol concentration in your blood?*

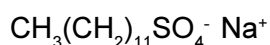
* You could discuss this in the bar after the practical (!).

Experiment 8

The determination of the critical micelle concentration of sodium sulphate from surface tension measurements

Introduction

Micellar solutions are formed by the aggregation of materials such as fatty acids which are soluble in both water and hydrocarbon solvents. Such surface active molecules ('surfactants') tend to orientate themselves at the air-water interface. Typical of this class of materials is sodium dodecyl sulfate or 'SDS':



In dilute aqueous solutions the surfactants behave as a normal solute - i.e. ionic as a normal electrolyte. When a specific concentration is reached, aggregates known as micelles are formed. This concentration is known as the critical micelle concentration or 'CMC'. These aggregates are roughly spherical and have the polar head groups pointing outwards:

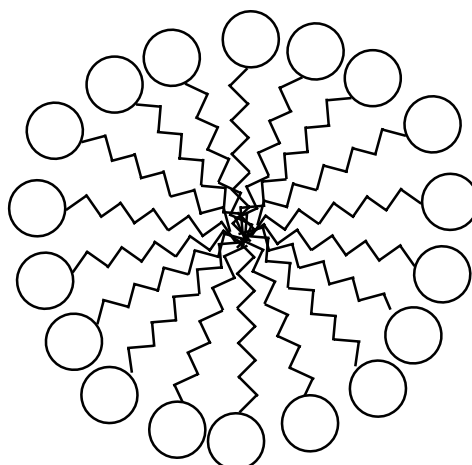


Figure 4.7: Illustration of the structure of a typical spherical micelle in an aqueous solution. Note all the polar head groups facing out and a minimum of internal space.

At the CMC, the physical properties of the solution change. There is more hydrogen bonding and the colligative properties of the solution are altered, as are the electrical properties such as conductivity.

Aim of the experiment

In this experiment the CMC of SDS is determined by monitoring the surface tension of an aqueous solution SDS. A series of solutions is prepared and from the resulting plot of surface tension v SDS concentration the CMC is determined.

Requirements

Film balance or tensiometer, suction pump for cleaning, sodium dedecyl sulphate, 1 clean 100ml volumetric flask, 10 clean 20ml beakers, chloroform, Kimwipes.

Experimental

Make up a 20 mmol/dm³ solution of SDS and from that stock make up solutions of 1, 2, 4, 6, 8, 10, 12, 14, 16, 18 & 20 mmol/dm³ in the 20ml beakers. The MW of SDS is 288.

Starting with pure water and then the least concentrated solution and working up to the most concentrated solution, measure the surface tension of each solution.

It is easiest to place the beaker with the solution under the pressure sensor and take the reading by gently lifting the paper plate out of the solution.

Note the temperature at which each of the measurements are made.

Plot a graph of surface tension against concentration of SDS.

Discussion and Questions

From the graph, determine the CMC of SDS. The CMC occurs at the break in the curve.

The surface tension after the minimum should tend to a constant value as the surfactant molecules have been removed into the micelles which are themselves not surface active and exist in the bulk of the solution.

Micellisation is an alternative mechanism to adsorption at the surface for surface active molecules, both decreasing the interfacial energy of the surfactant solution.

A value of the CMC of SDS at 40°C is quoted as being 8.6 mmol/dm³ on 'Surfactants and Interfacial Phenomena' by M.J.Rosen, Wiley, 1978.

There is no sharp transition between pre- and post-CMC behaviours. Why is a minimum usually observed?

How would the CMC be affected if the following were added?

1. Neutral salt.
2. An alcohol.

What effect would increasing the temperature of the solutions have on the CMC?

If an analog of SDS was used with a longer chain, what effect would that have on the CMC?

SOFTWARE

Introduction

This chapter is designed for reference only and need not be read completely. For a step by step guide of actual trough operation, please see the Tutorial chapter.

The operating software is organised as a graphics screen (the 'active screen') and a series of menus. All the 'action' takes place in the graphics screen in one of several axes such as 'pressure-area' as illustrated below.

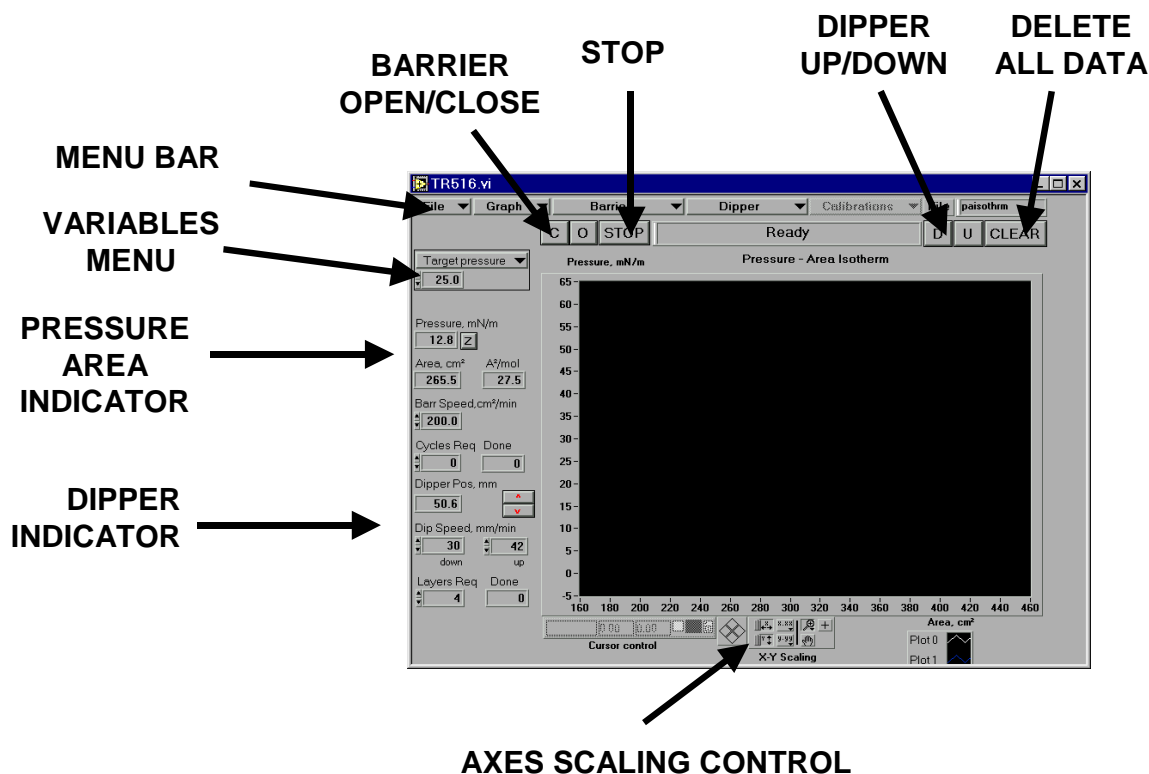


Figure 5.1: Main Screen of Nima Software

The active screen

The active graphics screen appears at power up. The main part of the screen is taken up by a graph. Then there is a menu bar running along the top with a series of 'drop down' menus. In the top right hand corner the most recently loaded file name is displayed - initially this is the 'standard' file. To the left of the graph is a margin displaying various sensor readings, such as surface pressure and area.

Other functions are available from the 'menu bar' running along the top of the screen. These menus are placed into logical groups such as 'File', 'Barrier', 'Dipper' etc.

Just below the menu bar are a series of large buttons. These are for often used functions such as opening the barrier ('O') or moving the dipper up ('U') or down ('D'). The same functions can be accessed via the menu bar. For instance to close the barrier, either click on the 'C' button or click on the 'Barrier' menu and then 'Close'.

The Variables Menu in the box at the top left of the screen allows access to less often changed variables, such as 'Target Pressure' or 'Cycle Max Area'. They can be changed

Menu Bar

'File' Menu

Load	Loads previously stored data
Save	Saves current data - give file name
Print	Gives print instructions - ALT-PrtScreen
Setup	Setup Menu - explained in detail later in this chapter
Signature	Nima address - in case you want to get in touch
Exit	Exit the program

'Graph' Menu

Pressure-Area	Selects pressure-area isotherm axes
P&A - Time	Selects pressure and area - time axes
Dipper-Area	Selects dipper-area axes (for deposition troughs only)
Transfer Ratio	Selects Transfer Ratio axes (for deposition troughs only)
Change Axes cm²<>Å²	Changes area axes between cm ² and Å ² /molecule (to values entered in Monolayer Menu)
Clear graphs	Clears all data in memory and from graphs

'Barrier' Menu

Monolayer Menu	Selects Monolayer Menu - explained in detail later in this chapter
Open	Moves barrier(s) to 'open to' area
Close	Moves barrier(s) to 'close to' area
Isotherm	Starts barrier moving and data logging
Pressure control	Compresses barrier(s) until target pressure is reached
Isocycle	Starts barrier moving under iso-cycle (see Monolayer Menu)
Coupled	Moves barriers in coupled mode (2B & MC option only)
Area control	Compresses barrier(s) until target area is reached
Stop	Stops barrier motor(s)

'Dipper' Menu

Dipper Menu	Selects Dipper Menu - explained in detail later in this chapter
Dipper Up	Moves dipper to top (or clockwise for alternate dipper)
Dipper Down	Moves dipper to bottom (or anti-clockwise for alternate dipper)
Program Dip	Starts pre-programmed dipping sequence
Dipper Stop	Stops dipper motor

'Calibrations' Menu

Interface Test	Runs interface diagnostic routine
Cali pressure sensor	Self
Cali potential sensor	evident
Cali temp sensor	- all
Teach barrier pos	explained
Cali barr speed	later in
Cali dip speed	this chapter!
Show cali data	Displays current area and speed calibrations.

'Variables' Menu

This menu changes the current variable available in the little box at the top left of the screen. It is useful to be able to change these 'secondary' variables without having to stop and enter a full menu.

Buttons

Keyboard

C	Closes barrier(s) to the 'close-to' area defined in the Monolayer Menu.	Home
O	Opens barrier(s) to the 'open-to' area defined in the Monolayer Menu.	End
STOP	Stops all motors	Esc
D	Down (<i>conventional dipper only</i>) moves dipper to bottom.	PgDn
U	Up (<i>conventional dipper only</i>) moves dipper to top.	PgUp
F	Forwards (<i>alternate dipper only</i>) moves dipper anti-clockwise.	
B	Backwards (<i>alternate dipper only</i>) moves dipper clockwise.	
CLEAR	Clears all data in memory and from graphs.	
A-B	A-B switch (alternate and multi-compartment troughs only) Switches action between A & B (when zeroing, opening/closing or displaying data).	
SYM	Symmetry button (2 independent barriers AND single compartment only) Switches between symmetrical and non-symmetrical compression of the barriers.	
Z	Zeroes pressure sensor-if AB switch present, then Z will zero either sensor A or B.	

Permanently Displayed Variables

Barrier Speed

Sets the barrier speed for isotherms. The range is approximately 5cm²/min to 1000cm²/min depending on trough type and gearbox ratio. It can be negative for expansions, annealing, hysteresis loops etc. The barrier speed can also be set in the Monolayer Menu.

Cycles Required Done

Sets the number of isotherm cycles required (only when iso-cycle function is selected in the Monolayer Menu). 'Done' displays the number already completed.

Dipper Speed up / down

Sets the dipper speed for depositions. The range is approximately 0.5mm/min to 50mm/min depending on dipper type (and gearbox ratio). The dipper speed can also be set in the Dipper Menu. For conventional dippers, separate 'up' and 'down' speeds are available.

Layers Required Done

Sets the number of layers required when dipping - can also be set in the Dipper Menu. 'Done' displays the number already deposited.

Variables Menu - selectedly displayed variables

These can be displayed by selecting the variables from the menu in the rectangular box at the top left of the screen.

Target pressure

This is the pressure at which the monolayer will be compressed to when running pressure control - can also be selected in the Monolayer and Dipper Menus.

Feedback gain

This is the speed of response under pressure control. The greater this number, the faster the barrier will compress the monolayer, according to the following algorithm:

$$\text{Barrier speed} = [\text{feedback gain}] * [\text{target pressure} - \text{actual pressure}]$$

If feedback gain is too large, the pressure control will oscillate out of control. Recommended values are 1.0 - 2.0 depending on aspect ratio of trough (the longer and slimmer the trough, the higher the gain).

Dip Top End

Sets the position to which the substrate will be raised (can also be set in the Dipper Menu)

Dip Bottom End

Sets the position to which the substrate will be immersed (can also be set in the Dipper Menu).

Cycle Max Area

The area to which the barrier(s) will be opened under iso-cycle control (but also check the 'Cycle Min Pressure' in the Monolayer Menu).

Cycle Min Area

The area to which the barrier(s) will be closed under iso-cycle control (but also check the 'Cycle Max Pressure' in the Monolayer Menu).

Target Area

This is the area at which the monolayer will be compressed to when running area control - area control is selected in 'Barrier' in menu bar.

Setup Menu

This is accessed from the 'File' Menu and allows you to configure the software to your particular trough.

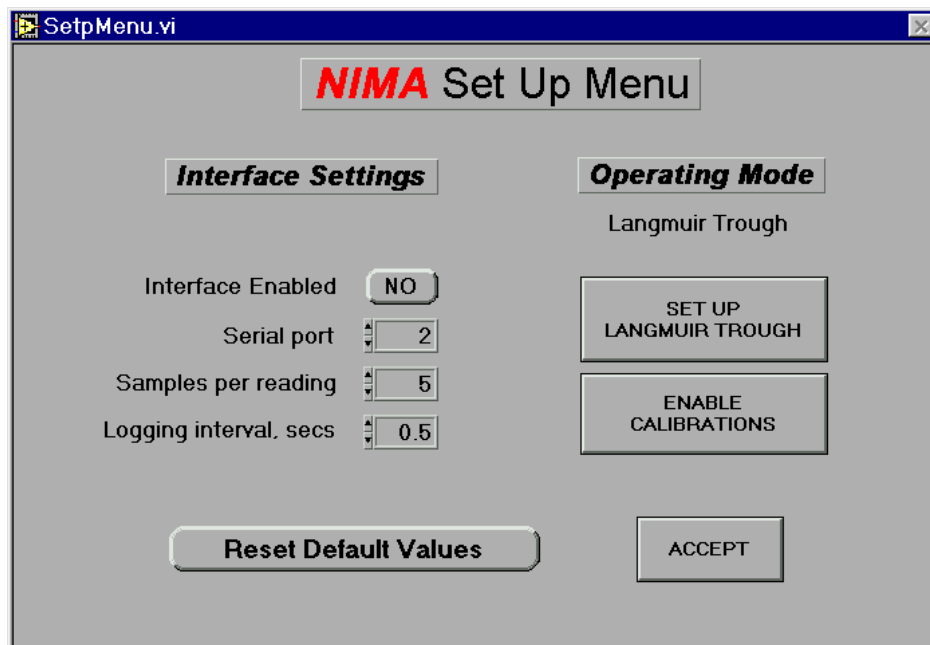


Figure 5.2: Setup Menu

- Interface Enabled** - **YES** if you want to control the trough.
NO if you want to run the software without the trough connected (for example when evaluating data in your office)
Please note that on some PCs the software will run very slowly when the interface is disabled AND there is no data loaded - so the software always loads a default isotherm on power up when the interface is disabled.
- Serial port** Selects the serial port on your PC that you have plugged the Nima interface into.
- Samples / Reading** This allows the PC to average the data returning from the interface, so the more samples the smoother the data, but the slower the response. Recommended value: 5
- Logging interval, secs** This is the time before the data is 'logged' into memory. If you are doing a long run, say overnight, you may wish only to log once every minute, so that your data files won't become too big. Typical value: 0.5 seconds.
- Set Up Langmuir Trough** Enters trough set up menu (described overleaf).
- Enable Calibrations** Gives access to 'Calibrations' in the menu bar.

Trough Setup Menu

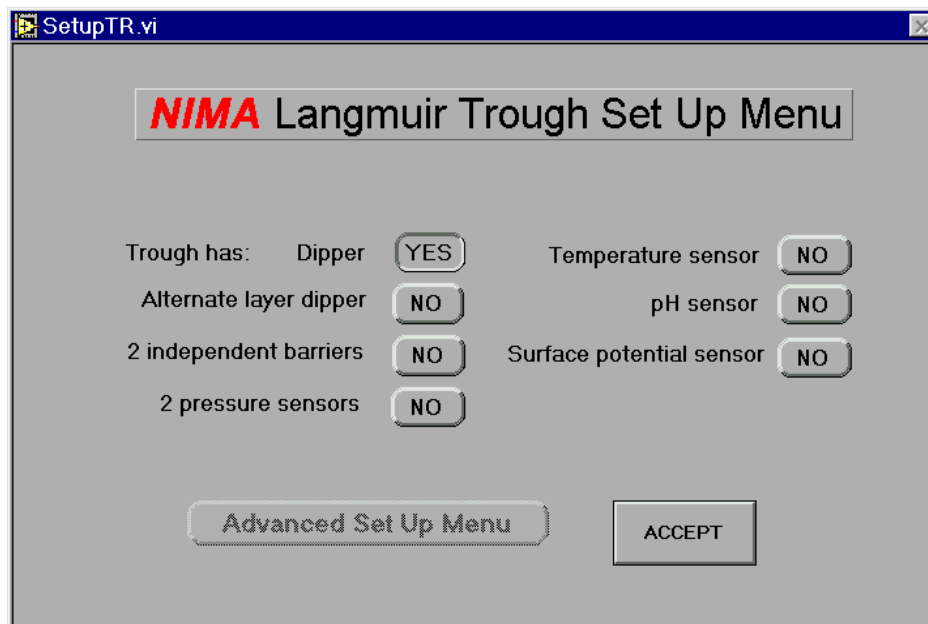


Figure 5.3: Trough Setup Menu

Dipper	YES if you have a dipper; NO if you don't
Alternate layer dipper	YES if you have an alternate layer dipper; NO if you don't
2nd independent barr.	YES if you have 2 barriers with 2 motors NO if you have only 1 motor (even if it's driving 2 barriers)
2nd pressure sensor	YES if you have an alternate layer trough NO for single compartment troughs
Temperature sensor	YES or NO
pH sensor	YES or NO
Surface potential sensor	YES or NO
Advanced Setup Menu	For custom made troughs To access this menu, download version 5.17 from our website.

Monolayer Menu

The Monolayer Menu is accessed from the 'Barrier' Drop Down Menu and is shown below:

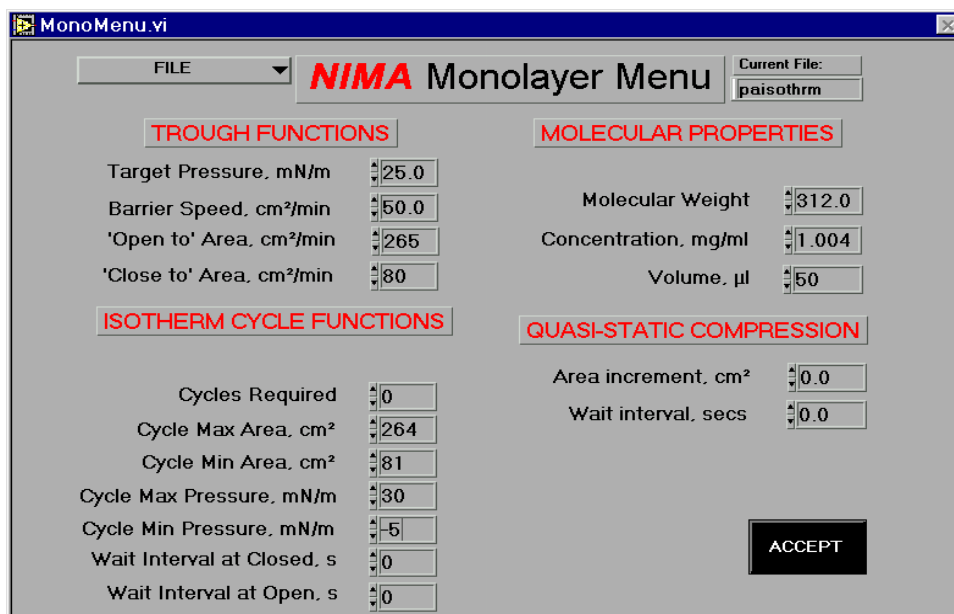


Figure 5.4: Monolayer Menu

This screen allows you to set up your isotherm run to your preferences. For instance you may wish to take a single isotherm or perform isotherm cycles. You may wish to move the barrier at a constant speed or in a 'quasi-static' way.

Entry of the molecular weight of your molecules, the concentration and volume of solution spread enables the software to calculate the absolute number of molecules spread on the subphase and hence convert the area on the subphase surface to an area per molecule.

TROUGH FUNCTIONS

Barrier speed The barrier speed of a compression run when taking an isotherm. Note that if you want to do a 'relaxation' (opening the barrier), please enter a negative barrier speed in the active screen.

Target pressure This is the pressure that the film will be compressed to under pressure control ('Pressure control' under 'Barrier' in the menu bar).

'Close to' area This is the minimum 'allowed' area. If your barrier moves to a smaller area, it will be stopped and 'barrier too closed' will be displayed. Click on 'O' to re-open it.

'Open to' area This is the maximum 'allowed' area. If your barrier moves to a larger area, it will be stopped and 'barrier too open' will be displayed. Simply click on 'C' to close it.

MOLECULAR PROPERTIES

Molecular weight Enter the MW of your molecule

Concentration, mg/ml Enter the concentration of your solution in mg/ml

Volume, μ l Enter the volume of your solution in μ l

Once the above data are entered, the computer can automatically label the area axes in area per molecule. MW and concentration are only printed to 3 decimal places but can be entered and are stored with greater accuracy.

A-B Switch between compartments (*alternate layer mode only*)

For an alternate layer trough (Model 622), molecule and solvent data are accessed one compartment at a time. Use this switch to select between compartment 'A' and compartment 'B'.

ISOTHERM CYCLE FUNCTIONS

It is possible to program the barrier(s) to compress and expand the monolayer repeatedly to observe hysteresis effects in isotherms. A choice of boundary conditions and the number of cycles is given. It is possible to cycle between defined areas (in cm^2) or defined pressures (mN/m) or between one of each. Please note that the barrier will reverse on the first parameter it meets, so you have to set both area and pressure parameters for the successful functioning of this routine.

Example 1

If you wish to cycle through the 'liquid-expanded' phase of a fatty acid, set the limit for minimum pressure to '0' mN/m and the limit for maximum pressure to about '30' mN/m. The area limits should then be set at points well outside the areas corresponding to these pressures, i.e. minimum area of 50 cm^2 and a maximum area of , say, 500 cm^2 (if you are using a 600 cm^2 trough).

Example 2

If you wish to cycle between the gaseous phase and the liquid condensed phase, typical values would be:

Max area: 500 cm^2 (for a 600 cm^2 trough).

Minimum π : -2 mN/m - better than 0 mN/m, as the pressure reading can on occasions drop below zero.

Min area: 50 cm^2 (or any low area value)

Maximum π : 45 mN/m - or whichever pressure you choose in the liquid condensed phase.

The barrier will then cycle between the max area and the max π limits.

Note - do not set the iso-cycle mode when dipping. Pressure will not be held constant and monolayer transfer will be inhomogeneous.

QUASI STATIC COMPRESSION

It is possible to make compression isotherms of monolayers 'quasi-statically' - that is to move the barrier by a defined area, wait for a defined time and then move the barrier again. This allows the monolayer to relax at each stage which is useful for stiff polymer films and for collapsing films. It can also help to improve the determination of phase changes during compression.

Select the size of area increment and the time interval between steps in this section. Then click on 'Isotherm' under 'Barrier' in the menu bar to perform a quasi-static compression.

FILE Saving and loading

The operating conditions can be saved and recalled on their own. If a particular set of conditions are frequently used, the 'standard' file can be overwritten to load these particular conditions at power-up. Please note that only the operating conditions file are saved/loaded here - no associated data files will be accessed.

Dipper Menu

The Dipper Menu is accessed from 'Dipper' in the menu bar and is shown below. This screen allows you to set up your LB deposition to your preferences. For instance you may wish to deposit a single layer or multiple layers. You may wish to move the dipper at a particular speed and wait a certain time between layers.

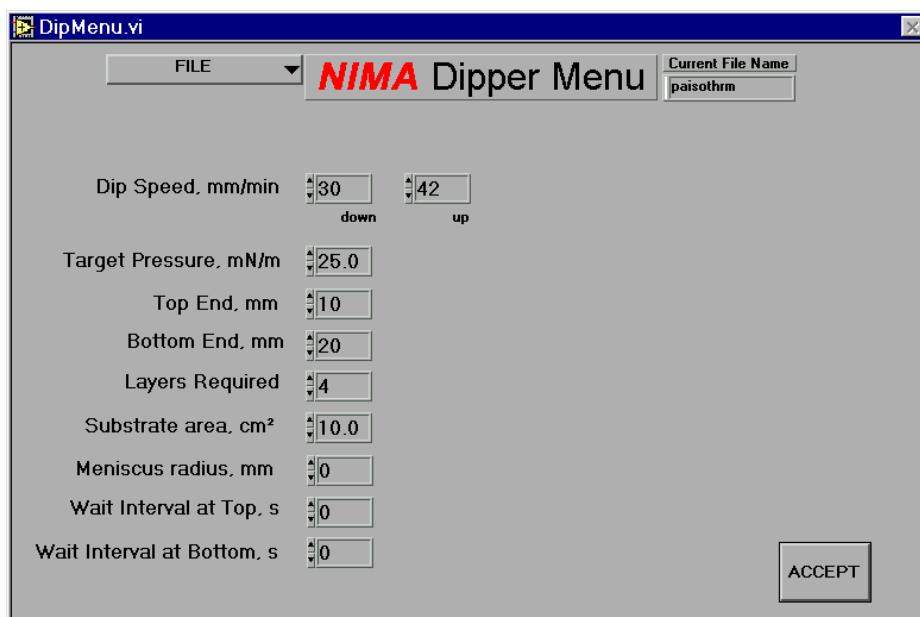


Figure 5.5: Dipper Menu (for conventional dippers)

Please note that the Dipper Menu for conventional LB dippers is shown here. The menu for the alternating dipper is shown in the 'Tutorial' chapter.

Dipper speed The dipper speed is the speed with which the substrate crosses the interface. Separate 'up' and 'down' speeds are available.

Target pressure This is the pressure that the film will be compressed to under pressure control. When the monolayer is transferred to the substrate, the barrier will be moved to keep the target pressure constant. This compensates for removal of monolayer from the surface during dipping.

Top End This is the level that the substrate will be raised to.
Dipper position is measured in mm immersion from the top - so a dipper position of 10mm means that the dipper is 10mm from the top. This is explained diagrammatically overleaf.

Bottom End This is the level that the substrate will be immersed to.

Layers Required This is the number of layers that will be deposited.

Wait at Top This value determines how long the dipper will wait at the top of its cycle.

Wait at Bottom This value determines how long the dipper will wait at the bottom of its cycle.

Substrate Area This value is used to determine if, after completion of an 'up' stroke, there is sufficient area left to deposit another 2 layers. If there is not, then 'Please open barrier and respread...' is displayed.

It is also used in the transfer ratio calculation (as explained in the 'Langmuir-Blodgetty' section). The substrate area is the total area immersed including both faces and the sides of your substrate (if thick enough), less the meniscus radius.

Hence, for rectangular substrates:

$$\text{substrate area} = 2 * ((\text{immersed length} - \text{meniscus radius}) * (\text{width} + \text{thickness}))$$

Meniscus Radius This value improves the accuracy of transfer ratio calculations. It is best to calculate the transfer ratio from the point at which the meniscus has 'flipped over', rather than the dip start position, as explained above and in the 'Langmuir-Blodgetty' chapter.

Setting 'top' and 'bottom' dipper positions - conventional dipper

The top and bottom positions are usually set so that the 'top' is where the substrate is entering the water subphase and the 'bottom' is where it is immersed.

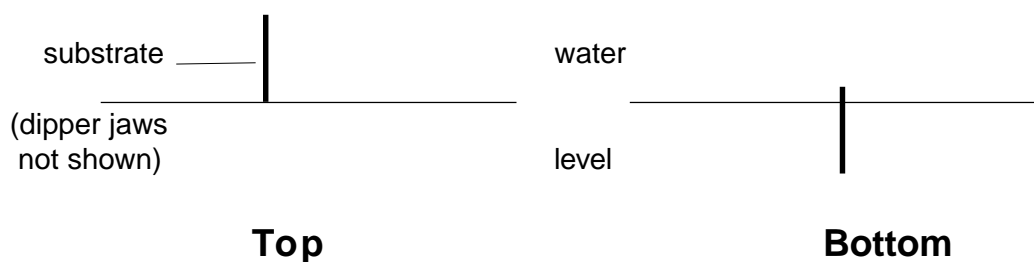


Figure 5.6: 'Top' and 'bottom' position for conventional dipper

Dipper Menu - alternate layer dipper

For alternate layer troughs the values of dip speed, target pressure and top & bottom ends are set separately. So, separate values for side 'A' and 'B' are displayed.

The 'top' and 'bottom' positions are illustrated graphically overleaf.

In addition, the following values need to be set as well:

Inter Dip Speed

This is the speed the dipper will move at in between side 'A' and side 'B'. This saves time, particularly when depositing large numbers of layers.

Alternate Layer Sequence

This is the sequence of layers deposited from side 'A' or side 'B'. Simply enter the sequence you require in the box. The number control in the little box lets you check exactly which number corresponds to which type of molecule.

Alternate layer dipper 'top end' & 'bottom end' positions

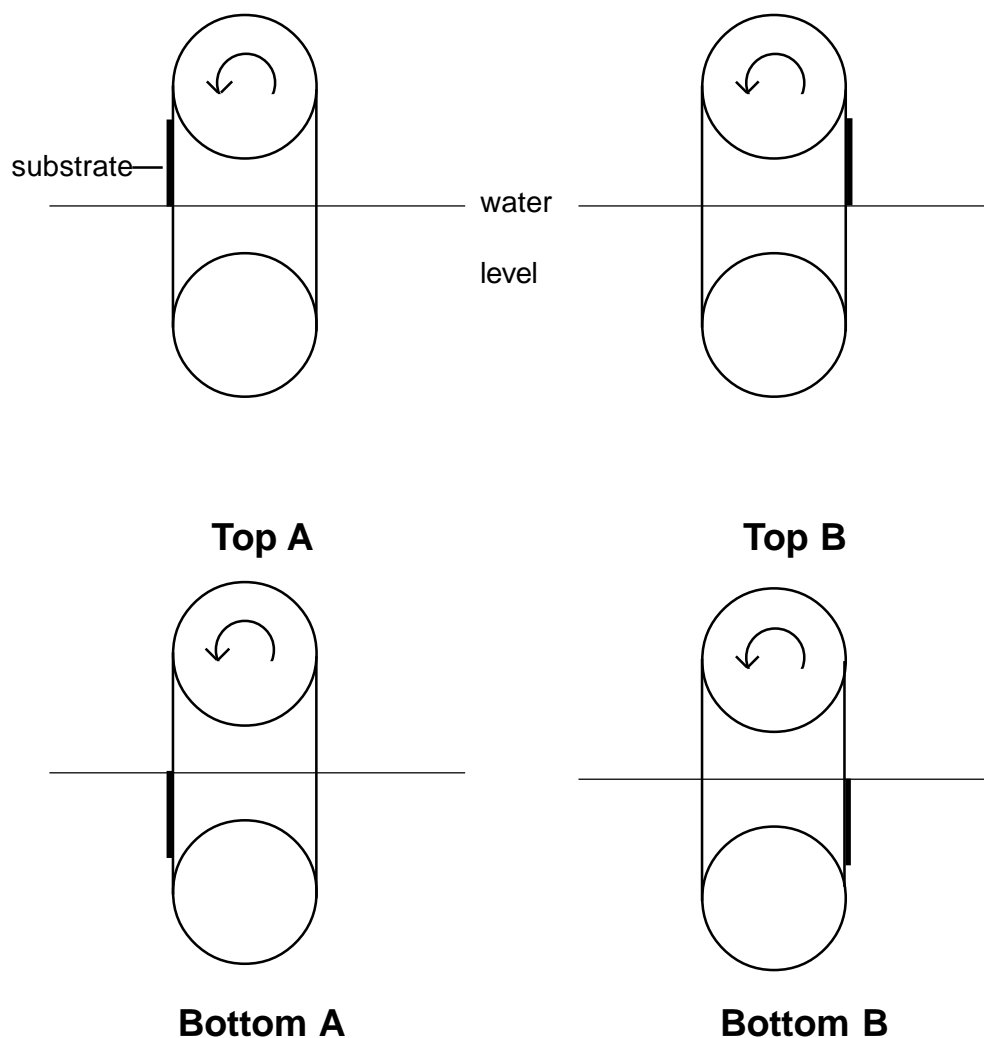


Figure 5.7: Alternate Layer Dipper 'Top' and 'Bottom' End Positions

The substrate is carried around the dipper - the arrows indicating the 'forwards' direction. The critical positions are illustrated above.

'Top A' is just as the substrate is about to be immersed in side A - typically 75mm.

'Bottom A' is when it is just fully immersed in side A - typically 100mm.

'Bottom B' is just before it emerges on side B - typically 190mm

'Top B' is immediately after it has completely emerged on side B - typically 210mm

These typical values are for a standard 76 x 26mm glass microscope slide. Other size substrates have different values, which are set before deposition commences.

Calibrations Menu

All motors and sensors are calibrated at Nima before despatch. Once calibrated, it is unlikely that the motors and potentiometers (position sensors) need to be calibrated again. However, the full calibration procedure is described here - just in case!

If you are updating your software, please load your new software into a new directory when installing the new version and then copy the old calibration files ('sensors.cal', 'install.dat' and 'standard.con') over to the new directory. This will save you having to recalibrate your trough.

The following options are given in the 'Calibrations Menu':

- Interface Test**
- Calibrate Pressure Sensor**
- Calibrate Potensial Sensor**
- Calibrate Temperature Sensor**
- Teach Barrier Positions**
- Calibrate Barrier Speed**
- Calibrate Dipper Speed**
- Show Calibration Data**

In order to gain access to the Calibrations Menu, please enable it in the Setup Menu.

Interface Test

This displays the 'raw' data as sent by the interface to your PC. It is also possible to move the motors 'manually' in this window. ***But take care - there are no safety stops and you can crash your barrier / dipper and you may cause damage to the gearbox.***

On entry, both interface and motors are disabled. Click on **Enable Interface** to start reading the sensors. The INPUTS should be reading real data and the 'V2' light on the interface should illuminate. If it does not, try changing the Serial Port No (bottom left of the screen).

Typical AD values are:

pressure sensor:	10,000 - 20,000
barrier:	15,000 - 25,000
dipper:	15,000 - 25,000

Click on **MOTORS DISABLED** to allow access to the slider controls on the right of the screen.

The following values apply:

0	▽	4095
open	STOP	close
up	STOP	down

ALWAYS STOP THE MOTORS BEFORE THEY REACH THE END OF THEIR TRAVEL!

Calibrate Pressure Sensor

It is good practice to check the calibration of the pressure sensor(s) before a series of runs, particularly if the data is to be published. It can be quickly checked by attaching the weighing pan and checking the indicated reading in mN/m for the calibration weight in the active screen - remember that for a 21.0mm perimeter Wilhelmy plate, 100mg is equivalent to -46.7mN/m.

To calibrate, select 'calibrate pressure sensor' from the 'Calibrations' menu and follow the instructions given on the screen. The readings of the pressure sensor are recorded with the empty weighing pan and with the calibration weight in the pan. These are then automatically stored on disc. The 100mg calibration weight (the small metal tab) and pan are to be found in the monolayer kit. Ensure that the correct calibration weight and plate perimeter are entered in the appropriate boxes. It is good practice to check the calibration weight on a 6 figure balance.

Calibrate Surface Potential

The surface potential probe is plugged into the 'PB' socket at the back of the interface. The surface potential option is enabled in the Setup Menu.

The software then guides you to bias the probe at two voltages 1.5V and 0.5V and the equivalent reading of this stored. Please note that the absolute value of voltage is not so important, as long as the difference is 1.0V. So you could choose 2.0 and 1.0V as well.

More details are given in the Technical Appendix.

Teach Barrier Positions

The 'minimum area' and 'maximum area' positions of the barrier have to be 'taught' to the PC. This is done by 'manually' moving the barrier to the correct position and then confirming the position and equivalent area of that position.

The barrier is moved with a slider control provided on the screen. There is also a STOP / CONTINUE button to instantly stop the barrier.

There are 4 different configurations for the various troughs made by Nima:

1. Standard - single barrier - Models 601A, 611M, 611D and 622(A&B separately)
2. 2 mechanically coupled barriers working symmetrically
- Models 601M, 601A/2B, 611M/2B, 611D/2B
3. 2 independent barriers working symmetrically but independently -Model 632/D1L
4. MC - 2 barriers with the ability to cross the centre line -Models 601/MC or 611/MC

These are explained in detail overleaf.

Teach Barrier Positions (continued)

1. Single barrier

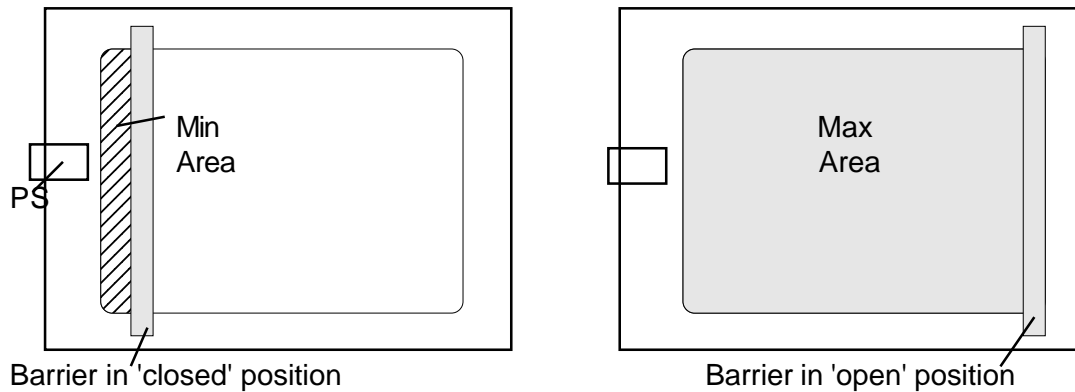


Figure 5.8: Teaching areas for single barrier troughs

The minimum area is the area at which the barrier is almost completely 'closed' - that is when it is nearest the pressure sensor ('PS' in the above diagram). It is good practice not to run the barrier to the end, so that when the minimum area is calculated, the curvature of the corners of the trough can be taken into consideration, thus giving a completely accurate area calibration.

To calculate the area, simply take an accurate ruler and measure the length x width. Please note that standard troughs have exact widths of whole numbers like 10 or 20cm. Most troughs have rounded corners of curvature of radius of 1cm. So $\frac{1}{2} \cdot (4 - \pi r^2)$ ($= 0.43\text{cm}^2$) has to be deducted.

The maximum area is that area where the barrier is furthest away from the pressure sensor and its trailing edge is just touching the edge of the trough. Again, measure the length x width less the area of the rounded corners.

Please note in the case of 622 troughs with 2 barriers and 2 separate compartments, this procedure is done twice, first for compartment A and then B (which has to use the same areas).

2. 2 barriers - symmetrical compression

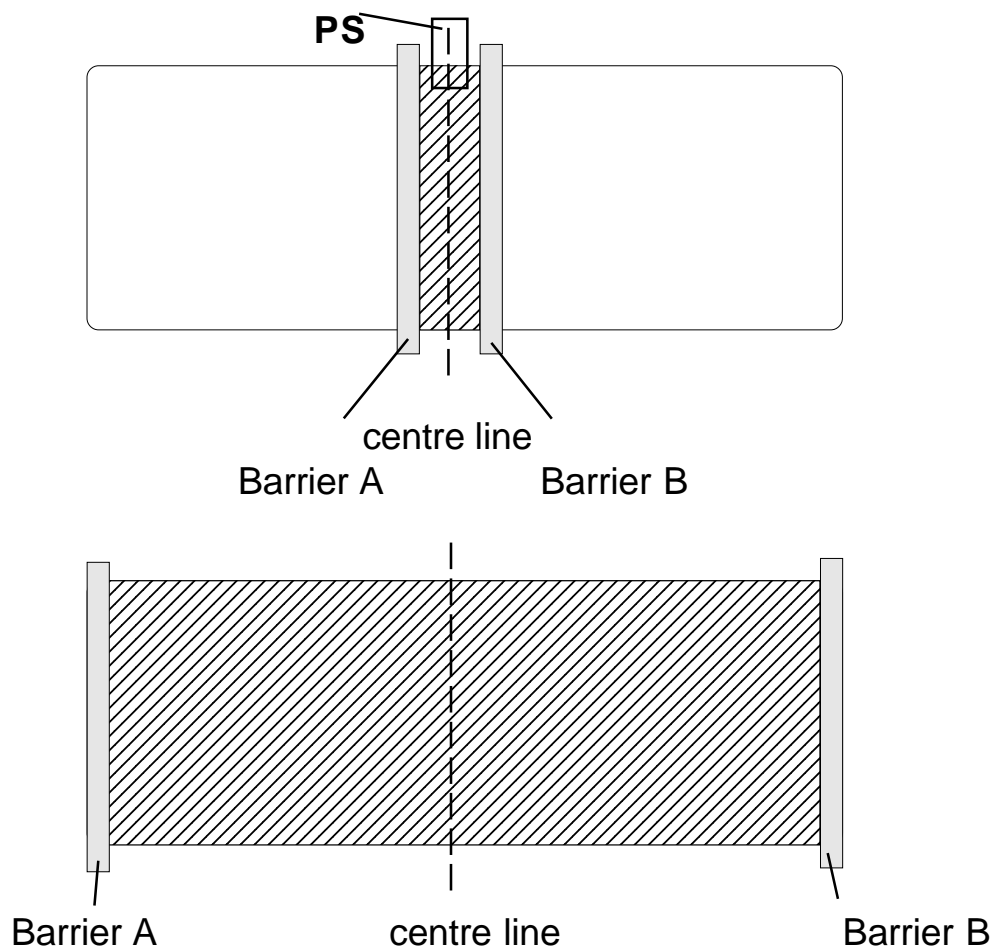


Figure 5.9: Teaching areas for troughs with 2 mechanically coupled barriers with symmetrical compression.

The minimum area is the area at which the barrier is almost completely 'closed' - that is when it is nearly at the centre line and almost touching the pressure sensor (PS).

To calculate the area, simply take an accurate ruler and measure the length x width. Please note that standard troughs have exact widths of whole numbers like 10 or 20cm.

The maximum area is that area where the barriers is furthest apart and their trailing (outside) edges are just touching the edge of the trough. Again, measure the length x width.

Teach Barrier Positions (continued)

3. 2 independent barriers

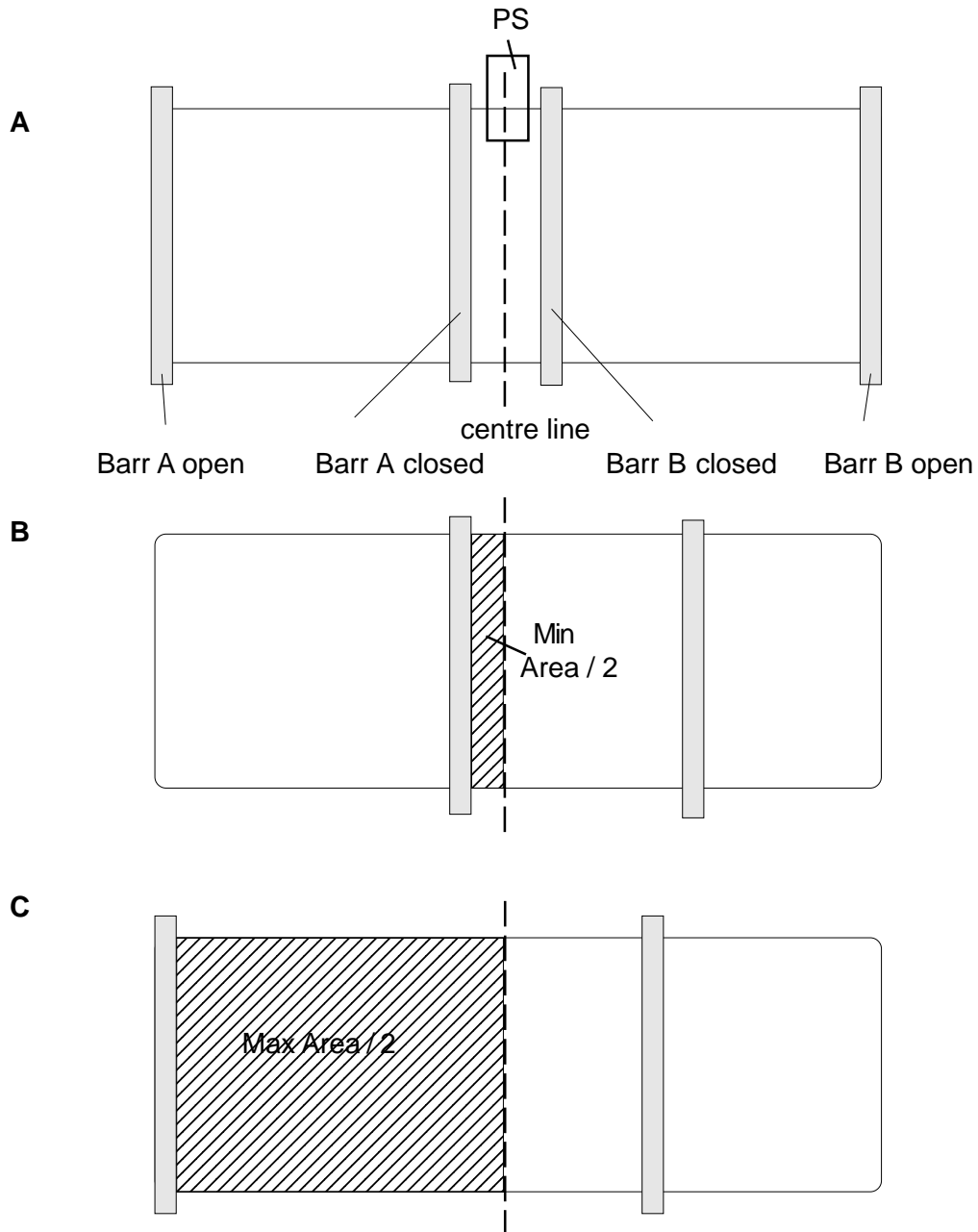


Figure 5.10:

Teaching areas for 2 independent barriers for symmetrical compression.

A: Typical minimum and maximum positions for both barriers.

B: Calculation of minimum area

C: Calculation of maximum area

- note that the shaded is only half the area!

The calibration procedure for 2 independent barriers is as follows:

1. Select 'Teach Barrier Position' from the Calibrations Menu and then click on 'A' for barrier A.
2. Click on 'CONTINUE MOTOR' and let the barrier move to its 'closed' position, as shown in Figure 5.10A.
3. Click on 'STOP MOTOR' when the barrier has reached its closed position. If necessary adjust the position of the barrier by clicking on 'CONTINUE MOTOR' and using the slider speed control to open or close it more slowly.
4. When it is at its 'closed' position, calculate the minimum area by measuring the area enclosed, as shown in Figure 5.10B. Measure the distance from the centre line to the leading edge of the barrier, as shown by the shaded area. Then double this area and enter this value in the 'minimum area' box. *You have to double the area, as it is the area enclosed by the 2 symmetrical barriers that is being measured.*
5. Now click on 'ACCEPT' and then run the barrier to its 'open' position. Measure the area as shown in Figure 5.10C from the centre line to the leading edge of the barrier. Again, double it and enter that area into the 'maximum area' box.
6. Finally, perform the whole procedure for barrier B. The only difference is that you will be given no choice of area to enter. So you have to run barrier B to the same positions (but their mirror image of course) as barrier A.

Teach Barrier Positions (continued)

4. 2 barriers - crossing over for multiple compartment option

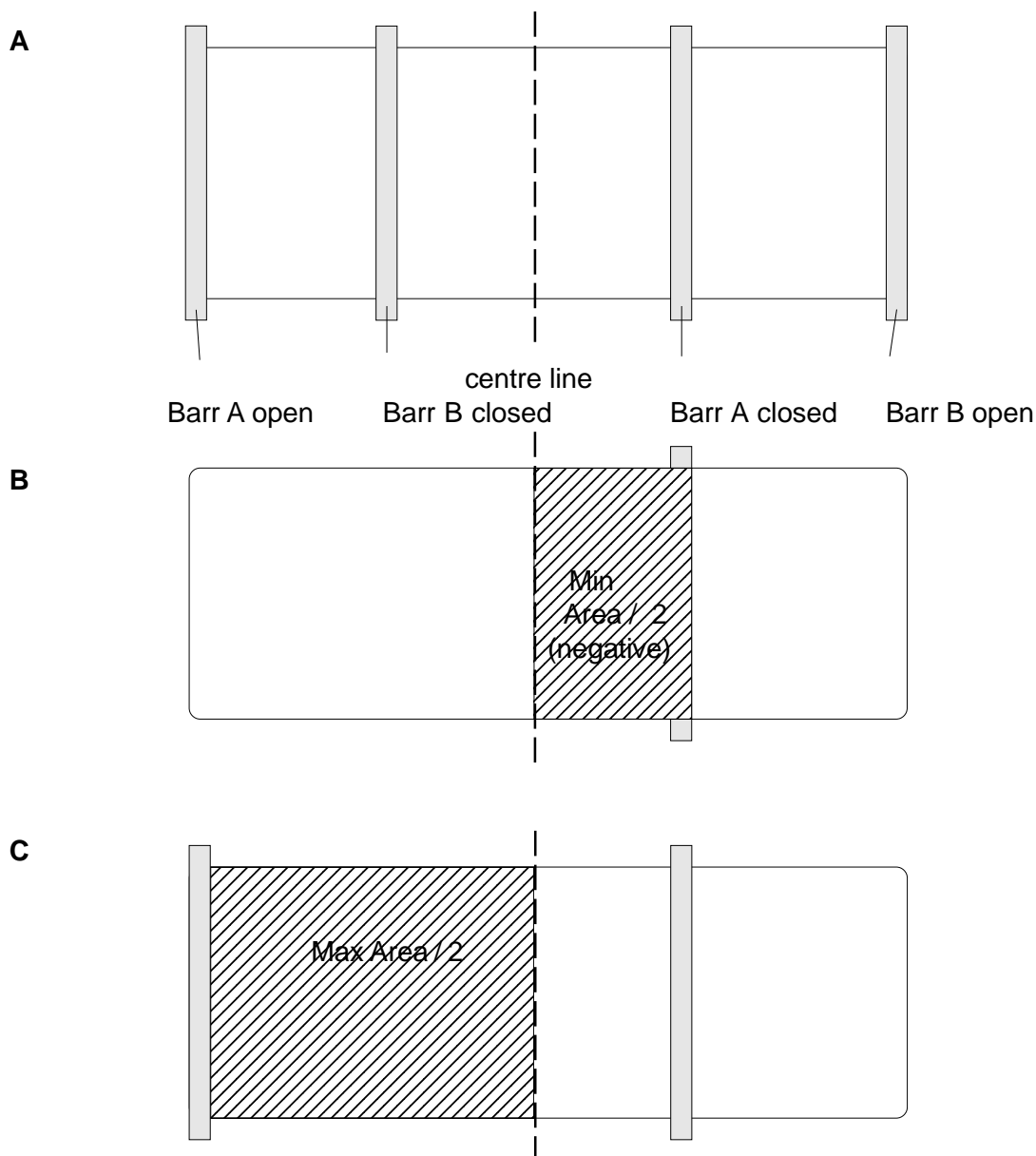


Figure 5.11

Teaching areas for 2 independent barriers for multiple compartment operation.

A: Typical minimum and maximum positions for both barriers.

B: Calculation of minimum area

C: Calculation of maximum area

- note that the shaded is only half the area!

In this variation, the barriers can cross over the centre line so that the monolayer can be compressed on one side and the transported over to the other. Hence the minimum area is now across the centre line and is actually a negative number.

The calibration procedure for 2 independent barriers crossing over is as follows:

1. Run barrier B to its fully open position (in the active graphics screen). It is now out of the way.
2. Select 'Teach Barrier Position' from the Calibrations Menu and then click on 'A' for barrier A.
3. Click on 'CONTINUE MOTOR' and let the barrier move to its 'closed' position, as shown in Figure 5.11. This will be well over the centre line. Make sure the barrier does not hit barrier B or its belt drive.
4. Click on 'STOP MOTOR' when the barrier has reached its closed position. If necessary adjust the position of the barrier by clicking on 'CONTINUE MOTOR' and using the slider speed control to open or close it more slowly.
5. When it is at its 'closed' position, calculate the minimum area by measuring the area enclosed, as shown in Figure 5.11B. Measure the distance from the centre line to the leading edge of the barrier, as shown by the shaded area. Then double this area and enter this value in the 'minimum area' box. *You have to double the area, as it is the area enclosed by two barriers that is being measured.*
6. Now click on 'ACCEPT' and then run the barrier to its 'open' position. Measure the area as shown in Figure 5.11C from the centre line to the leading edge of the barrier. Again, double it and enter that area into the 'maximum area' box.
7. Finally, perform the whole procedure for barrier B. The only difference is that you will be given no choice of area to enter. So you have to run barrier B to the same positions (but their mirror image of course) as barrier A.

Calibrating barrier speed

1. Select 'Calibrate Barrier Speed' from 'Calibrations' on the Menu Bar.
2. Click on Start and the calibration will run automatically.

Please ensure that the barrier is physically moving when 'moving at the slowest speed'. So, when the software displays 'Moving Barrier at Slowest Speed', check that you can see the position indicator actually decrease (slowly!). If it's not changing, increase the 'Min Barrier Speed' from the default value of 50, until you can see it change. For greatest accuracy, run this routine twice, if you have changed the Min Speed during calibration, so that this speed is measured over the full 60 second calibration time.

Calibrating dipper speed

1. Select 'Calibrate Dipper Speed' from 'Calibrations' on the Menu Bar.
2. Check that the correct dipper stroke and dip factor have been entered. Typical values are given below and will be written in your calibration certificate:

Dipper type	Stroke	Dip factor
mini	25mm	8.28
standard	75mm	4.10
alternate	38mm	1.006

3. Click on Start and the calibration will run automatically.

Please ensure that the dipper is physically moving when 'moving at the slowest speed'. So, when the software displays 'Moving Dipper at Slowest Speed', check that you can see the position indicator actually decrease (slowly!). If it's not changing, increase the 'Min Dipper Speed' from the default value of 40, until you can see it change. For greatest accuracy, run this routine twice, if you have changed the Min Speed during calibration, so that this speed is measured over the full 60 second calibration time.

Calibrate Temperature Sensor

The temperature sensor is plugged into the 'pH/Temp' socket at the back of the interface and the temperature option is selected in the Setup Menu.

The software then guides you to immerse the sensor at two temperatures (approx 5° and 50°C) and the readings of these are stored.

Software Updates

Updates are regularly made available on our website - free of charge.

Please follow the instructions on the website - they:

Download the program from our website at: www.nima.co.uk/softwaree

Unzip the installation files.

The file unzips to smaller floppy sized files ('setup.exe', 'data.001', 'data.002' etc and 'Nimahelp.txt') that fit onto 2 floppy discs. So you can copy and install it on another PC.

Set up. Click on Setup.exe and the Nima software will be installed for you. You can install it to any directory and there are no dynamic link libraries to worry about.

If you are upgrading, please install the new software into a new directory, for instance, 'c:\nimanew'.

Then copy the 3 calibration files 'install.dat', 'sensors.cal' & 'standard.con' from your existing 'nima' directory to the new one. This will save having to re-calibrate all the motors and sensors.

Conclusion

If you read the whole section at one sitting - well done!

Otherwise, just use this section as a reference if you ever get stuck.

TECHNICAL APPENDIX

Introduction

A list of frequently asked questions is presented in this chapter. These questions were prepared by listening to several generations of research students learning their Langmuir films at Cranfield University, England.

This chapter also explains the detailed functioning of the various motor and sensor assemblies. If a problem does ever occur, please don't hesitate to contact us on:

info@nima.co.uk

Frequently asked questions

General

What does 'Barrier A/B too open/closed' mean?

The barrier has moved outside its 'allowed' range. This range is given by the 'open-to' and 'close-to' areas, as set in the Monolayer Menu. Simply open or close the barrier to bring it into range by typing 'O' or 'C' as appropriate.

Why does 'Pressure too low / too high' appear?

The value from the pressure sensor is outside its 'allowed' range of 0 - 2.5V. Usually, this means that there is nothing hanging from the little suspension point. Just add the Wilhelmy plate and you should be ok.

If this problem persists, check the 'Pressure Sensor' section, later in this chapter.

How full should the trough be?

The trough should be filled so that the water just brims over the top, say 2mm. The barriers will work effectively over a wide range (at least ± 2 mm), because of the water's surface tension. A full trough allows plenty of leeway for cleaning without needing to top the subphase up.

When I switch the trough off, do I need to leave it in any particular state?

No, it doesn't matter how the trough is left, though it is good practice to leave it empty and thoroughly clean, with the barriers open and the dipper at the top for future users.

How do I start?

To take a pressure-area isotherm, select the 'Barrier' Menu from the Menu Bar and click on 'Isotherm'. The barrier(s) will move at the speed given in the 'Barrier Speed' control box, on the left of the graph.

How do I escape from a command I don't want to execute?

The 'ESC' key will STOP all motors moving. This has the same effect as clicking on the 'STOP' button.

How do I clear the screen?

Click on the 'CLEAR' button or select 'Clear Graph' from the 'Graph' Menu on the Menu Bar. A confirm will be requested, as this will wipe out all the data from your memory and the graphs.

How often is the surface pressure / all data sampled?

Surface pressure (and all sensor inputs) are continually sampled. Usually 5 readings are taken and these are then averaged and displayed on the screen. The number of readings can be changed in the 'Set up' Menu, selected from the 'File' Menu on the Menu Bar.

How do I configure the trough for multiple users?

Install the software as many times as there are users. During installation, you are given a choice of directory to load the software to. (The default directory is c:\Nima). Enter the directory name of your choice and then run the software from that directory. You can, of course, create the associated short-cuts and place them on the main screen of WIN95.

How can I display a directory of stored isotherms?

Use the 'Load' or 'Save' commands (from the File menu) which displays the contents of your working directory. Click on 'Cancel' if you don't want to load or save anything.

The interface is not responding

Examine the connections of the serial lead to interface unit and to the computer. The most common reasons for the interface not working are:

1. Wrong serial port selected.
Please try another serial port - there are 4 to choose from com1..com4. Usually com1 or com2 are used. Use 'Interface Test' from the Calibrations Menu to select the com port.
2. Serial port driver clash with mouse or network.
If communications are intermittent and/or sluggish, the interrupts may not be set properly in your PC set up. Check the System/Device Manager/ Ports/ Resources / Interrupts in your WIN Control Panel.

Pressure sensors

Does the degree of waterlogging of the filter paper affect the pressure readings?

Yes, for a couple of minutes after the filter paper has been immersed, it will soak up water and cause the pressure sensor reading to drift.

Does the length of filter paper used affect the pressure readings?

No, because the pressure sensors can be zeroed to offset the weight of the plate. The change in force is all that is important.

How can I measure the pressure of a very stiff film?

This can be difficult with single barrier troughs. Try experimenting with the pressure sensor position; putting pressure sensors on top of the barriers so that the measurement is made at the point of compression prevents premature collapse of a rigid film. Of course, if you have a 2 barrier trough, then the pressure sensor is mounted on the centre line of your trough and this problem is eliminated.

Why are the Wilhelmy plates being dragged towards the trough edge?

This could be because the floating Langmuir film is very stiff or it could be because of static charge on the PTFE or the acrylic cover. In the latter case, try an anti-static gun or spray.

Why does the pressure sensor reading appear to drift slowly when the trough is first used?

For a couple of minutes after the filter paper has been immersed, it will soak up water and cause the pressure sensor reading to drift.

Why doesn't the pressure sensor reading change very much?

The Wilhelmy plate may have fallen off or may be out of the water. If you suspect a hardware fault, suspend the empty weighing pan from the sensor, zero the display and add the 100mg calibration weight to the pan. The surface pressure should change by 46.7mN/m.

Isotherms

How can I plot a hysteresis loop?

There are 2 ways:

1. Compress as normal then use a negative barrier speed to run the expansion.
2. Select the isocycle function in the 'Barrier' Menu.
- the 'isocycle' parameters are set up in the 'Monolayer Menu'.

My isotherm appears vastly expanded/compressed / has vanished Not all the run appears on the screen

It is likely that the isotherm has been loaded without choosing the 'auto-scaling' of the axes set to 'auto'. Right-click over the graph and select 'auto-scaling' for both X and Y axes. If you're running in alternate mode - check that you're in the right compartment (A-B switch at top left).

How do I get a pressure-time plot?

Select 'Pressure&Area - Time' from the 'Graph' Menu on the Menu Bar. Then set the barrier speed to 0cm²/min and click on 'Isotherm' on the Barrier Menu. The trough will be doing an isotherm at zero barrier speed - i.e. a pressure-time plot.

Why do pressure-area isotherms occasionally have spikes?

This is probably because of external vibrations or air currents jolting the pressure sensors. If spikes are visible on the screen, the Langmuir film will have been disturbed.

Why are pressure-area isotherms sometimes 'jumpy' / climbing in discrete steps?

The pressure sensor consists of a galvanometer movement. A suspension wire is attached to the meter arm from which the Wilhelmy plate or balance pan hangs. The meter arm or suspension wire can get slightly bent out of shape and catch on the inside of the meter housing. The resulting friction causes jumpy rather than smooth changes in recorded pressure. Open the cover plate and free the suspension wire with the tweezers provided.

Why does the pressure reading not return to zero / drop below zero when the barriers are opened after a compression?

The surface was probably not thoroughly cleaned before spreading or the monolayer has collapsed.

Why is the area-per-molecule wrong?

There could be several reasons. The solvent used may be miscible with water, carrying some material into the water with it, the chemical may be impure (high purity materials must be used), the concentration and volume of solution need to be checked, the film may be collapsing prematurely, etc. Each possible cause needs to be investigated thoroughly and in a logical sequence.

Dipping***What pressure do I dip at?***

Generally, it is best to dip at in the liquid condensed phase, just above the liquid expanded-liquid condensed transition point. At this point, the film is packed almost as tightly as it can be, yet minor excursions in pressure will not result in premature collapse. Deposition can be monitored by watching the meniscus as the substrate crosses the interface - an even meniscus usually implies good transfer. The film must not, obviously, collapse at any stage.

Why are the transfer ratios wrong?

There are several possible reasons. If the substrate has not been properly cleaned and treated prior to deposition, the film may be repeatedly deposited and peeled off the substrate. If the 'dipstart' and 'dipend' positions or the area have been wrongly entered, the computer will be working from incorrect data.

It may be that the barriers are not sufficiently clean so that material is escaping under them. It may be that the monolayer is collapsing continually under pressure - check this on the area-time axes, while holding it at the deposition pressure. With a conventional dipper mechanism, the 'up' and 'down' deposition ratios will always be different, as the meniscus will always take a finite distance to reverse directions.

See also 'Interpreting Transfer Ratios' in the 'Tutorial' section of this manual.

Why does the barrier continually move inwards with pressure control on?

The floating monolayer could be collapsing, the Wilhelmy plate may be out of the water or material may be escaping under the barriers if these are not clean.

How can I prevent the barrier of an unused compartment of an alternate layer trough drifting to become 'too closed'?

If during deposition only one compartment of an alternate layer trough is used, the barrier for the other compartment can slowly drift over a period of time and become 'too open' or 'too closed'. This drift can be controlled by occasionally making the target pressure for the unused compartment negative by adjusting it downwards using 'Target Pressure' controls (top left of screen), accessed from the Variables Menu. Alternatively, the feedback gain can be set to zero for the relevant compartment.

Why does the dipper position not go through '0' mm?

With, for example, a standard alternate layer dipper mechanism attached the dipper position jumps from around 250mm to around 10mm. This is because the potentiometer used to monitor the dipper position has a dead area of a few degrees around 'top dead centre' (of the possible measuring systems, this method nevertheless has the fewest drawbacks). A filter mechanism is built into the software to prevent this from confusing the dipper control procedure.

Conclusion

We hope this has helped you with any questions or problems you may have had. The most frequent problems we are asked about are the software settings. If you are in doubt, the simplest thing to do is to re-install the software on your PC from the master diskette supplied with your trough. This will have all the default settings and those specific to your trough included.

Please don't hesitate to contact us at Nima, if you still have problems:

info@nima.co.uk

Barrier Mechanisms

Introduction

Barriers are driven along the trough by a toothed belt, as illustrated below:

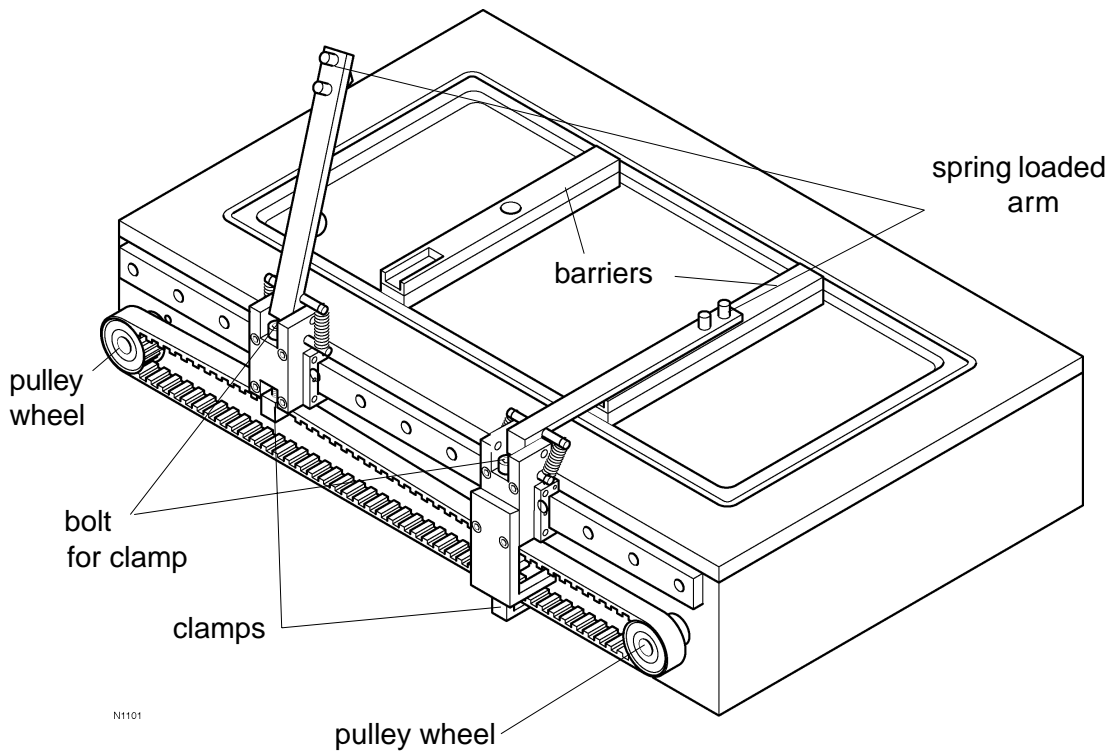


Figure A1: Barrier Assembly. Troughs can have 1 or 2 barriers - 2 barriers shown here.

Each PTFE barrier is located on the Langmuir trough by a spring loaded arm. This arm can be raised to allow the easy removal of the barrier from the trough for cleaning.

The arm runs on a precision linear rail and is driven along the trough by a toothed drive belt mechanism. The arm is attached to the belt by means of a clamp, which is tightened by a bolt.

The belt mechanism is moved by a precision dc motor/gearbox combination turning a pulley wheel at one end of the belt. The barrier position is detected by a potentiometer (called 'pot' in this manual) attached to the back side of the drive shaft. A second pulley wheel, the 'idler pulley' is located at the other end of the belt - this is located in a slot and allows the belt tension to be adjusted.

The following pages are written to help you repair or replace any components in case of problems.

Barriers - trouble-shooting

Symptoms

There are 2 major symptoms associated with a faulty barrier:

- a) barrier not moving - either motor or gearbox faulty
- b) barrier moving but area display incorrect - area not calibrated properly or potentiometer faulty

However, before you take everything apart, it is worth checking some obvious things first:

Wiring & connections

If your barrier is completely 'dead', check that the cables are plugged into their correct sockets in the interface unit - barrier A into 'Barrier A' and barrier B into 'Barrier B'.

Check the wires at the motor and potentiometer - sometimes these can come loose but still be held in place by the protective rubber sleeving. Just give each wire a gentle tug, to make sure that it is attached properly.

Mechanical action of barrier

Now check the mechanical action of the barrier. There is a hexagon bolt on the end of the barrier, which tightens a small clamp onto the belt, Figure A1. When this is tightened, the barrier moves along with the belt. When this is loose, the barrier can be pushed manually and should run freely along the whole of its length. Please check that the barrier can do this.

If it is not running smoothly, please check for signs of scratching or pitting on the surface of the barrier rail. Also check for any other obstructions interfering with the free movement of the barrier.

Then move the barrier near the centre of its travel and tighten the locking bolt gently, so that the belt is clamped firmly but not so tight that the belt is squashed out of shape.

Testing motor/gearbox

Symptoms of faulty motor/gearbox:

- *Motor not responding under computer control - no noise, no movement*
- *Noise coming from motor but barrier not moving*

Run the 'Interface Test' routine (under 'Calibrations' on the menu bar). The barriers are controlled by slider controls on the right side of the screen. When the slider is in the middle, the barriers are stopped. Moving them left and right makes the barriers move open or closed. There is also a MOTORS ENABLED/DISABLED button which acts as an override for emergency stops.

Locate the appropriate barrier control ('A' or 'B') on the top right of the screen and move the slider to the right. The barrier should move towards its 'closed' position - the further you move the slider control from the middle, the faster the barrier will move.

Take great care not to leave the barrier moving. As there are no safety controls in this test routine, the barrier can crash into its end stop and may be damaged. Always stop the barrier!

Click on MOTORS ENABLED to stop it again.

If the barrier is not moving at all and there is no noise coming from the motor, it may be broken and will have to be replaced. *Please note these motors are usually very reliable and care should be taken that everything is plugged in properly, before taking it all apart.*

If there is a noise coming from the motor but the barrier is not moving, then the gearbox may be broken and will have to be replaced.

Replacement of the motor/gearbox is described overleaf.

Testing the barrier potentiometer ('pot')

Symptoms of faulty pot:

** Area-time plot is non-linear*

** Barrier not moving, even though motor/gearbox is ok*

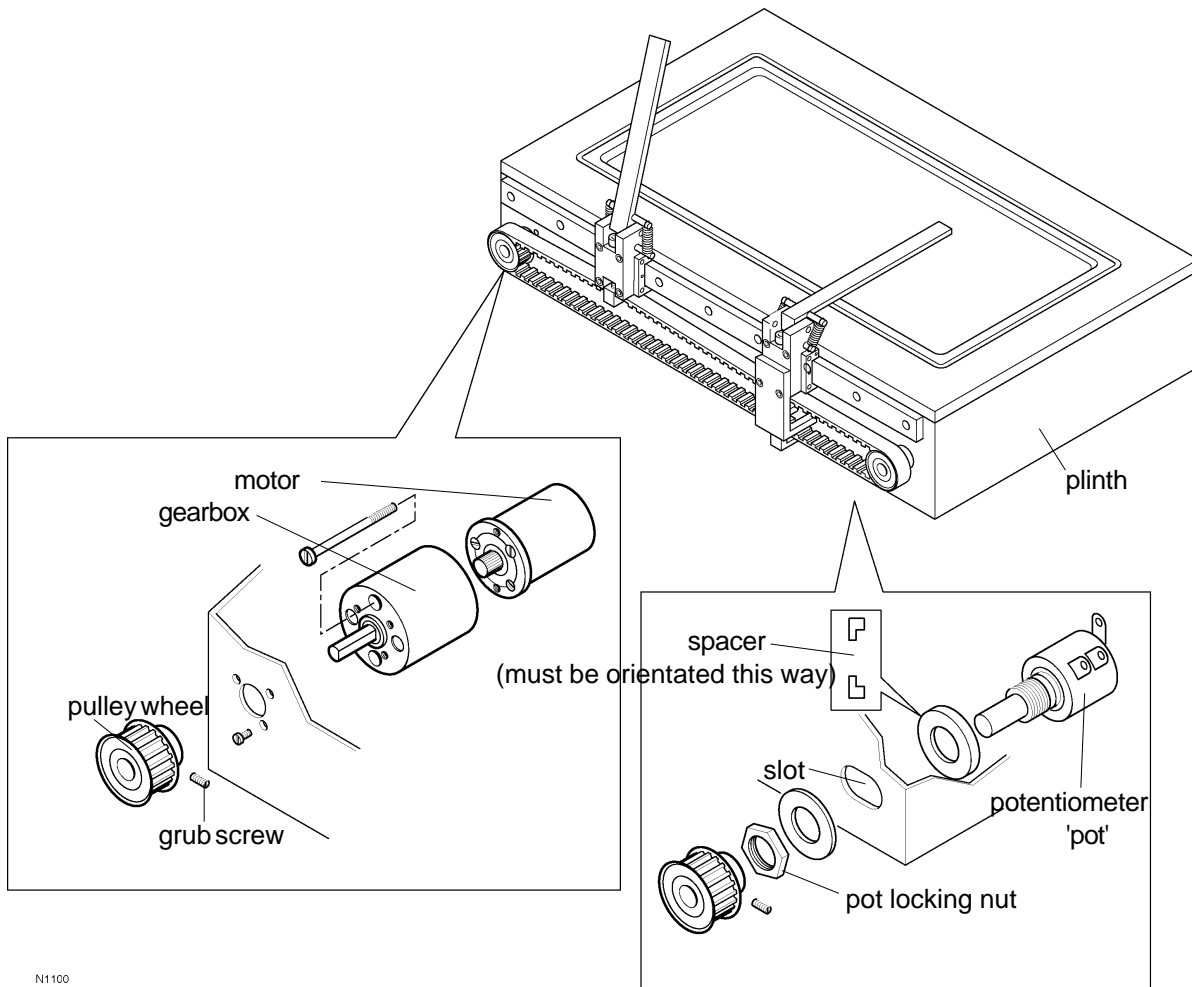
** Pot difficult to turn by hand (after belt has been removed)*

If the barrier is moving without problems but the area display is inaccurate, the barrier may have slipped on the belt. So, please re-calibrate the areas first, as described in the Software chapter of this manual.

If the areas have been calibrated properly and the area display is erratic, please take an area-time plot of the barrier position. Select the area & pressure v time axes and click on 'Isotherm' under 'Barrier' in the menu bar to take an area time plot. If you do not see a straight line of area-time, then the pot is faulty and will have to be replaced.

Replacement of the pot is described overleaf.

Replacement of barrier motor/gearbox and potentiometer



N1100

Figure A2:

Exploded view of barrier assembly - showing motor/gearbox and potentiometer

1. Slacken the barrier clamp again and slip the belt out of the clamp.
2. Undo the grub screw of the pulleys (the little aluminium wheel with teeth for the belt) attached to both the pot and the motor/gearbox. The grub screw is a little hexagon socket screw that needs a 1.5mm hex key (supplied in our toolkit).
Note: if this grub screw is already loose, it may be that this is the problem. Tighten it up and test the action of the barrier.
3. Using a 13mm (½ inch) spanner, gently loosen the locking nut that holds the pot to the trough plinth (or the polished cover in a 601M). This will ease the tension in the belt, as the pot is located in a slot, not a hole.
4. Gently pull the pulley wheels off the pot and gearbox shafts, so that the belt and pulley wheels come away completely.

Replacement of motor/gearbox

1. Unscrew the 3 little screws holding the gearbox onto the trough plinth (or cover for 601M).
2. With the wires still attached to the motor, try to run it again. Is the output shaft turning? If yes, try to stop it by hand - does the shaft stop turning? If yes, then maybe the gears in the gearbox are slipping.
3. If only the gearbox is to be exchanged, then unscrew the 2 long screws that hold the gearbox to the motor and replace with the new gearbox.
4. If the motor is to be replaced, unsolder the wires from the motor, taking note of the wiring configuration. This wiring configuration will depend on the gearbox and trough type you have. But there are only 2 wires, so you can't go far wrong!
5. Replace the motor/gearbox assembly.

Replacement of pot

1. Completely unscrew the pot locking nut and remove the pot from the trough.
2. Disconnect the wires, making a note of the wiring configuration. This should be:

pin 1	red
pin 2	yellow
pin 3	blue

The red and blue wires may be switched over, depending on the direction of movement of the barrier.

3. Replace the new pot, resolder the wires in the same way and fix it to the trough, but don't yet tighten the pot locking nut completely.

Re-fitting the drive belt

1. With the pot locking nut still loose, attach the pulley wheels and belt as one unit, making sure that there is no undue force on the pot shaft. Too much force will damage the bearing and cause the pot to jam up.
2. Now gently push the pot pulley wheel towards the end of the trough, so that some tension is put on the belt - tight enough for the belt not to slip on the teeth of the wheels, but not so tight that there is excessive force on the pot shaft. Then tighten the pot locking nut.
3. Now, while the barrier belt clamp is loose and not driving the barrier, move the barrier motor with the slider control until the barrier '16 bit decimal INPUT' reads $25,000 \pm 100$ units. Then manually push the barrier to its 'open' position and gently tighten up the barrier clamp.
4. Re-calibrate the areas, as described in the Software chapter of this manual.

Dipper Mechanisms

There are 2 Nima dipper mechanisms - conventional and alternate. In this context, 'conventional' means that the substrate is oscillated vertically through the liquid-gas interface while the alternate layer mechanism immerses the substrate through one monolayer and withdraws it from another.

Both dippers come in 2 standard sizes:

D1L-25 miniature dipper for small substrates up to 25mm long.

D1L-75 standard conventional dipper for microscope slides and 3" (75mm) wafers.

D2 - standard alternate layer dipper for microscope slides.

D2-3" large alternate dipper for 3" (75mm) diameter wafers.

The 'L' in 'D1L' stands for linear, to differentiate it from the old 'D1S' dipper which was sinusoidal. This is now out of production.

Setting the Linear Dipper, Model D1L

The standard conventional linear dipper, Model D1L, consists of a substrate clamp that is magnetically attached to an arm which is driven up and down by a belt and pulley system.

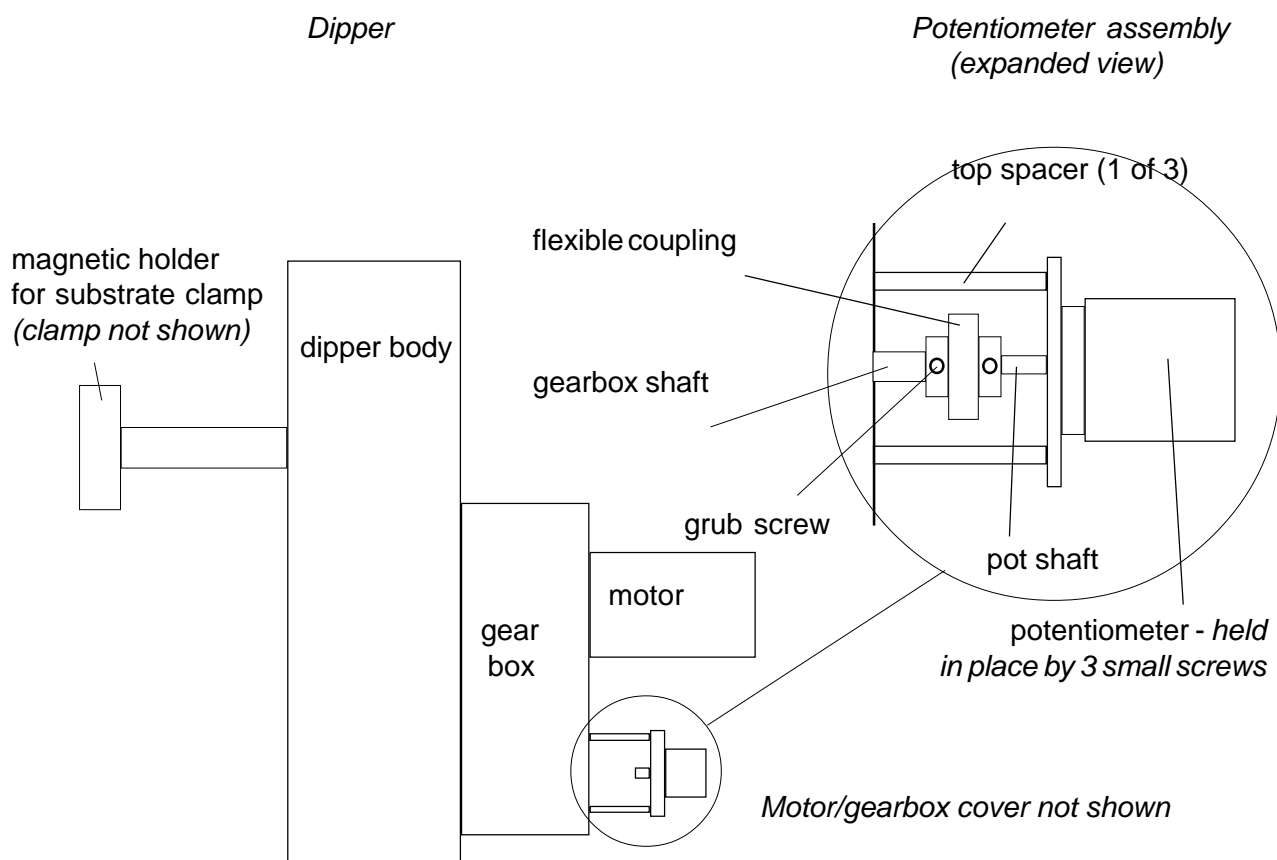


Figure A3: Illustration of Dipper, Model D1L-75

Setting the conventional dipper potentiometer position

1. First remove the round black cover by unscrewing the 2 screws..
2. Identify the flexible coupling which connects the pot to the gearbox, Figure A3. This has 4 little grub screws - 2 pinching on the pot shaft and 2 on the gearbox shaft.
3. Slacken the 2 gearbox shaft grub screws with the 1.5mm hexagon key provided. If access to the grub screws is not possible, rotate the dipper until it is.

Run the 'Interface Test' routine (under 'Calibrations' on the menu bar). The dipper is controlled by a slider control on the right side of the screen. When the slider is in the middle, the dipper is stopped. Moving it left and right makes the dipper move up or down. There is also a MOTORS ENABLED/DISABLED button which acts as an override for emergency stops.

Move the slider to the right. The dipper will move towards its 'down' position - the further you move the slider control from the middle, the faster the dipper will move.

Take great care not to leave the dipper moving. As there are no safety controls in this test routine, the dipper can crash into its end stop and may be damaged. Always stop the dipper!

4. In the 'Interface Test' program, slide the 'Dipper' control to the left to move the dipper to the top.
5. When it reaches the top i.e. when dipper height = 75mm for a standard dipper or 25mm for a mini dipper, stop the motor by moving the slider to the centre.
6. If necessary, move the dipper down again by sliding the control a little to the right and then back to the centre to stop it again. Repeat until the correct height is reached.
7. Check that the grub screws of the other side of the flexible coupling are tightened onto the pot shaft and rotate the whole assembly so that the '16 bit decimal INPUT' on the screen reads $25,000 \pm 100$ units.
8. Re-tighten the grub screws on the flexible coupling and replace the outer cover.
9. Quit the Interface Test program and click on 'Calibrate Dipper Speed':

Set the stroke and factor as follows:	Dipper	Stroke	Dip Factor
	D1L-75	75mm	4.10
	D1L-25	25mm	8.28

If in doubt, check your calibrations certificate for the stroke and factor or contact us - we keep records of your settings.

12. Click on START and the dipper speed will be calibrated as normal. The dip factor and stroke will be saved along with the speed calibration data.

Alternate Layer Dipper, Model D2

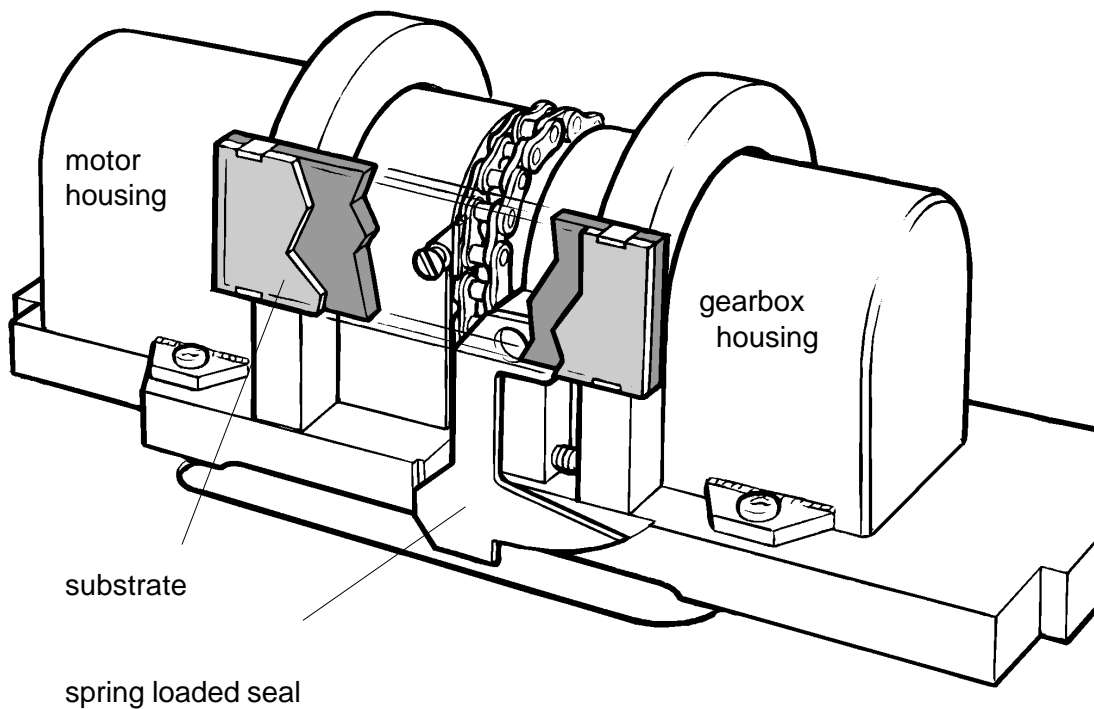


Figure A4: Alternate layer dipper, Model D2

The alternate dipper mechanism has its potentiometer in the smaller of the 2 stainless steel housings. First, the dipper needs to be moved to its 'top' position:

1. Run the 'Interface Test' program.
2. Slide the dipper control to the left or right to move the dipper. It's not important which way, as the substrate can go round indefinitely.
3. Stop when it reaches its top position by clicking on MOTOR ENABLED.
4. Undo the 2 screws holding the steel cover in place and remove the cover.
5. Loosen the 2 small screws holding the potentiometer in place.
6. Rotate the pot until its maximum value is displayed. In principle, this is 32,767, but because of the 'dead band' of the pot, this is usually around 30,000. It is not important if you have not adjusted it to the exact 'top dead centre' - as you will be setting the 'dip start' and 'dip end' position in the Dipper Menu anyway.
7. Tighten the three little screws and replace the cover.

Then its speed needs to be calibrated:

1. In the main graphics screen, click on 'Calibrate Dipper Speed' under 'Calibrations' in the menu bar.
2. For the standard D2 dipper, set the stroke to 49.0mm and dip factor to 1.006.
3. Click on START and the dipper speed will be calibrated as normal.
The dip factor and stroke will be saved along with the speed calibration data.

Pressure sensor, PS4

This pressure sensor is the fourth generation of our sensors. It combines very high accuracy with stability and reliability. It uses a taut-band meter movement which gives very low friction. The design of the electronic circuit allows infinite loop gain giving zero compliance i.e. whatever the load, the Wilhelmy plate remains at the same level. Hence it is ideal for surface tension measurements.

However, as a result of the small forces being measured, some of the component parts are delicate and can be bent out of shape. This technical note aims to help the user repair the sensor without having to return it to the manufacturer.

Mechanical setup

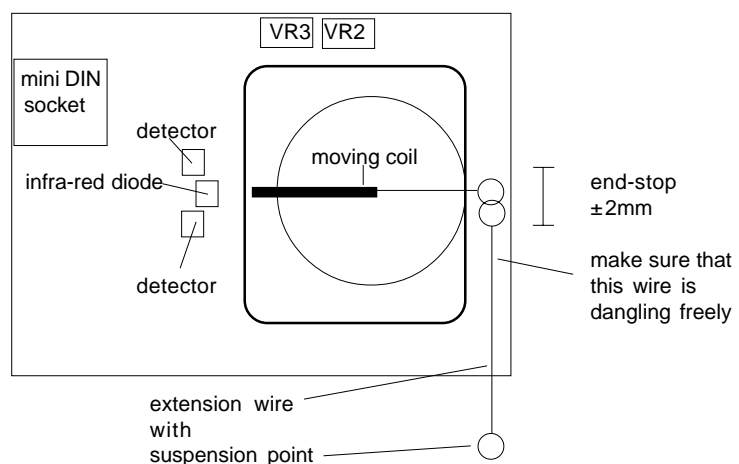


Figure A5: Illustration of PS4 - cover removed.

The sensor should be set up as in the diagram above.

For proper operation the following points should be observed:

1. The moving coil must be able to move freely .
2. The extension wire must be dangling freely and must not be touching the inside of the housing.
3. The moving coil should reach the horizontal position when the sensor is powered up.

Electronic setup

There are 2 potentiometers to adjust:

- | | |
|-----|--|
| VR2 | offset of output signal - turn clockwise for increased output |
| VR3 | gain of output signal - turn anti-clockwise for increased gain |

When powering up, the coil should automatically reach its horizontal 'balance' position. There is a wire end stop to prevent it moving by more than $\pm 2\text{mm}$ from the horizontal, to keep it in range.

If the meter does not come to its 'balance' position, push the diode a little towards the coil, so that the optical signal (reflecting from the edge of the coil into the detectors) is a little stronger. Then the electronics will take over.

VR2 (offset) and VR3 (gain) should be adjusted, so that the output level matches the appropriate operating mode:

Suggested values are:

Force suspended from sensor	Approximate output (Volts)	
	Tensiometers	Troughs
Output with empty weighing pan:	0.2	0.8
Output with pan + 100mg:	0.6	1.6

Adjust the blue potentiometer labelled 'VR2' until 0.8V is displayed. Add the 100mg weight and adjust VR3 until 1.6V is displayed. Remove the weight and check the output. Adjust VR2 again if necessary. Repeat in an iterative manner until the required output voltages have been achieved.

Completion

Finally, replace the cover and calibrate in the usual way. Note that the voltages need not be set exactly, as the sensor will be calibrated anyway. It is also possible to reduce the gain when wider plates are used or increase the gain for greater accuracy.

Pressure sensor out of range - if this message appears, it means that the pressure signal has gone outside the AD range. Usually this is not serious, as it only happens when there is no load on the sensor i.e. when the plate and hooks have been detached. To prevent this occurring, simply suspend a paper plate from the pressure sensor.

Temperature sensor

Any commercially available temperature sensing system can be used with Nima troughs.

If you want to log the data on the PC, there is an input on the Nima interface. The only criterion is that the output of your meter be in the range 0 - 2.5V.

The following 'pin-outs' apply on the 'pH/Temp' input on the Nima IU4 interface:

pin 1	temp
pin 2	ground
pin 3	pH

Magnetic Stirrer, Model MST

The magnetic stirrer consists of a steel pin encased in an PTFE disc which is located in a 1mm deep recess in the trough. It is rotated by rotating a magnet below the trough with a dc motor. Speed control is effected from a small control box with a single turn dial. The wire from the motor is plugged into the control box using the 5 pin DIN plug labelled 'MS'.

Power is supplied to the control box from the 9V encapsulated supply. Usually a little '1 into 2' box is supplied, so that the trough interface and the magnetic stirrer are supplied from 1 power supply.

To operate, simply place the stirrer disc in its location on the trough and rotate the control knob until the required speed is reached.

Surface potential sensor - Trek Electrometer 320

Introduction

If you have bought a Trek electrometer (either separately or through Nima), the following section will show you how to install it.

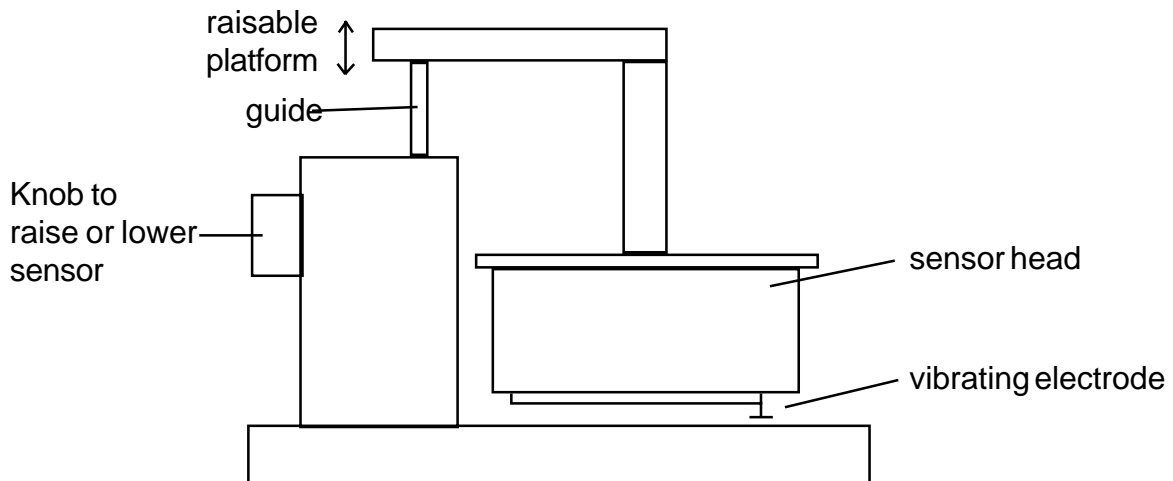


Figure A6: Trek vibrating electrode mounted on Nima raisable platform

1. Carefully unpack the sensor and meter and set the sensor up as in the diagram above.
Read the Trek manual thoroughly.
2. Ensure that the sensitivity switch on the front panel of the meter is set to '10V' and the NULL VOLTAGE switch to '+'.
Read the Trek manual thoroughly.
3. Ensure that the RESPONSE dial on the back of the meter is turned all the way to 'slow'.
4. Lower the sensor head to its bottom position by rotating the knob on the back of the body, so that the vibrating electrode is about 1mm above the ground plate.
5. Connect the probe lead from the sensor to the large plastic socket on the back of the meter and the ground lead from the ground plate to the GND socket on the back of the meter
6. Turn the meter ON.
7. Adjust the NULL VOLTAGE dial until the displayed reading is 0.00 V.
If the dial comes to the end of its range before 0.00 V is reached, flip the Null Voltage switch over to '-' and continue the adjustment.
8. The unit is now ready for use.

When taking readings, keep the vibrating electrode as close as possible to the test surface without actually touching it. The RESPONSE switch on the back of the meter can be adjusted to give optimal compromise between speed of response and noise of signal.

Never touch the vibrating electrode - it may have a high potential on it.

Checking absolute potential against a reference

Take the 1.5V battery and place it in series with the earth wire between the GND socket and the ground electrode, as in the diagram in below:

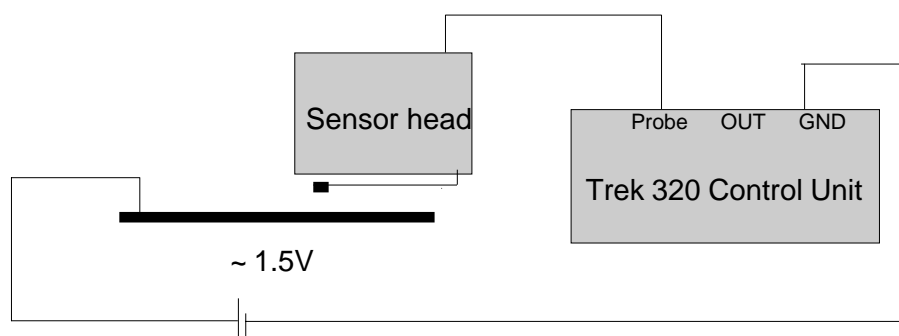


Figure A7: Electrical connections to test the surface potential sensor

A 1.5V potential step has now been placed on the plate and this should be displayed on the meter. Remember to check the difference in voltage - not the absolute value. Check the battery voltage with a conventional meter and compare the reading on the control unit. The change noted on the meter should be within 10mV of the displayed signal.

Using with the Langmuir trough

It is now necessary to lay the ground plate into the subphase, as otherwise the high surface energy of the PTFE trough will swamp the small electric field of the monolayer. The ground plate also acts as a reference for the surface potential signal.

1. Place the stainless steel ground plate in the (empty) trough and plug the 2mm 'banana' connector provided on the earth lead to make good contact with the plate. The socket on the plate connector consists of a 2mm stainless steel socket with a PTFE skirt. The PTFE skirt prevents the connector from short-circuiting the monolayer.

There are 2 possible positions for the connector in the ground plate, depending on the geometry of the trough. A single barrier trough should use the end position, while a 2 barrier trough should use the central position.

The other end of the ground lead has to be plugged into the 'GND' socket of the interface.

2. Connect the co-axial cable between the 'OUT' socket of the Trek meter and the 'PB' socket' on the Nima interface.
3. Run the 'Interface Test' routine and check the 'Pressure B' reading. Adjust the output voltage of the Trek with the voltage offset dial. Check that when the output display reads 0.0V on the display of the Trek, 0.0V \pm 0.1V is displayed by the

Pressure B reading. Note that it is not important if the voltage displayed on the screen and the Trek meter are not exactly the same - this is why you will be calibrating the output precisely.

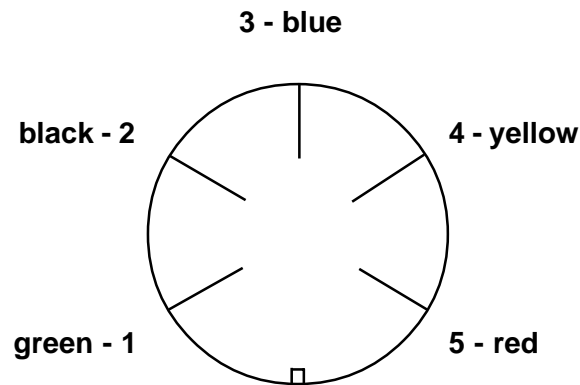
4. Go to the Setup Menu and enable the 'Surface Potential' option in 'Setup Langmuir Trough'
5. Select the 'Calibrate potential sensor' from 'Calibrations' in the menu bar. Follow the instructions on the screen: adjust the output on the Trek to read +0.5V, click on the button to accept and then adjust it to read +1.5V and click again. The software now knows what reading corresponds to a difference of 1V.
6. Isotherms of pressure and potential can now be captured, plotted and stored simultaneously. Just click on 'Isotherm' to take the isotherm in the usual way.

Notes for best results

1. Compared to surface pressure measurements, changes in surface potential readings are much more leisurely and need more experimental finesse. They require the same kind of patience as do precise pH readings. Hence considerable care during operation and interpretation is required.
2. It is easiest to make surface potential measurements of ionic solutions. Pure water is a very good insulator and there are considerable higher stray (and variable) capacitances on pure water subphases. Signal noise is proportional to the square of ionic concentration.
3. Particular care must be made not to charge surfaces unnecessarily, as charges will invariably leak to other surfaces near the probe and cause drift in the measured readings. Ideally, antistatic protection should be worn (such as found in semiconductor fabrication areas) and antistatic mats should be placed around the trough bench. In addition, a simple Faraday cage should be erected to prevent stray charges interfering with measurements.
4. Place the vibrating plate of the probe about 2mm from the test surface. Should it touch the water, remove the droplet with the aspirator and start again. If the probe is too far from the test surface, the signal will be too noisy for satisfactory measurements. Don't be afraid to experiment - no damage will be done to the probe.

Cable connections

5 pin DIN socket (240°)



Viewed from the outside of the interface unit or from inside the DIN plug.
(Pin numbers are marked on both plugs and sockets)

The colours identify the five wires used inside the six-wire screened cable running to each motor/sensor.

The connections of the wires to the LB trough devices to the DIN plug/socket pins are shown below. The potentiometers have pins marked 1,2,3 or a,b,c.

Wire \ Device	601, 611 622 side B	622 side A	Alternate Dipper	Conventional Dipper D1L
Motor (+)	green	black	green	green
Motor (-)	black	green	black	black
Pot pin 1 or a	red	blue	blue	red
Pot pin 2 or b	yellow	yellow	yellow	yellow
Pot pin 3 or c	blue	red	red	blue
Pressure sensor PS4, mini DIN socket				
Ground	black (pin 2 on IU4 DIN socket)			
-V	white (pin 3 " " ")			
Output	red (pin 4 " " ")			
+V	yellow (pin 5 " " ")			

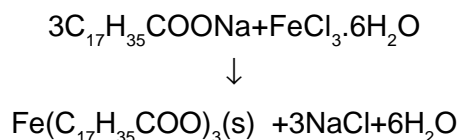
Synthesis of ferric stearate

Ferric stearate is used to make the substrate surface hydrophobic (as described in the Tutorial chapter). A small sample of this is supplied with your trough and it is also commercially available*.

If you prefer to synthesise it in your own lab, the following process takes about an hour and a half:

- Make up a solution containing 1g of sodium stearate in 50ml of ultra-pure water.
- When all the solid has dissolved, pour the solution into a clean burette.
- Make up a second solution containing 0.3g of ferric chloride (iron (III) chloride) hexahydrate in 50ml of ultra-pure water.
- When all the ferric chloride has dissolved, pour the solution into a second clean burette.
- Simultaneously add the solution from each burette to a beaker containing approximately 10ml of pure water.

Stop every few millilitres to gently stir the contents of the beaker and to check that the pH of the resultant solution does not vary from pH7. If the pH is too acidic the product of the reaction will be white stearic acid; if it is too basic, the product will be dark grey ferric hydroxide. The reaction taking place is:



- On addition of all the reagents, stir the solution gently and leave to stand for a few minutes. The ferric stearate should precipitate out of the solution as a pale brown solid.
- Pour off the excess liquid above the ferric stearate.
- Wash the product with pure water a couple of times.
- Leave the product to dry in air on a filter paper for about an hour.

The yield of ferric stearate product should be 1g.

* **Commercially available from TCI Co Ltd, Tokyo, Japan. Fax (+81)(3)3270 8466**

INDEX

A

Active screen 94
 software 94
Alcohol 18
Alkanoic acid
 dissociation 30
Alternate layer deposition 66
Alternate layer dipper 130
Alternate layer dipper enable 99
Alternate layer mode 101
Amines 18
Amphiphatic balance 28, 76
Amphiphiles 76
Amphiphilic 18
Anti-reflection coating 48, 60
Anti-vibration table 36
Arachidic acid 49, 56
Area
 per molecule 100, 121
Area control 95, 97
Argon ion plasma 49

B

Babylonians 20
Bare skin 35
Barrier 11
 holdtime 100, 103
 opening in software 94
 speed 100, 103
Barrier mechanisms 123
Barrier menu 11
Barrier positions
 calibration of 107
Barrierspeed 96, 100, 114
 calibration 114
 setting 53
 under pressure control 57
Barrier 'too open/closed' 118
Bench space 2
Biotechnology 21
Blank spreading 39
Blodgett 21
 original paper 48
Boltzmann 25
Bottom end 103
Bottom position
 setting dipper 104
Buttons
 software 96

C

Cable connections 137
Cadmium
 contamination 72
Cadmium arachidate 48
Cadmium chloride 48, 87
Calcium fluoride
 For IR studies 40
Calibration

 of barrier positions 107
 of barrier speed 114
 of dipper speed 114
 of pressure sensor 107
 of surface potential 107
 weight 107
Calibration certificate 114
Calibrations Menu 95, 106
Carboxylic acid 18
Change axes
 area units 95
Cholesterol
 monolayer properties of 89
Chromic acid 40
Clapham Common 20
Cleaning 37, 73
 aspirator/pump 51, 74
 plasma etching 40
 trough 36
 water surface 51
Cleanliness 35, 72
 for experiments 72
Clear graphs 95
Clear memory 11
Clear screen 119
Close to area 100
Coatings
 Anti-reflection 21
Collapse
 of monolayer 62
Collapse pressure 83
Com port 119
Compression 53. *See also* Isotherm
 of monolayer 53
Concentration 101
Containers
 For water 38
Contaminants 37
Contamination
 surface active 38
Copyright 72
Coulomb 18
Coupled barrier operation 65
Cursor control 55
Cycle Max Area 97
Cycle Min Area 97
Cycles required 96

D

Decon-90 37
Deposition 13, 56, 57. *See also* Dipper
 alternate layer 34
 and peeling off 32, 62
 first monolayer
 onto hydrophilic substrates 32, 61, 62
 onto hydrophobic substrates 19, 31
 head to head and tail to tail 33
 quality 58
 Types: X, Y and Z 33
Detergent Cleaning 37

Devaux, H. 21
Dip Bottom End 97
Dip Top End 97
Dipper 11
 adjustments 128
 making LB film 56
 mechanism
 questions 122
 moving in software 94
Dipper enable 99
Dipper mechanisms
 setup 128
Dipper Menu 11, 95, 102
Dipper position 122
Dipper positions
 setting top & bottom 104
Dippers speed 96, 103
 calibration 114
Dipper start/end
 positions 63
Dipper-Area graph 95
Dipping 121
Display directory 119
Disposal
 solvents 35
 toxic materials 72
Duplex film 76

E

Easy cleaning 54
Esc key 50
Exit software 95

F

Fats 18
Fatty acid
 dissociation 30
 saturated 83
 unsaturated 85
Feedback gain 11, 97
Ferric stearate 49
 hydrophobic surface 40
 synthesis 138
File
 loading and saving 54
File Menu 95
Film balance
 cleaning 73
 preparations 72
Film quality
 streaky 53
Filter paper 119. *See also* Wilhelmy plate
Filters
 for clean labs 35
First layer
 on up stroke. *See* Deposition
Franklin, B. 20
Fume cupboard 72

G

Gaines, G.L. 21
Gas detectors 21
Gauges
 Step-thickness 21
Gelatin 20
Gold
 Hydrophobic surface 40
Graph
 changing type 54
Graph Menu 95
Graphics
 screen 94
Ground plate
 for surface potential 135
Grunfeld, F 62

H

Hardy 21
Head to head and tail to tail 33
Helmanex 37
Help site - www.nima.co.uk/help 8
Hexamethyl disilazane 40
HHTT 33
Homologous series
 of fatty acids 85
Horizontal streaking
 during deposition 32
Hydrocarbon 18, 28
Hydrocarbon chain
 area 82
 isomers 85
 length 29
 minimum length 85
Hydrophilic 18, 28
 molecules in subphase 62
 surface preparation 40
Hydrophobic 18, 28
 surface preparation 40
 tail structure 85
Hysteresis loop 120

I

Ingestion 35
Installation 9
 hardware 4
 software 8
Interface 119
Interface Enabled 98
Interface Test
 software 106
Interface unit
 setting up 7
Interference colours 48
Ionic equilibria 30
Isotherm 12, 24, 50, 55, 82, 119, 120
 arachidic acid 54
 in tutorial 50
 of similar fatty acids 85

Isotherm cycle 101

K

Kelvin probe

surface potential sensor 134

Kimwipes 12, 36, 49

USA 14, 49

Kuhn, H. 21

L

Laboratory

requirements 2

Langmuir, I. 21

Layers Required 96, 103

LB film

deposition 56

Levelling 7

Lipids 18

Liquid condensed phase 55, 56

Liquid crystal 25

Liquid expanded phase 55

Liquid-gas 18

Liquid-liquid 18

Load file 95

Loading

operating conditions 102

Loading a file 13, 54

Logging interval 98

M

Marbling 20

Materials

for experiments 72

Memory

clear 11

Meniscus 31, 32, 58, 76

during deposition 32, 58, 62

Meniscus radius 59, 63

Menu bar

software 94

Micelles 37

Micro-balance 131

Möbius, D. 21

Molecular

mountain ranges 62

Molecular area

determination 80

zero pressure 25

Molecular electronics 21

Molecular flow 78

Molecular weight 101

Monolayer

acid to salt conversion 87

annealing 36

cholesterol 89

collapse 25, 62, 77, 83

elasticity 77

flow 78

peeling off 62

physical presence 76

reactions 87

spreading 76

stability 29, 62, 76

viscosity 79

Monolayer Menu 95, 100

Multi-compartment troughs 65

Multilayer 19, 56. *See also* Deposition

Multilayer deposition

in tutorial 56

Multiple users 10, 119

N

Nature 21

Non-centro-symmetric 34

Non-linear optical films 34

O

Oleophilic 18

Open to area 100

Operating Conditions Menu 52

Operating modes

multiple users 10

P

P&A-Time 54, 59, 60, 95

PC requirements 8

Peeling off

of monolayer 62

Peroxide 40

Phase changes

determination in monolayers 102

Piston oil 22

Plasma etch 49

Plotting an isotherm 54

Pockels, A. 21

Polar media 18

Port

com port 119

Position detection 130

Potassium octanoate 37

Potentiometer 123

dipper 129

Powder

monolayer flow 78

Preparations

for experiments 72

Pressure

equilibrium spreading 23

Pressure control 121

for dipping 57

setting 54

Pressure sensor 7, 118, 119

adjustment 131

calibration 107

questions 119

setup 131

zeroing 51, 74

Pressure sensor out of range 132

Pressure too low 118

Pressure-area graph 95

Pressure-area isotherm 12
Pressure-time 120
Print screen 95
Printing 13
Program Dip
 software command 57
PS4 131
PTFE 73
 Troughs 36
Pump 2
Pyroelectric films 34

Q

Quasi static compression 102
Questions 118

R

Rayleigh, Lord
 John William Strutt 21
Refractive index
 changing in LB films 60
Removable top 5
Repeated compressions 101. *See also* Isotherm
 cycles
Requirements
 for tutorial 48
 laboratory 2, 35
Run time variables 11

S

Safety 35, 72, 87
Samples 119
Samples / Reading 98
Saving
 operating conditions 102
Saving files 13, 95
Schaefer 22
Sensors 21
Serial port 7, 119
Serial port driver 8
Setup Menu 95, 98
Signature
 software 95
Silk
 waxed thread 22
Sodium hydroxide
 substrate preparation 40
Software 8, 94, 106
 active screen 94
 buttons 96
 commands in tutorial 50
 menu bar 94
 organisation 8
 updating 10, 115
Solution
 molecules in subphase 62
Solvents
 boiling points 39
Soxhlet 40
Spreading 53, 76

Stop 11
Subphase
 Cadmium ions in 29
 cleaning 51, 74
 metal ions in 87
 solution of molecules 62
 trivalent ions in 88
Substrate
 cleaning 40
 hydrophilic 31
 preparation 49, 138
Substrate area
 calculation of 103
Sumi-nagashi 20
Surface
 active 18, 37
 cleaning 62
 with aspirator / pump 77
 preparation 40, 138
 plasma etch 49
 pressure 23
 pressure too high 62
Surface potential sensor 134
Surface tension 23
Surfactants 18, 37
Switching area axis
 $\text{cm}^2 \leftrightarrow \text{Å}^2$ 53

T

Target area 95, 97
Target pressure 11, 97, 100, 103
 setting for deposition 56
Teach barrier positions 107
Tectonic plate
 monolayer model 77
Temperature control 7
Tikopur 37
TopEnd 103
Top position
 setting dipper 104
Transfer ratio 32, 60, 63, 121
 incorrect 121
Transfer ratios
 interpreting 62
Traube's rule 29
Trek electrometer 134
Trivalent metal ion
 in subphase 88
Trouble-shooting
 barriers 124
Trough
 filling 118
 preparation 49
 storage 58, 73
 transport 73
Trough top 5

U

Ultrasonic bath 40
Unpacking 3

Updating software 10, 115

V

Van der Waal 18, 24

Variables

 permanently displayed 96

Variables Menu 56, 95

Volatility

 of solvents 39

Volume 101

W

Wait interval

 dipping 103

Water 2, 38

Waveguides 21

Website 9

Weight

 calibration 107

Whatman's

 Chromatography paper 26

Wilhelmy plate 24, 26, 107, 120

 setting up 7

X

X type deposition 63

X-ray diffraction

 head group spacing 63

Y

Y type deposition 33

Z

Z type deposition 33, 63

Zero

 pressure sensor 51

Zero pressure

 molecular area 55

