

Insoluble Monolayers: Preparation, characterisation and use in functional surfaces and nanotechnology

Dr. Tapani Viitala

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Why ?

- Thin organic films of a thickness of a few nanometers (a monolayer) are the source of high expectations as being useful components in many practical and commercial applications such as sensors, detectors, displays, coatings and electronic circuit components
- Nowadays materials can be synthesized almost without any limitations with desired functionality \Rightarrow Combined with LB enables the production of electrically, optically and biologically active components on a nanometer scale
- Powerful technique for mimicking molecular binding, transport and interactions in biological membranes
- Not only restricted to organic materials anymore – solid nano- and microparticles and fibers has been used as film forming materials

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Why ?

- Promising deposition technique for monolayers due to its advantages compared to other techniques i.e.
 - Enables precise control of the monolayer (thin film) thickness and packing density,
 - Homogeneous deposition over large areas
 - Enables multilayer structures with varying layer composition
 - Deposition can be made on any kind of solid substrate
- Enables also the study of interactions between materials on a molecular level

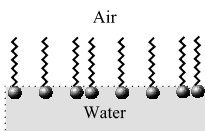
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Basic concepts in Langmuir and Langmuir-Blodgett technology

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Insoluble Monolayers

- Make use of the ability of surfactants to lower the surface tension of water based subphases
- There exists a wide range of surfactants with an amphiphilic nature which drastically lower the surface tension of water
- Surfactants with longer hydrocarbon chains than 14-16 are practically insoluble in water
- These amphiphilic substances can with the help of a volatile and water insoluble solvent easily be spread on a water surface to form an insoluble monolayer at the air/water interface: Langmuir film



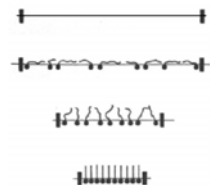
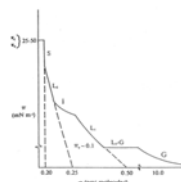
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Surface pressure, π

- Surface pressure is the decrease in surface tension of a water subphase when a monolayer is spread and compressed on the air-water interface

$$\pi = \gamma_0 - \gamma$$

γ_0 = surface tension of subphase without any monolayer
 γ = surface tension of subphase with monolayer present



Surface tension decrease

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Surface potential, ΔV

- Caused by changes in the orientation and accumulation of dipole moments at the air-water interface

$\Delta V = \mu_d / \epsilon \epsilon_0 A$

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Langmuir film balance

- Balance + movable barriers in a feedback loop
- Wilhelmy plate electrobalance measures the surface pressure, simultaneously as the barriers reduces the available surface area.

$F = \rho_p g l w_p t_p + 2\gamma(t_p w_p)(\cos) - \rho g t_l w_p h_l$

$\Pi = -\Delta\gamma = -[\Delta F / 2 (t_p + w_p)] = -\Delta F / 2 w_p$, if $w_p \gg t_p$

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Compression isotherm

- The recorded data are usually plotted as Surface pressure versus Mean Molecular Area, which results in the compression isotherm

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Compression isotherm

- The phase behaviour of the monolayer is mainly determined by:
 - The physical and chemical properties of the amphiphile
 - The subphase temperature and pH
 - The subphase composition i.e. salt concentration, type of salt, small molecules, biomolecules...
 - Compression speed
- An increase in the chain length increases the attraction between molecules, condensing the π -A-isotherm. On the other hand, if an ionizable amphiphile is used the ionisation of the head groups induces repulsive forces tending to oppose phase transitions.

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Compression isotherms - Hysteresis

- Can be used to evaluate how well the monolayer material can retain its configuration during its expansion after a compression, or how mixed monolayers behave by squeezing out smaller molecules
- Monolayer compressed to a predetermined pressure and then decompressed

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Compression isotherms – Relaxation isotherms (Stability)

- Monolayer compressed to a predetermined pressure and then kept at this
- Monolayer compressed to a predetermined pressure at a certain area and then kept at constant area

Constant area

Constant pressure

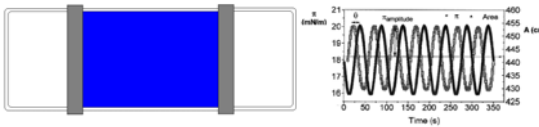
Comparison of relaxation isotherms for high- and low-molecular-weight asphaltene monolayers relaxed at a surface pressure of $\pi^* \approx 25$ mN/m at 20.0°C.

The kinetic stability curves for stearic acid monolayers on CaCl_2 at three different pH values.

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Compression isotherms – Oscillating barriers (interfacial elasticity)

- Monolayer compressed to predetermined surface pressure after which the barriers is started to oscillate
- Visco-elastic parameters of the monolayer can be obtained by using the oscillating barrier method (dilatational properties)



$$E^* = E' + iE'' = |E| \times \cos\phi + i|E| \times \sin\phi$$

$$|E| = \gamma_A / [A_A / A_{mean}]$$

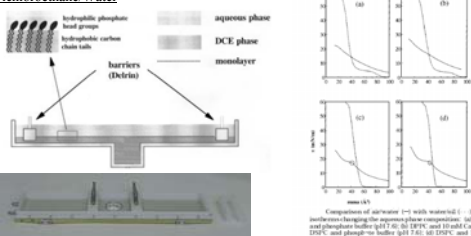
$$\theta \rightarrow \begin{cases} E_s = |E| \cos\theta \\ E_v = |E| \sin\theta \\ \tan\theta = E_v / E_s \end{cases}$$

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Compression isotherms – Water/Oil

- Isotherms measured at water-oil interface resembles more closely real life situations

Dichloroethane/Water



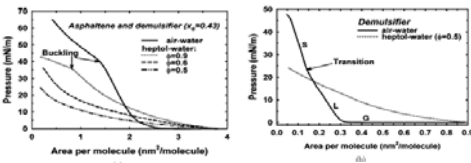
hydrophilic phosphate head groups
 hydrophobic carbon chain tails
 barriers (debris)
 aqueous phase
 DCE phase
 monolayer

Compression of air/water (1:1) with water/DCE (1:1) isotherms showing the aqueous phase compression: (a) DPPC and phospholipid (DPPC) at 10°C, (b) DPPC and 10 mM SDS at 10°C, (c) DPPC and 10 mM SDS at 20°C, and (d) DPPC and 10 mM SDS at 30°C.

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Compression isotherms – Oil/Water

- Isotherms measured at oil-water

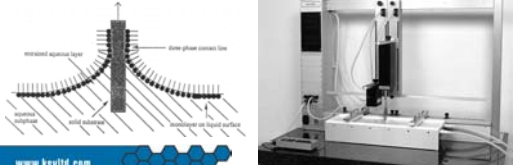


Comparison of pressure-area (p-A) isotherms of asphaltene ($\phi_A = 0$) and demulsifier ($\phi_A = 1$) monolayers, at the heptol-water and air-water interfaces: (a) asphaltene monolayers at heptol-water interfaces for $\phi = 0.5, 0.6$ and 0.9 and at the air-water interface; (b) demulsifier monolayers at the heptol-water interface for $\phi = 0.5$ and at the air-water interface.

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LB Deposition

- The floating monolayer or Langmuir film can also be deposited on a solid substrate for building up highly organised multilayers of the used monolayer material: Langmuir-Blodgett films
- Done by successively dipping a solid substrate up and down through the monolayer while simultaneously keeping the surface pressure constant by a computer controlled feedback system between the electrobalance measuring the surface pressure and the barrier moving mechanism



monolayer spreader
 solid substrate
 monolayer on liquid surface
 monolayer transfer
 monolayer on solid surface

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LB deposition

- The LB deposition is traditionally carried out in the “solid” phase. The surface pressure is then high enough to ensure sufficient cohesion in the monolayer
- The surface pressure value that gives the best results depends on the nature of the monolayer and is usually established empirically (10-40 mN/m)
- When the solid substrate is hydrophilic (glass, SiO₂, etc.) the first layer is deposited by raising the solid substrate from the subphase through the monolayer, whereas for a hydrophobic solid (HOPG, silanized SiO₂, etc.) the deposition is started from air
- The quantity and the quality of the deposited monolayer on a solid support is measured by a so called transfer ratio, t.r. This is defined as the ration between the decrease in monolayer area during a deposition stroke, A_f , and the area of the substrate, A_s . For ideal transfer the t.r. is equal to 1

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LB deposition

- Several parameters affect what type of LB film is produced:
 - Nature of the spread film
 - Subphase composition, pH and temperature
 - Surface pressure during the deposition
 - Deposition speed
 - Type and nature of the solid substrate
 - The time the solid substrate is stored in air or in the subphase between the deposition cycles

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Classical LB deposition

- Vertical deposition

Hydrophilic substrate Hydrophobic substrate

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Alternate LB deposition

- Special case of normal LB deposition – 2 different monolayer materials can be deposited in any configuration

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Horizontal deposition

- Sometimes vertical deposition unwanted
- Alternative is horizontal deposition (Langmuir-Schaeffer)
- Basically the same preparative procedures as for vertical depositions

Cadmiumstearate, C18COOH-Cd

$\pi = 35 \text{ mN/m}$
T.R. = 2.06 ± 0.1

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Utilizing the Langmuir and Langmuir-Blodgett films

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Compression isotherms

- Differences in chain conformation:
 - Stearic acid (C_{18}COOH)
 - Petroselaic acid, one double bond (trans6-C18COOH)
 - Elaidic acid, one double bond (trans9-C18COOH)
 - Oleic acid, one double bond (cis9-C18COOH)

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Compression isotherm + ΔV

- Effect of added salt in subphase:
 - Petroselaic acid, one double bond (trans6-C18COOH)

The πA isotherms of petroselaic acid on (a) $5 \times 10^{-4} \text{ M}$, (b) $5 \times 10^{-3} \text{ M}$, and (c) 10^{-2} M TiCl_3 and (d) pure water ($\text{pH} = 2$).

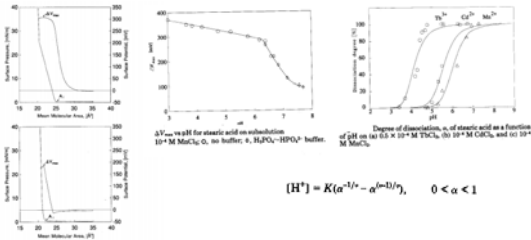
ΔV_{max} vs salt concentration for (a) petroselaic acid on (c) TiCl_3 , (d) MnCl_2 , and (a) CoCl_2 solutions at $\text{pH} = 5.7$.

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Compression isotherm + ΔV

- Effect of different pH with constant salt concentration:
– Stearic acid (C18COOH)



$$[H^+] = K(\alpha^{1-\alpha} - \alpha^{1-\alpha}/\gamma) \quad 0 < \alpha < 1$$

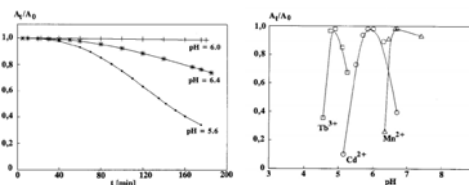
$$K = (aK_a^*K_b[M^+])^{1/2} \gamma^{1/2}$$

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Compression isotherm - Stability

- SA on subphases with constant concentration of different ions but different pH



The kinetic stability curves for stearic acid monolayers on CaCl₂ at three different pH values.

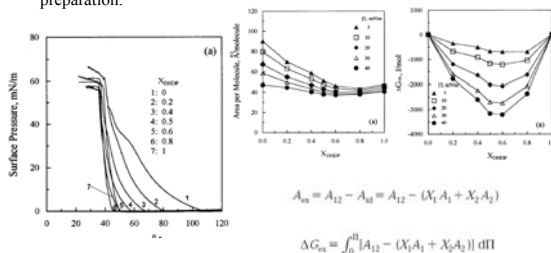
The stability of stearic acid monolayers as a function of pH on TbCl₃, CdCl₂, and MnCl₂ subphases. The time t at which A_t/A_0 was determined was 100 min for the Tb subphase and 175 min for Cd and Mn subphases. The surface pressure was 32.5 mN m⁻¹ for the subphases containing divalent ions and 30 mN m⁻¹ for the Tb subphase.

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Compression isotherms - Thermodynamics

- Mixing of monolayer materials: Dipalmitoylphosphatidylcholine (DPPC) and dihexadecyl phosphate (DHPD). Lipids used for liposome preparation.

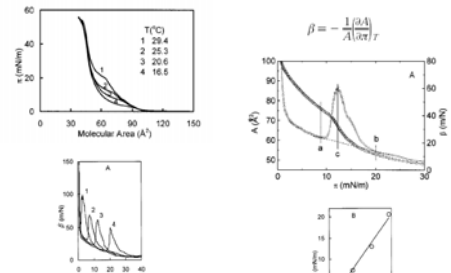


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Compression isotherms - Thermodynamics

- DPPC: Temperature dependence and compressibility

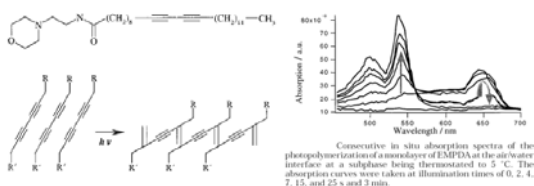


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Monolayer Polymerization

- UV induced polymerization of diacetylenes

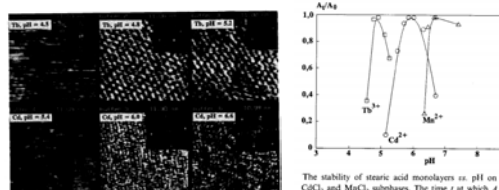


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Deposition - Stability

- Quality of deposited film improved by tuning the stability of monolayer



The AFM images show the quality of the deposited films on different subphases.

The stability of stearic acid monolayers as a function of pH on TbCl₃, CdCl₂, and MnCl₂ subphases. The time t at which A_t/A_0 was determined was 100 min for the Tb subphase and 175 min for Cd and Mn subphases. The surface pressure was 32.5 mN m⁻¹ for the subphases containing divalent ions and 30 mN m⁻¹ for the Tb subphase.

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Deposition - Biomembranes

- Polymerized monolayer with functional group for covalently immobilize antigens

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Deposition - Microparticles

- Polystyrene particle deposition

| Mw x 10^-6 | Area (Å^2) | Area (Å^2) | Area (Å^2) |
|------------|------------|------------|------------|
| 6.77 | 19 | 69 | 77 |
| 2.34 | 20 | 70 | 30 |
| 7.1 | 84 | 110 | 130 |
| 7.1 | 40 | 60 | 66 |

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Deposition - Nanowires

- Nanowire deposition with LB technique

Silver

Silicon

Scanning electron microscopy images (at different magnifications) of the silver nanowire monolayer deposited on a silicon wafer.

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Deposition - Nanoparticles

- Fe₂O₃ nanoparticle deposition with LB technique

| Area (Å^2) | Area (Å^2) | Area (Å^2) | Area (Å^2) |
|------------|------------|------------|------------|
| I | II | III | IV |

Double layer

Monolayer

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Practical/Commercial Applications?

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Basic properties of biomembranes

- Monolayers simple models of biological membranes
- Main components of mammalian plasma membrane and cell membranes are different lipids; phospholipids, sphingolipids, cholesterol etc.
- Studies with monolayers can help understanding the behaviour and role of different lipids in biological membranes

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Interaction of biomolecules with membranes

- Basic research topics to understand and control the mechanism and interactions at molecular level
- Implications to biotechnology, pharmaceutical & cosmetic industry
 - Biocompatible surfaces
 - Incorporation of biomolecules in artificial membranes
 - Surface epidermal cell interactions
 - Drug delivery
 - Enzyme interactions
 - Respiratory Distress Syndrome (RDS)



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Sensors

- Chemical sensors of LB films are developed for gas, bio, food, beverage etc applications.
- Gas and volatile organic compound (VOC) sensors requires 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 for these sensors.
 - Gas sensors have been developed for example for NO_x , SO_2 , CO , Cl_2 , NH_3 etc.
 - VOC sensors have been developed for example for acetic acid, citric acid, glutamic acid, ethanol, n-butyl acetate, hexanal, saxitoxin, sucrose quinine etc.
- Biosensors should be able to use small amount of analytes which is possible with LB film based sensors as they are nanoscale layers. Furthermore, the LB technology have been proven to enable controlled oriented immobilization of active biomolecules by using linker lipids or streptavidin-biotin-lipids.
 - Immunological assays; antibody-antigen reactions
 - Detection of biotin functionalized biomolecules

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Technological Applications

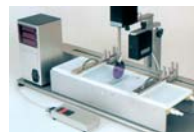
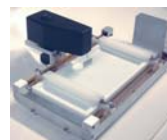
- The capability of fabricating dimensions to mono-molecular tolerances and their ability to incorporate different molecular architecture give LB films some unique advantages for technological applications.
 - Optical waveguides and signal processing devices based on thin organic films are being developed for computing and communications applications due to their nonlinear optical properties and fast response times
 - Organic photoactive and/or conductive layers are being developed for organic light emitting diodes, organic solar cells, liquid crystal displays, optical information storage, optical switching etc...
 - CdS and TiO_2 nanoparticles are studied due to their excellent photocatalytic properties.
 - Magnetic nanoparticles (magnetite Fe_3O_4 and maghemite Fe_2O_3) are of great interest for applications in information storage systems, catalysts, ferrofluids, and medical diagnostics.
 - Nanoparticles and -wires are being used as templates for nanoscale photoresists
 - Hybrid materials of clays and amphiphilic cations are being studied for ion-exchange materials and catalysis applications

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KSV LB Trough Models

- MiniMicro
- Minitrough
- KSV2000

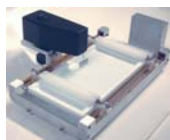


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KSV MiniMicro

- The smallest miniaturized Langmuir/Langmuir-Blodgett trough on the market
- Standard trough size; 170 mm (l) x 80 mm (w) x 5 mm (d) = 68 ml, other trough sizes by request
- Transportable and quick setup; exchangeable troughs for modularity
- Full size software enabling all most common Langmuir film studies from compression (expansion) isotherms, isobars, dilational elasticity and Langmuir-Blodgett deposition
- Maximum substrate size for deposition; 25 mm (w) x 30 mm (l)
- Compatible with major thin film characterization techniques; Brewster Angle Microscopy, Fluorescence Microscopy, UV-Vis, IRRAS and Synchrotron beam line measurements of floating monolayers

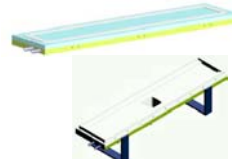


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KSV MiniTrough

- The most sold Langmuir/Langmuir-Blodgett trough system in the world
- Cost efficiency without compromise
- Standard trough size; 330 mm (l) x 75 mm (w) x 5 mm (d) = 125 ml, other trough sizes by request
- Low volume (from 15 ml), oil/water, microscopy, enzyme kinetics trough options
- Full size software enabling all most common Langmuir film studies from compression (expansion) isotherms, isobars, dilational elasticity and Langmuir-Blodgett deposition
- Maximum substrate size for deposition; 35 mm (w) x 60 mm (l)
- Compatible with major thin film characterization techniques; Brewster Angle Microscopy, Fluorescence Microscopy, UV-Vis, IRRAS and Synchrotron beam line measurements of floating monolayers



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KSV 2000

- The cost effective, full size modular and open design Langmuir/Langmuir-Blodgett trough system
- Expands from a full size conventional Langmuir film balance to a high performance Langmuir film deposition system or to a fully equipped alternating multilayer Langmuir-Blodgett instrument; MiniAlternate Option (trough volume 1 L instead of 6 L)
- Compatible with all the special trough options of the KSV MiniTrough
- Standard trough size; 580 mm (l) x 150 mm (w) x 7 mm (d) = 610 ml
- Full size software enabling all most common Langmuir film studies from compression (expansion) isotherms, isobars, dilational elasticity and Langmuir-Blodgett deposition
- Maximum substrate size for deposition; 100 mm (w) x 100 mm (l)
- Compatible with most thin film characterization techniques; Brewster Angle Microscopy UV-Vis and IRRAS measurements of floating monolayers



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Langmuir film characterisation methods

BAM



PM-IRRAS



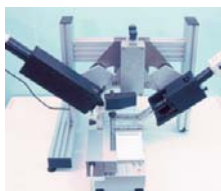
ISR



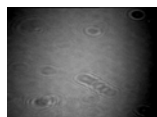
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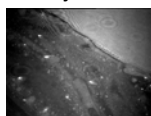
Brewster Angle Microscope, BAM KSV Optrel BAM300



film absent



formation of monolayer



resolution – 2 μm

angle of incidence 45-75 degree

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Use of BAM – morphology of monolayer

- Gibbs adsorption isotherm
- crystallization

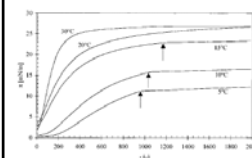
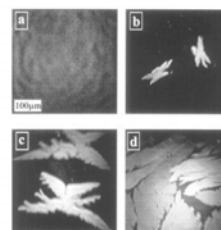


Figure 2. π/Γ adsorption isotherms of 1.5×10^{-5} M aqueous DIBAA solution at different temperatures: 1–5, 2–10, 3–15, 4–20, and 5–30 °C. The appearance of the phase transition point and its coordinates are a function of the temperature T .



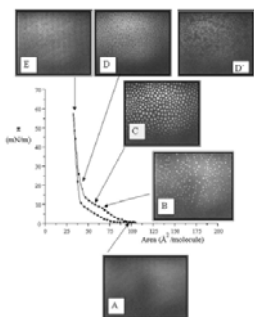
D. Vollhardt, V. Melzer, *J.Phys.Chem.B*, 101(1997)3370.

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Use of BAM – morphology of monolayer

Dipalmitoyl phosphatidyl glycerol (DPPG)



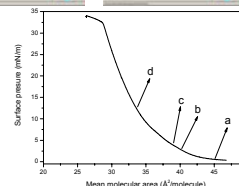
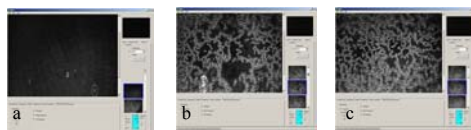
J. Minones Jr., P. Denarowicz Łątka,
J. Minones, J.M. Rodriguez Patino,
E. Iribarnegaray,
J.Coll.Interface Sci., 265(2003)380.

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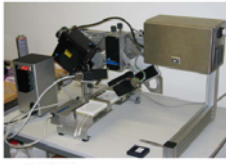
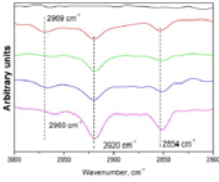
Use of BAM - monolayer polymerization

- Condensation polymerization, Octadecyltrimethoxysilane (ODTMS) on pure water, pH = 2.1



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(Polarization modulation) - Infrared Reflection Absorption Spectroscopy, PM-IRRAS New!!

air/water or air/solid

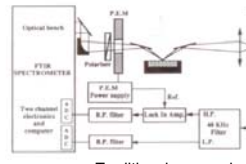
'tiny' and easy to use!

Resolution – 8 cm⁻¹
Spectral range 800 – 4000 cm⁻¹
Angle of incidence 40-85 degree

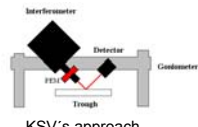
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PM-IRRAS

- Optical techniques widely used in surface characterization
- Advantage of optical techniques that they are non-invasive
- Molecular scale analysis of thin films at air-water, air-solid, and even liquid-solid interfaces
- Enables quantitative analysis of film properties



Traditional approach



KSV's approach

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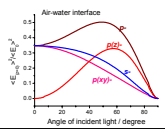
IRRAS vs PM-IRRAS

IRRAS

- Reference spectrum taken without a sample (e.g. clean subphase) is used to resolve sample's response from instrument's spectrum

PM-IRRAS

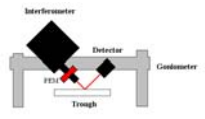

- Utilizes the fact that light's polarization state changes in reflection thus yielding differing spectra for differing polarization states
- Since atmospheric disturbance (H₂O and CO₂) is isotropic, i.e. has no polarization preference, its contribution to IRRAS measurement can be greatly reduced



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PM-IRRAS

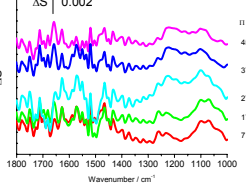
- Usual choice is to modulate polarization between *s* and *p* –states and record spectra for both states *S_s* and *S_p*
- Define differential reflectivity spectrum $\Delta S/S = (S_s - S_p) / (S_s + S_p)$
- Isotropic disturbance is in theory cancelled out from differential spectrum
- Sample's isotropic absorption cancelled

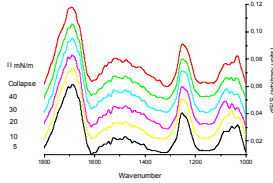
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IRRAS vs PM-IRRAS of DPPC on pure water – Polar Part

IRRAS



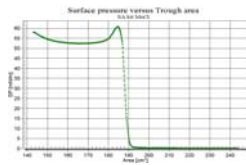
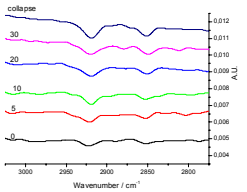
PM-IRRAS



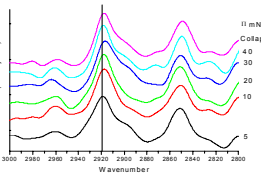
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SA on MnCl₂ subphase

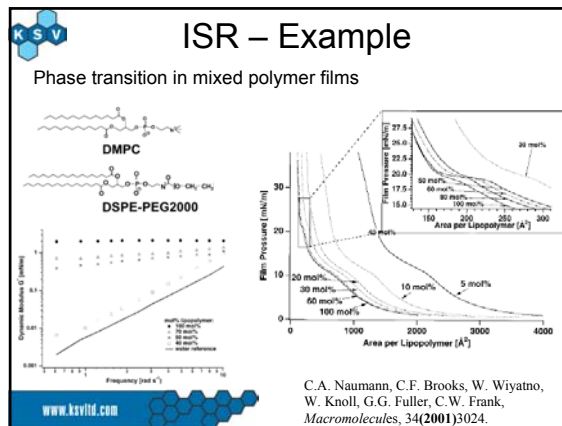
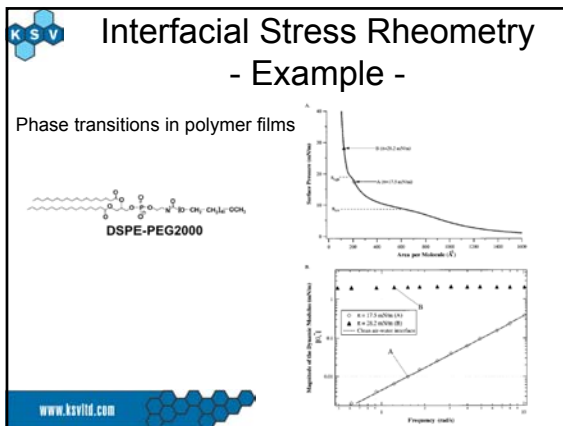
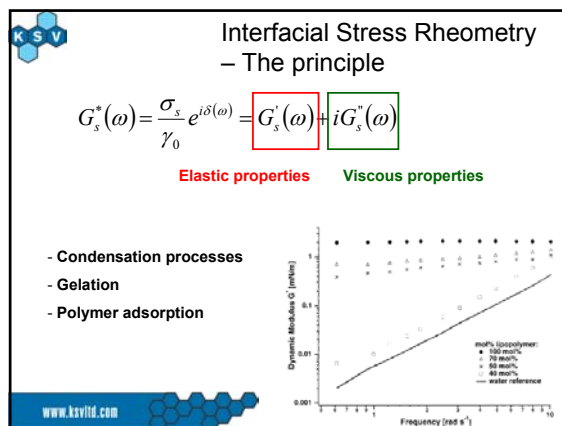
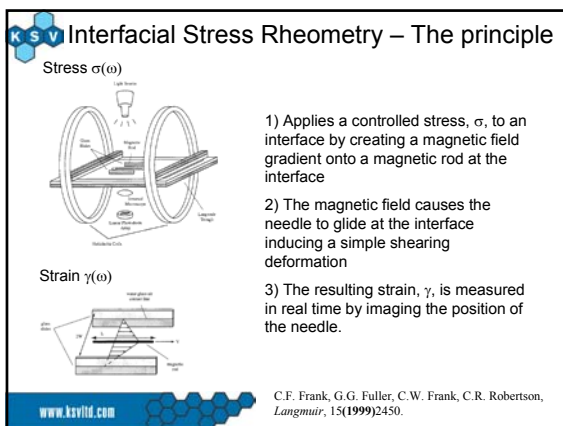
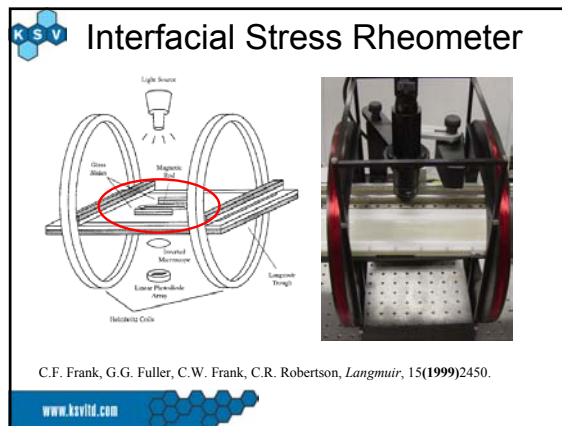
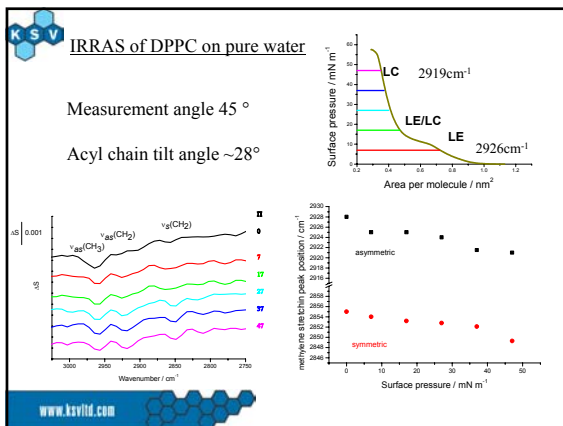
IRRAS

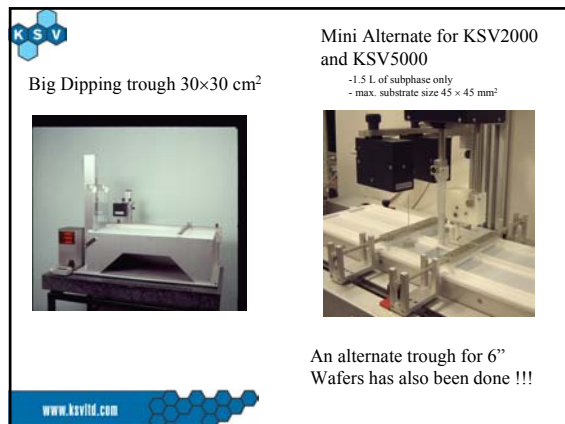
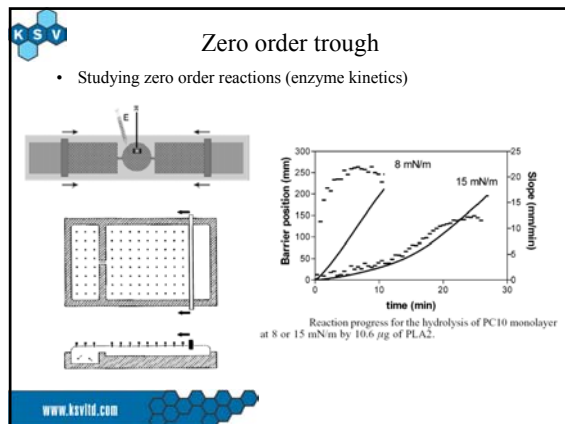
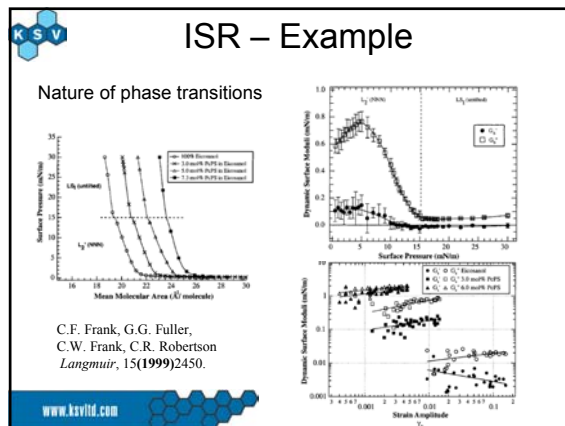
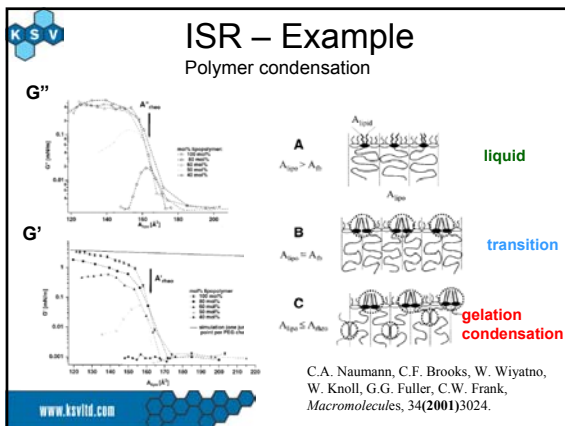



PM-IRRAS



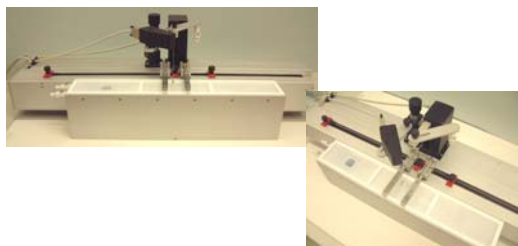
www.ksvild.com







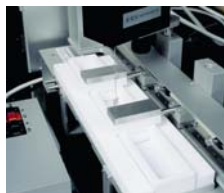
Fromhertz trough



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Interfacial trough – Oil/water Trough with electrode in the subphase



[Example 1](#)

[Example 2](#)

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MiniMicro trough



Big Dip Coater



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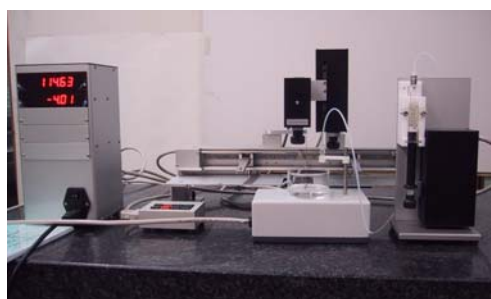
6" wafer Alternate Dipping trough



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Converting Minitrough to a CMC measuring tensiometer



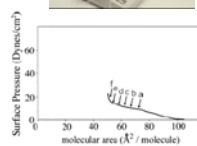
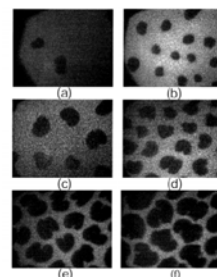
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Fluorescence microscopy



L-DPPC



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