

# Acoustic Waves for Gas and Liquid Phase Sensing

Glen McHale

School of Science  
The Nottingham Trent University  
Nottingham NG11 8NS, UK

# Overview

## 1. Acoustic Waves

- Acoustic wave modes
- Principles of sensing (QCM/SAW)

## 2. Literature Examples

- SAW for dew/frost point sensing
- QCM for monolayer phase transitions

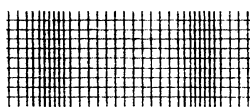
## 3. Our Recent Work

- Steroid and particulate detection
- Combined optical-SAW
- Love waves and biosensing: Theory & Experiment
- Super-hydrophobicity and acoustic waves

# Acoustic Wave Modes

## Acoustic Waves

bulk longitudinal wave



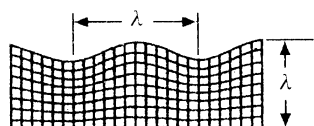
$$v_p = 4000\text{--}12000 \text{ m s}^{-1}$$

bulk transverse wave



$$v_p = 2000\text{--}6000 \text{ m s}^{-1}$$

surface (Rayleigh) wave



$$v_p = 2000\text{--}6000 \text{ m s}^{-1}$$

## Basic Sensor Devices

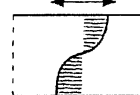
QCM



top

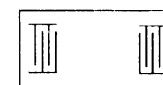


side

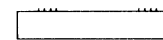


side

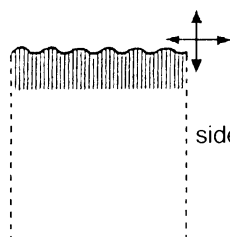
SAW



top

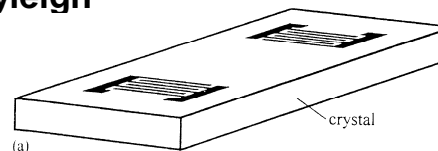


side



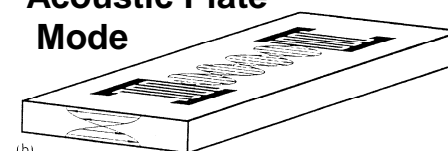
side

Rayleigh



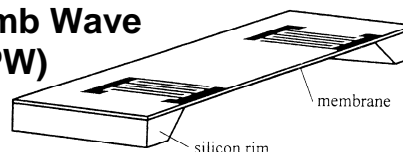
(a)

Acoustic Plate Mode



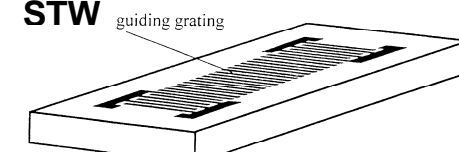
(b)

Lamb Wave (FPW)



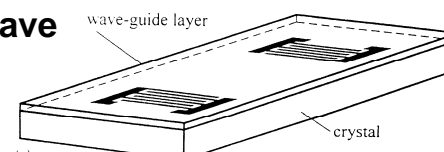
(c)

STW



(d)

Love Wave



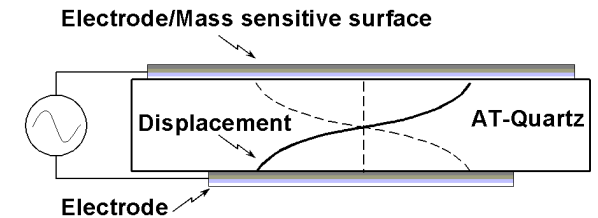
(e)

Delay Line Config's ⇒

# Sensing Principles

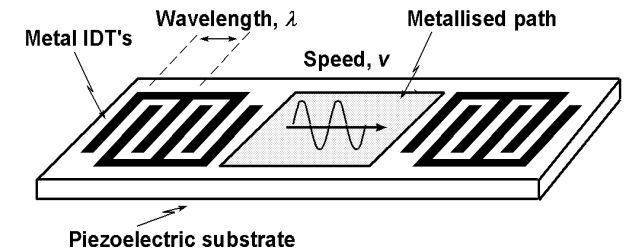
- Quartz Crystal Microbalance (QCM)

Thickness shear mode  
oscillation



- Surface Acoustic Wave (SAW)

Mechanical wave travelling  
along a surface (+electric field)



- Create resonator or measure impedance/spectrum

QCM/SAW determines oscillation freq.

$$v = f\lambda$$

- Mass (thin film) loading

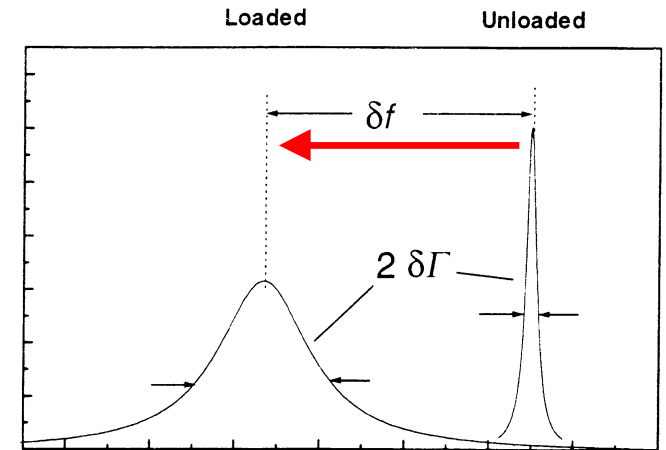
Main effect is change in frequency

Sauerbrey equation  $\Rightarrow$

$$\Delta f \propto f^2 \Delta m/A$$

- Surface Loading Alters Resonance

Mass loading reduces frequency  
 Non-rigid mass (e.g. polymers)  
 broadens resonance/creates  
 damping  
 (senses shear modulus)



- Liquid Loading & Penetration Depth

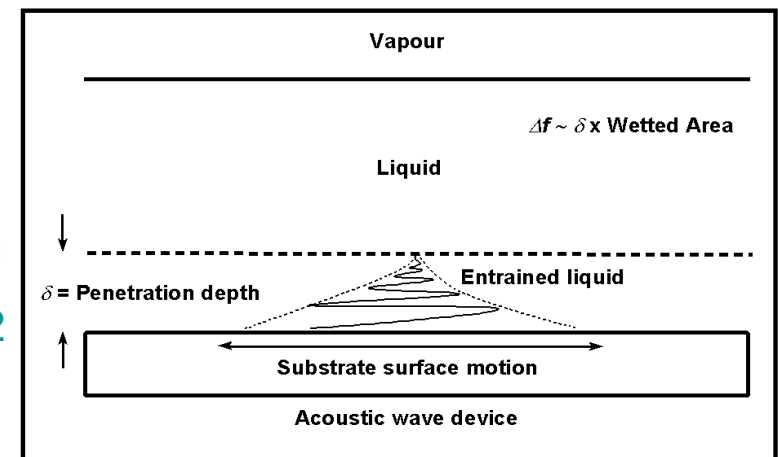
Need shear mode devices  
 (QCM, Shear type SAWs)

Penetration depth  $\delta = (\eta / \pi f \rho)^{1/2}$

Sense mass in penetration depth

Kanazawa  $\Rightarrow \Delta f \propto \sqrt{(\eta \rho)} f^{3/2}$

For water  $\delta \sim 250$  nm (at 5 MHz)



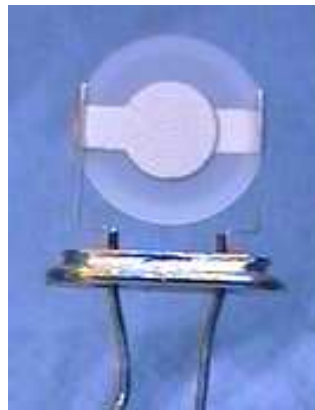
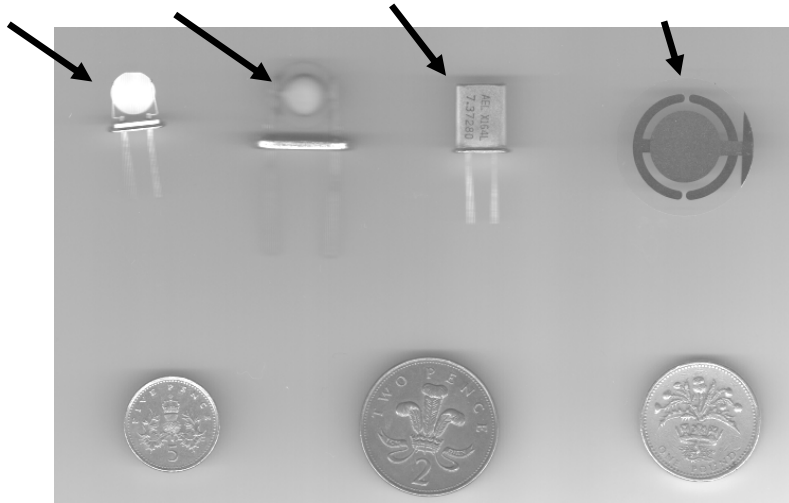
# Devices

## QCMs

Quartz (IQD)  
Blank/ with Contacts Package

RS 7MHz  
Package

Specialist Quartz  
Crystal/5 MHz



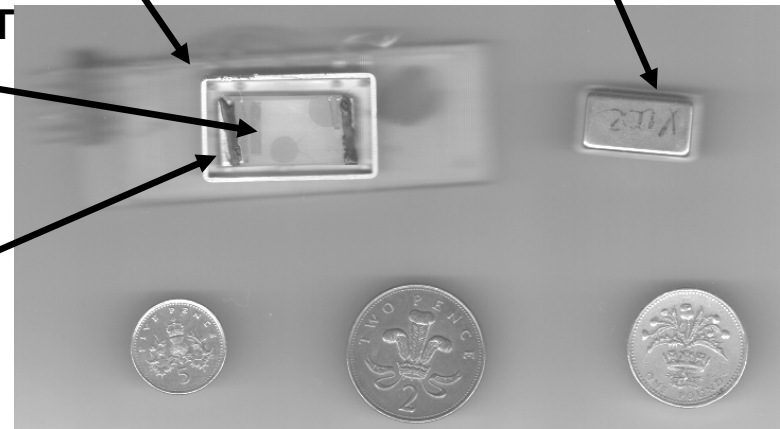
## SAWs

50 MHz RACAL MESL

SAWTEK Package

Apodized IDT  
Offset IDTs  
Multistrip  
Coupler

Acoustic  
Absorber



Dual delay  
line with  
one side  
coated

110 MHz  
SAW

Contact  
Pads

Sensing  
Area

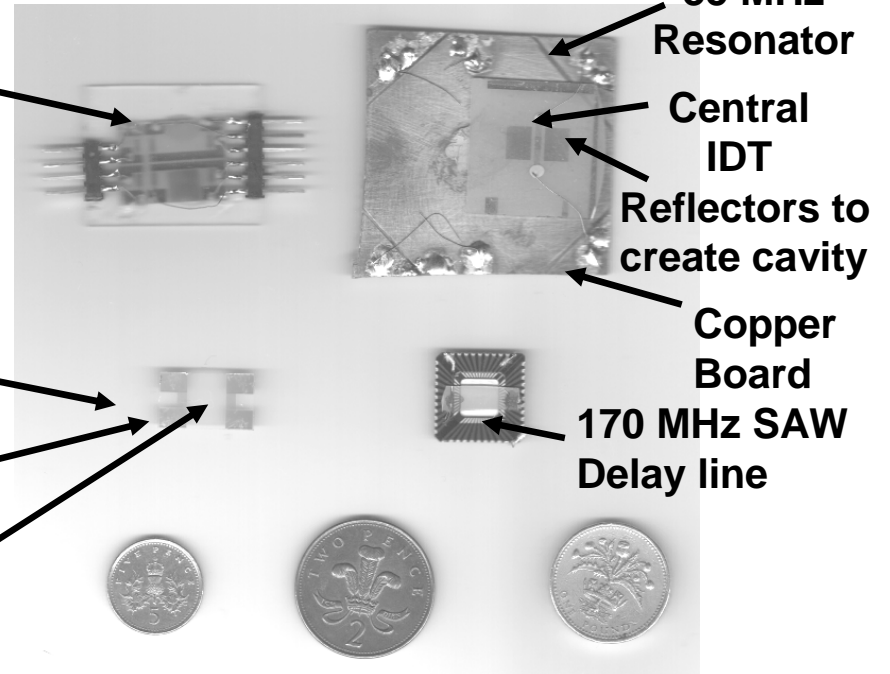
35 MHz  
Resonator

Central  
IDT

Reflectors to  
create cavity

Copper  
Board

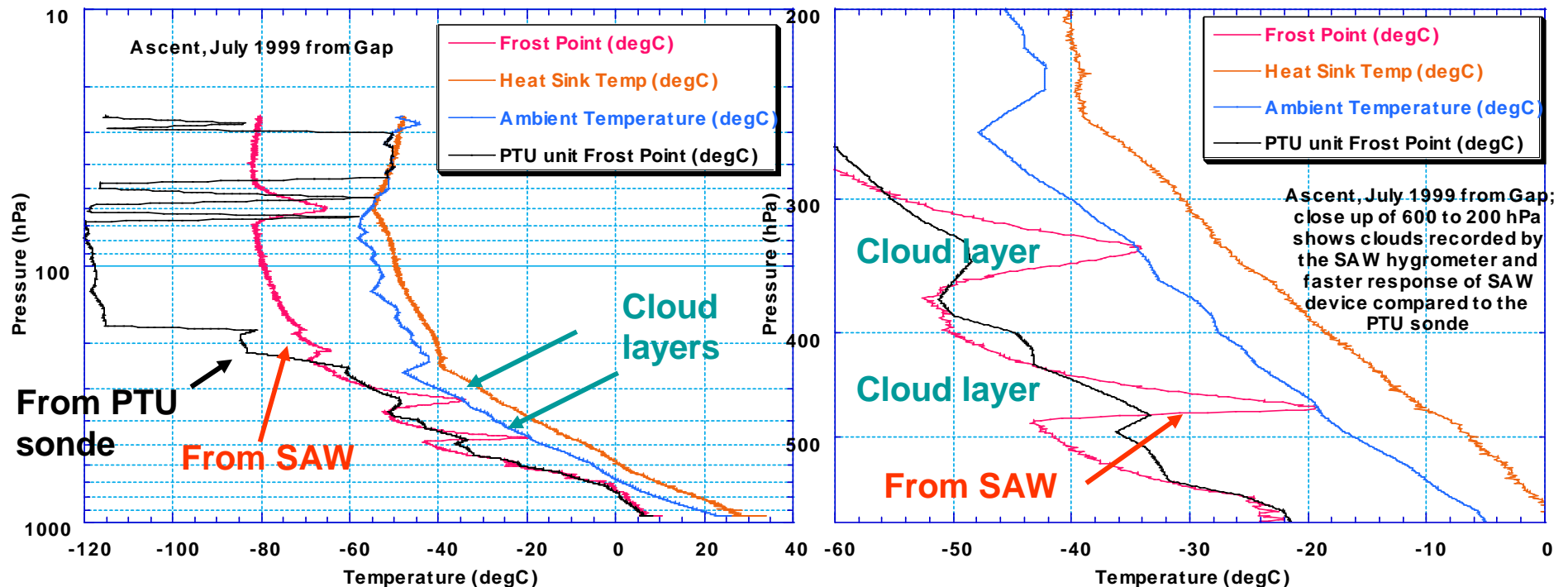
170 MHz SAW  
Delay line



# Two Example Applications from the Literature

# Atmospheric Data

- 400 MHz Saw Based Frost Point Hygrometer  
Dr Rod Jones – Cambridge, UK  
Cycle temperature of substrate using a Peltier  
– loss of SAW resonance gives frost/dew point  
Deployed in a weather balloon



# Monolayer Phase Transitions

- 8 MHz QCM

Prof. J Krim

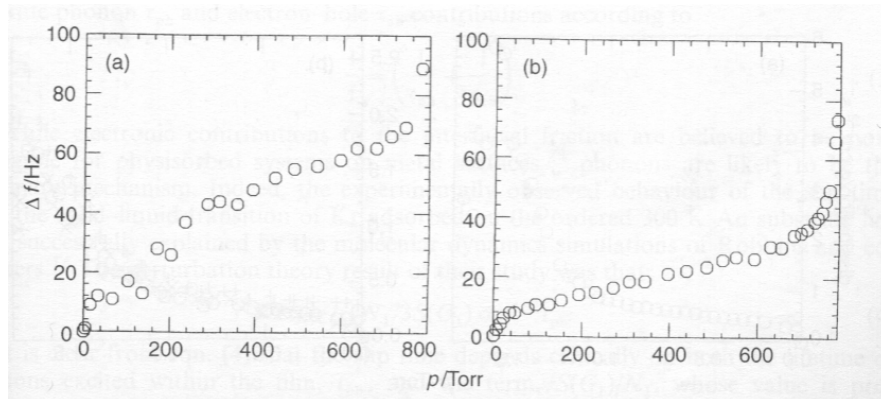
Sliding friction on gold surfaces via monolayer adsorption in UHV

## Nitrogen adsorption (77.4 K)

Au film deposited at

(a) 80 K

(b) 300 K



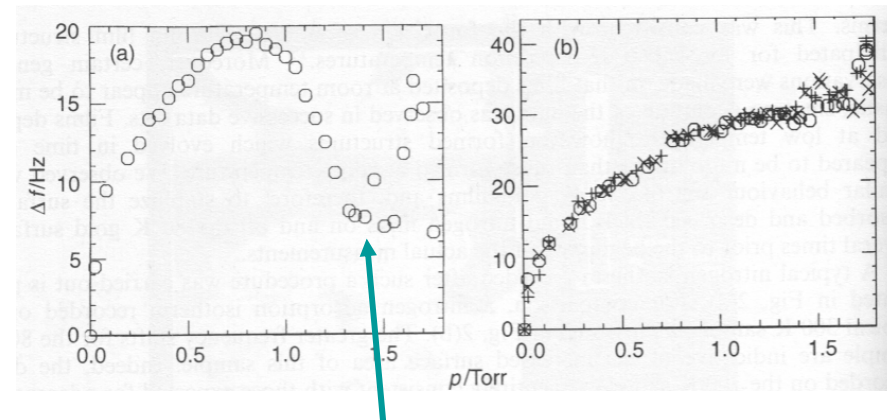
Larger surface area for 80 K deposited Au gives larger frequency shift

## Krypton adsorption (77.4 K)

Au film deposited at

(a) 80 K

(b) 300 K



Liquid to solid monolayer transition point

# NTU Based Acoustic Wave Research

# Overview

- Experimental

  - QCMs

    - MIPs for steroids, terpenes & amino acids, SAMs for PAHs

      - Selectivity*

    - Surface texture & hydrophobicity

      - Wetting*

  - SAWs

    - Electrostatic precipitation of atmospheric particulates

    - Spreading oils and Rayleigh-SAWs

      - Instrumentation*

    - Love waves for biosensing

    - Multiple modes and layer-guided SH-APMs

      - Sensitivity*

- Theoretical

  - Acoustic wave response to multiple viscoelastic layers

  - Interfacial slip and interfacial layers of water*

  - Hydrophobic effects*

## Two of Our Applications

# Molecularly Imprinted Polymers

- Target Applications (*Liquid Phase*)

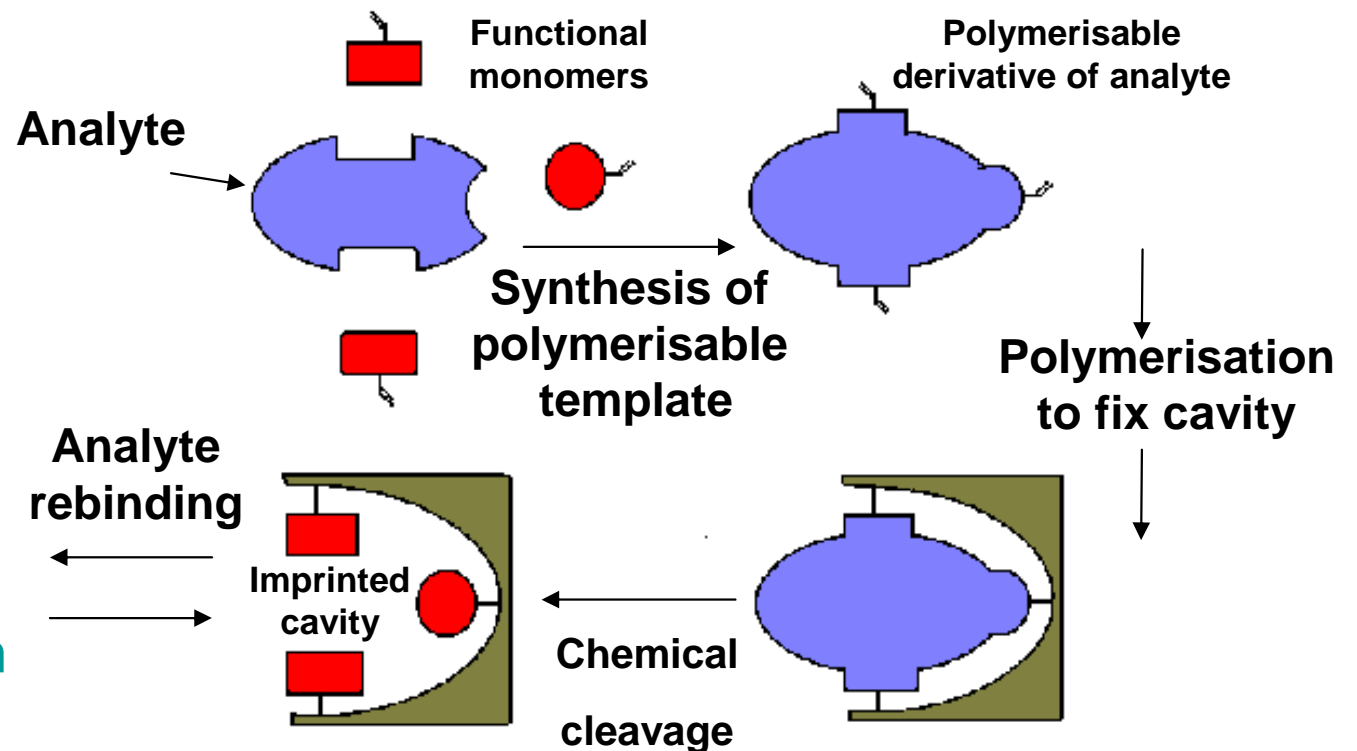
Applications: monoterpenes, amino acids, *topical steroids*  
Tailor made enantioseparation materials

- MIP - Polymer Type Artificial Receptor

Emil Fisher's 'Lock and Key'  
(enzyme analogy)

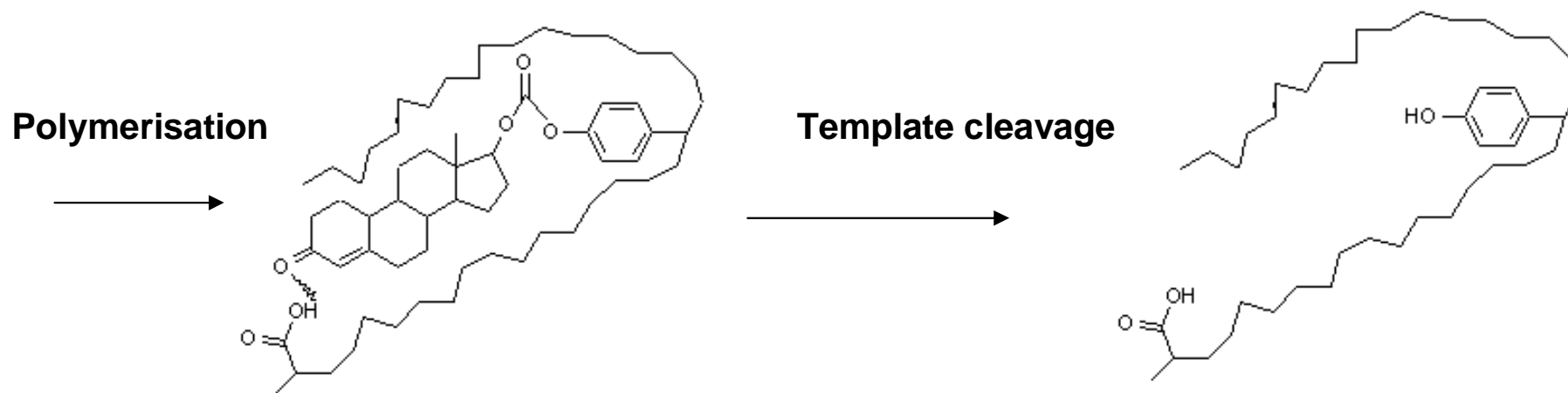
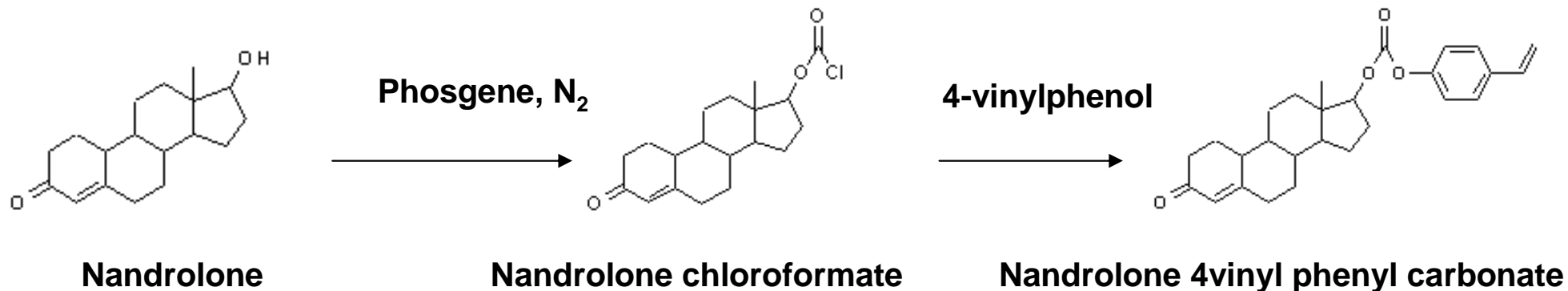
Specific to target analyte in terms of their spatial and electronic environment

Diagram shows a covalent approach



# Synthesis of Nandrolone MIP

- Covalent Approach (Scheme 1)



Gives non-covalent recognition sites

# Selectivity to Nandrolone

- QCM Coating

Spin coated/cast layer  
Covalent imprinting strategy

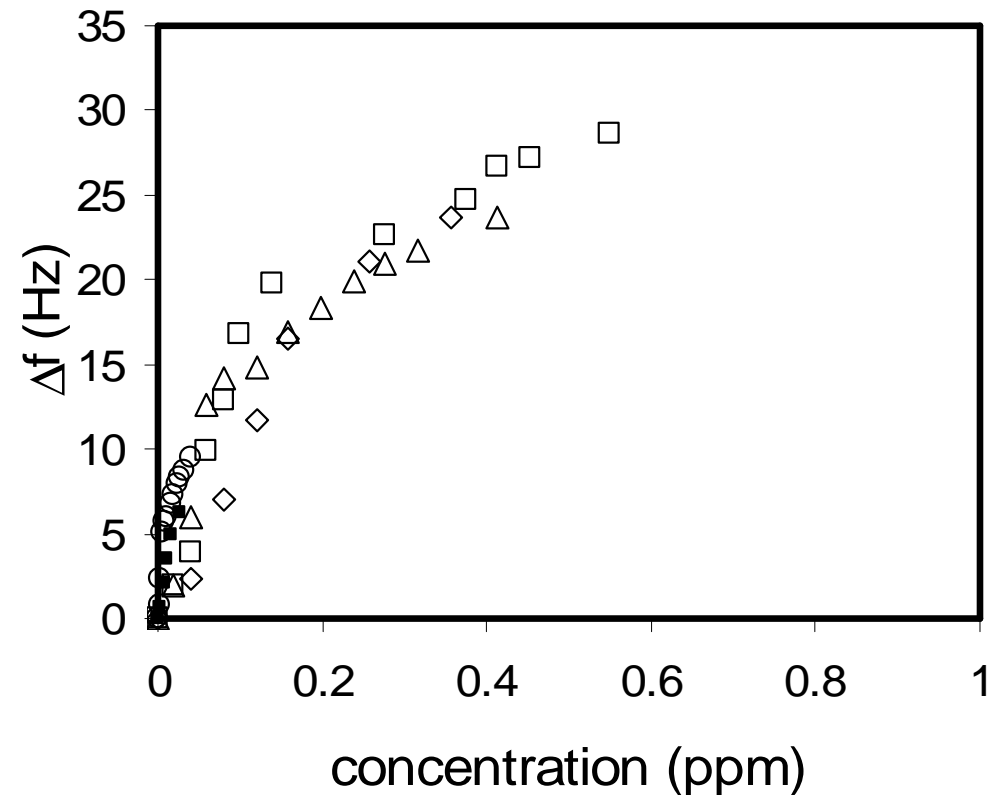
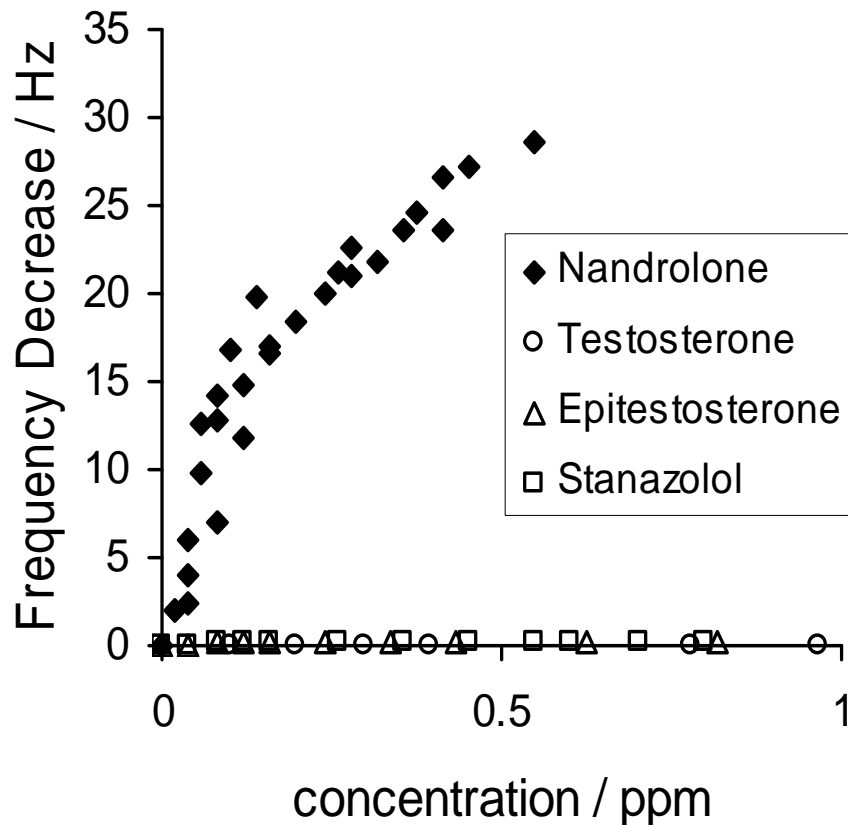
Polymer 1 - Imprinted

Polymer 2 - Non-Imprinted

- Response to Replicates

One-shot screening

Test data for 5 crystals



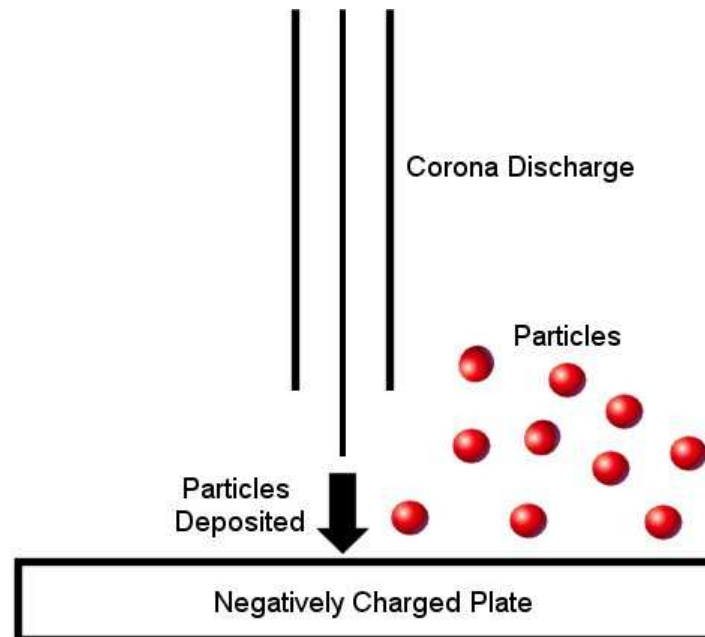
# EP-SAW for Atmospheric Particulates

- **Electrostatic Precipitation**

Charged particles deposited on a collector plate

Established principle for atmospherically borne microorganisms

High (99-100%) efficiency



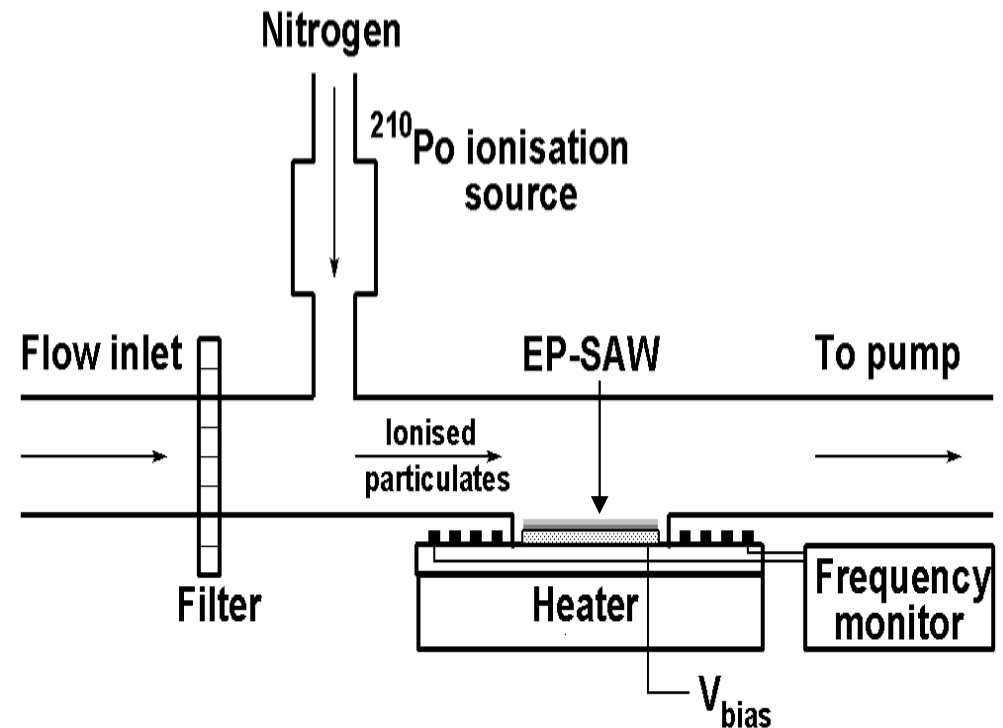
- **System Design**

Air sampled via filter

Particles ionised by  $N_2^+$

Particles collected onto path of biased metallised SAW

**i.e. Electrostatic precipitation**



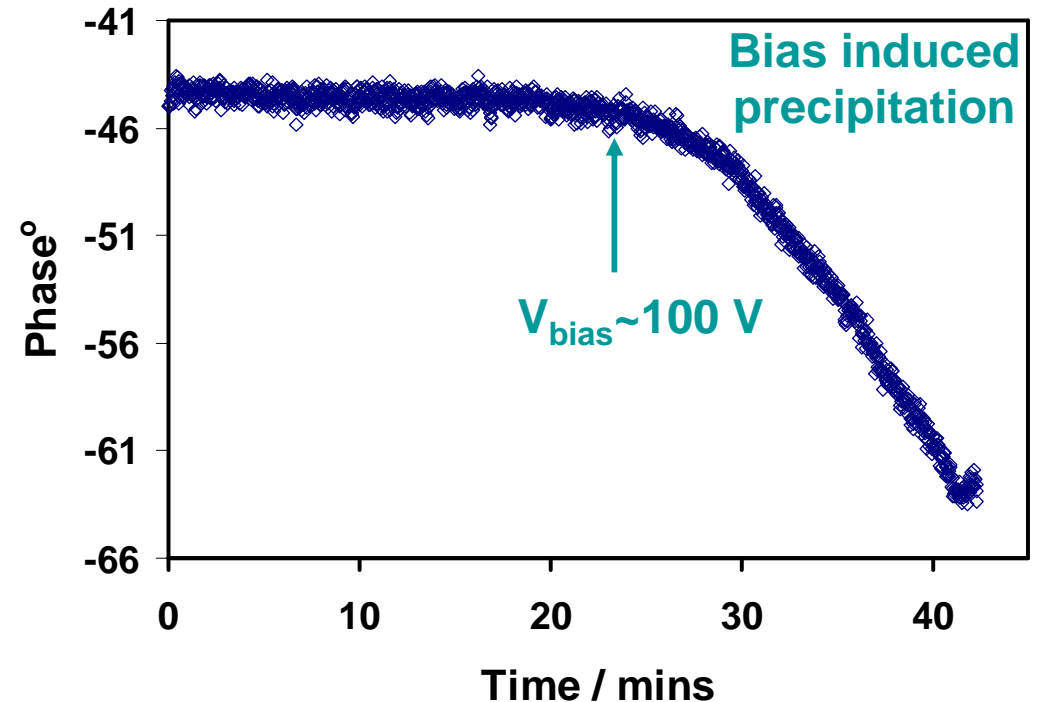
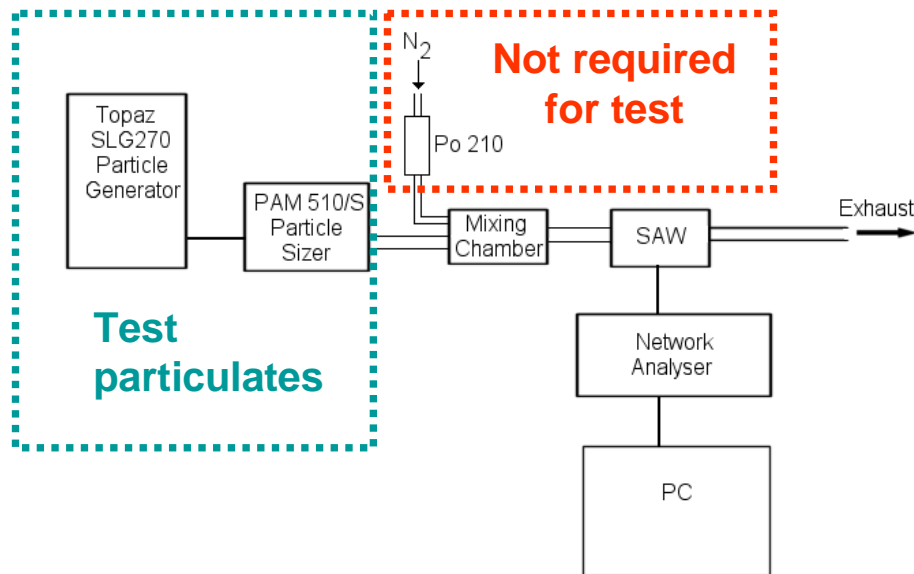
# Particulate Response with Bias

- **Test Device Configuration**

LiNbO<sub>3</sub> - Rayleigh-SAW,  $\lambda \sim 45 \mu\text{m}$   
86 MHz & 253 MHz  
Test particulates via a mono-disperse  $\sim (2.0 \pm 0.1) \mu\text{m}$  NaCl aerosol

- **Preliminary Results**

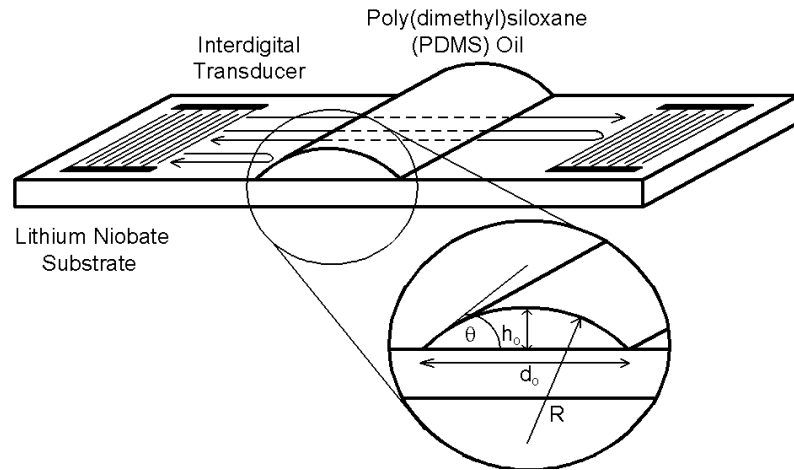
Voltage of plate increased to  $> 120 \text{ V}$  in 20 V steps  
 $\Rightarrow$  **Phase changes**



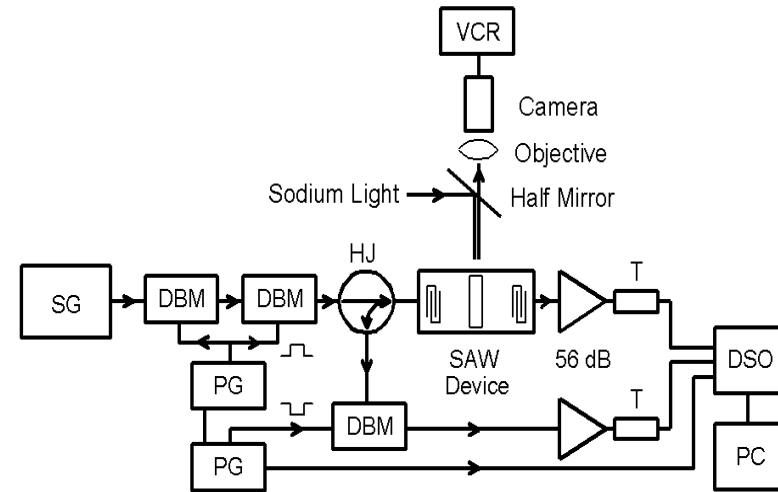
# Our Historical Development

# Dynamic Wetting and SAWs

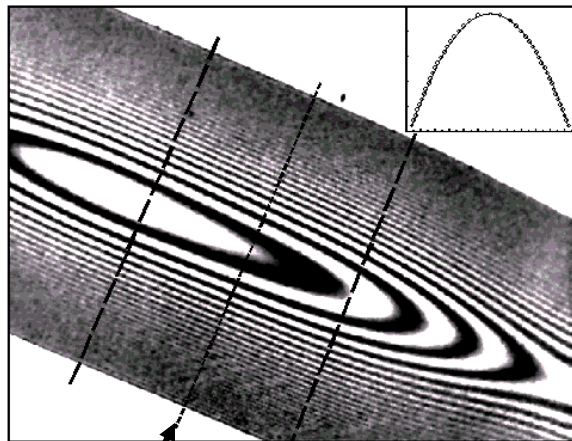
## Concept of the Experiment



## Schematic of Experiment

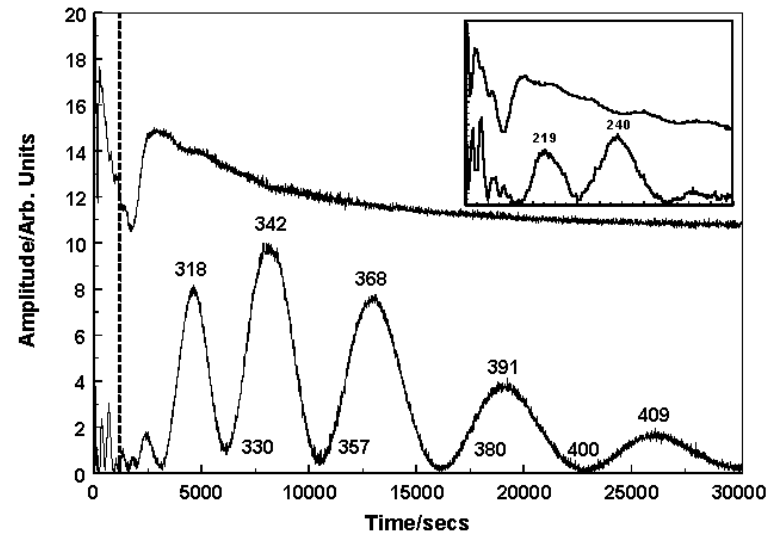


## Interferometry



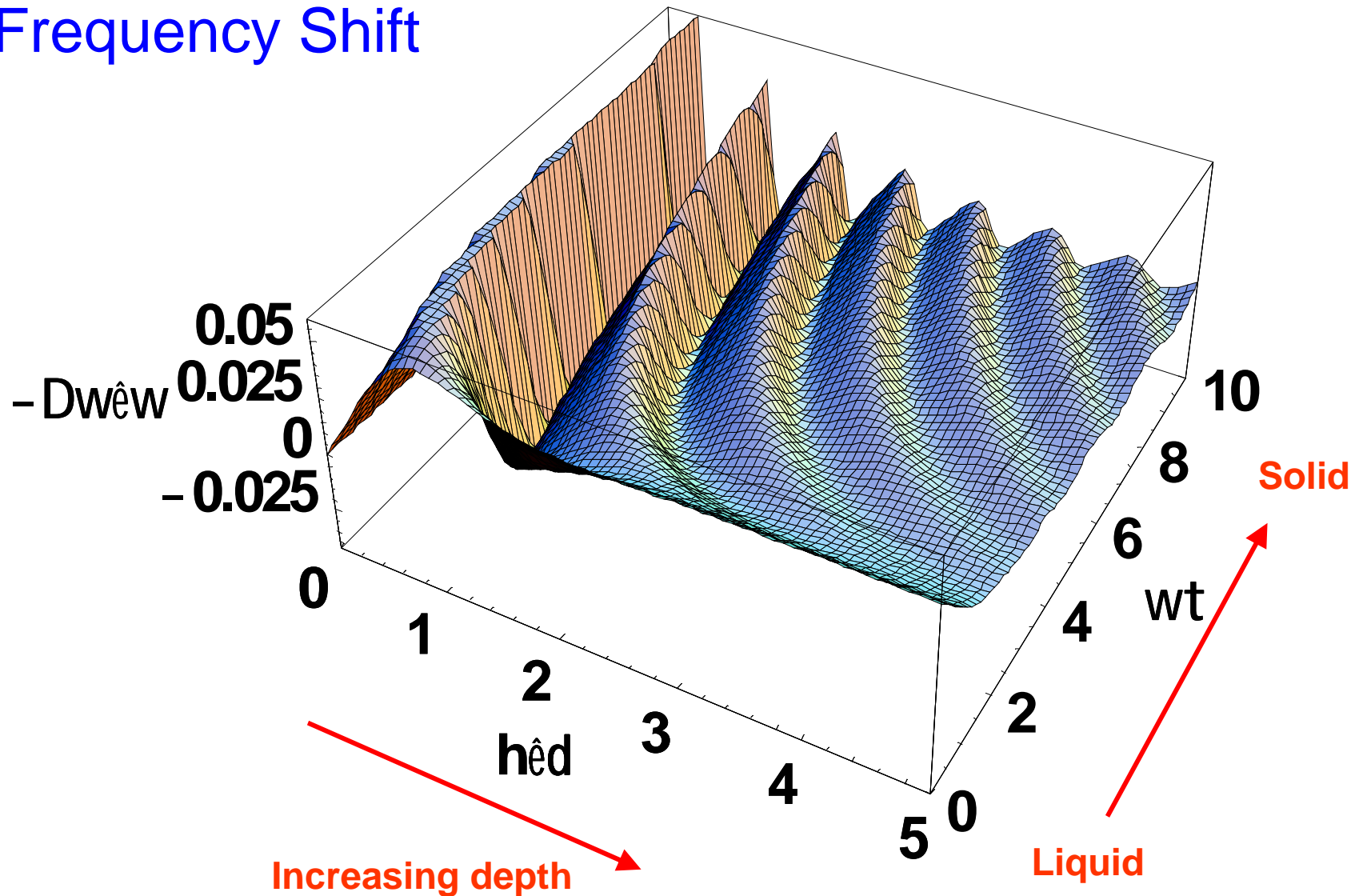
SAW propagation direction

## SAW Reflection



# Viscoelastic Layer on QCM/SAW - Theory

## Frequency Shift



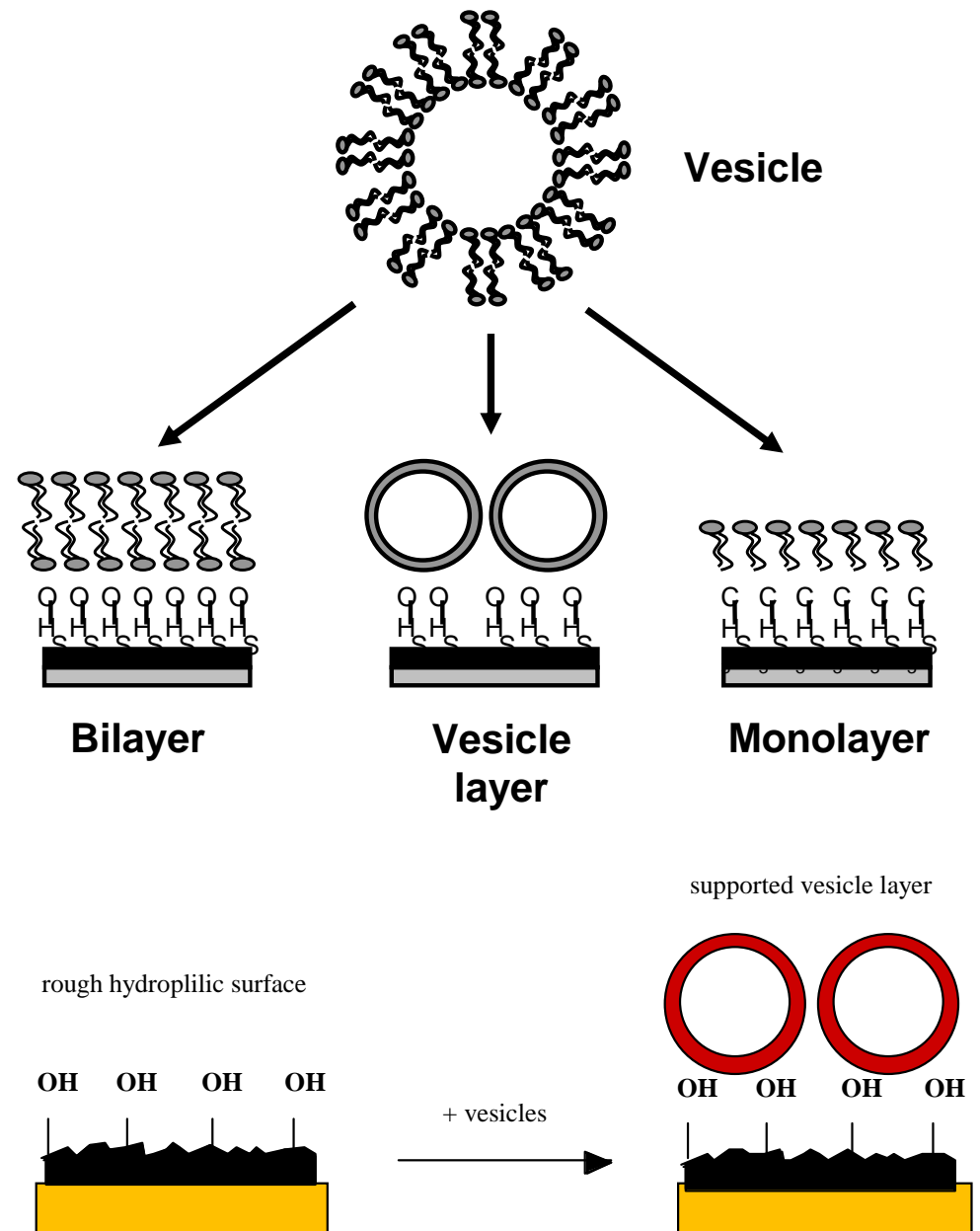
# Biological Mass and Vesicle Deposition

- **Concept**

Vesicle deposition to give bilayers and monolayers

- **Experiment**

Flow through system  
Water, buffer solution,  
vesicle deposition (POPC),  
detergent



# Vesicle Deposition on Love Wave Devices

- Love Wave Devices

110 MHz (+ 330 Harmonic)

Pulse (and CW) mode

Flow cell used

IL and phase measured

- Experimental Sequence

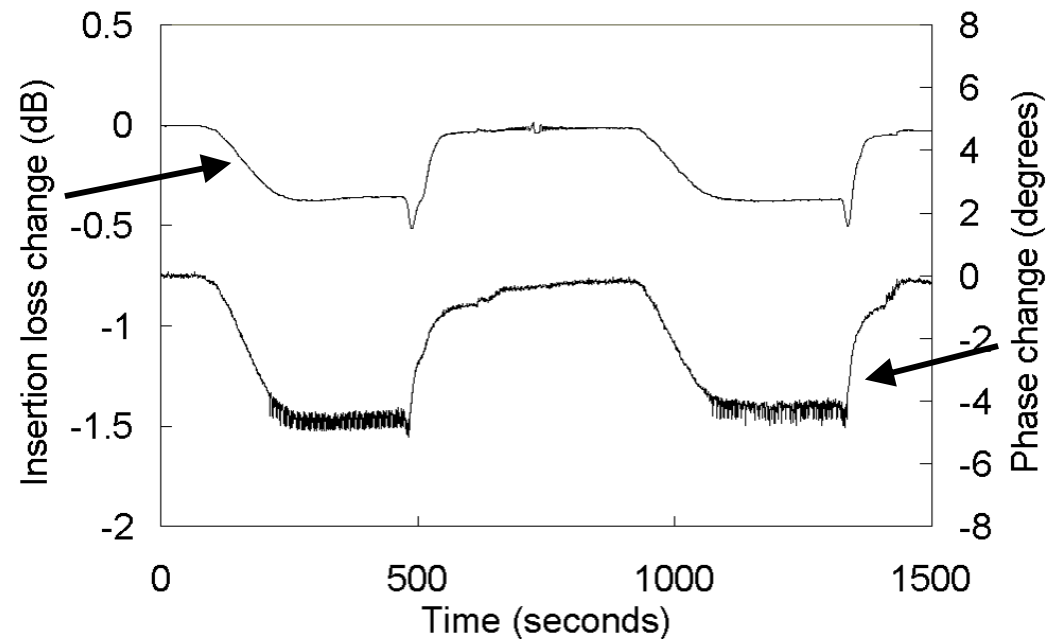
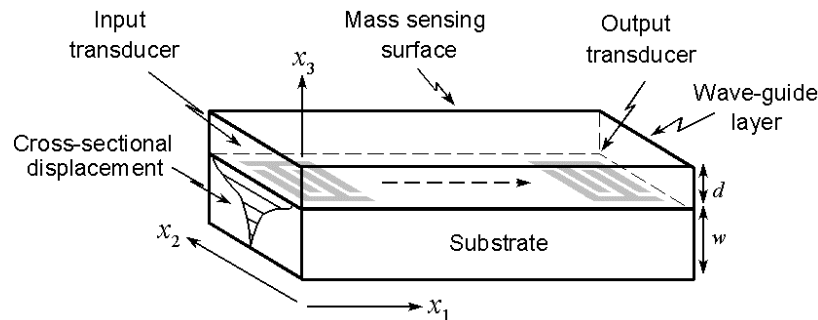
Water

Buffer solution (PBS)

Vesicle deposition (POPC)

Detergent

Repeat



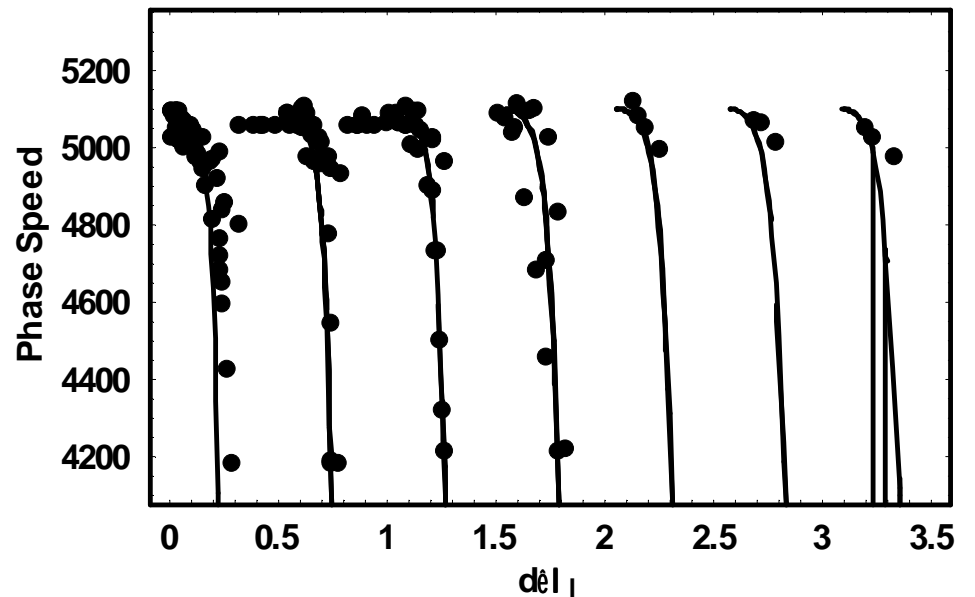
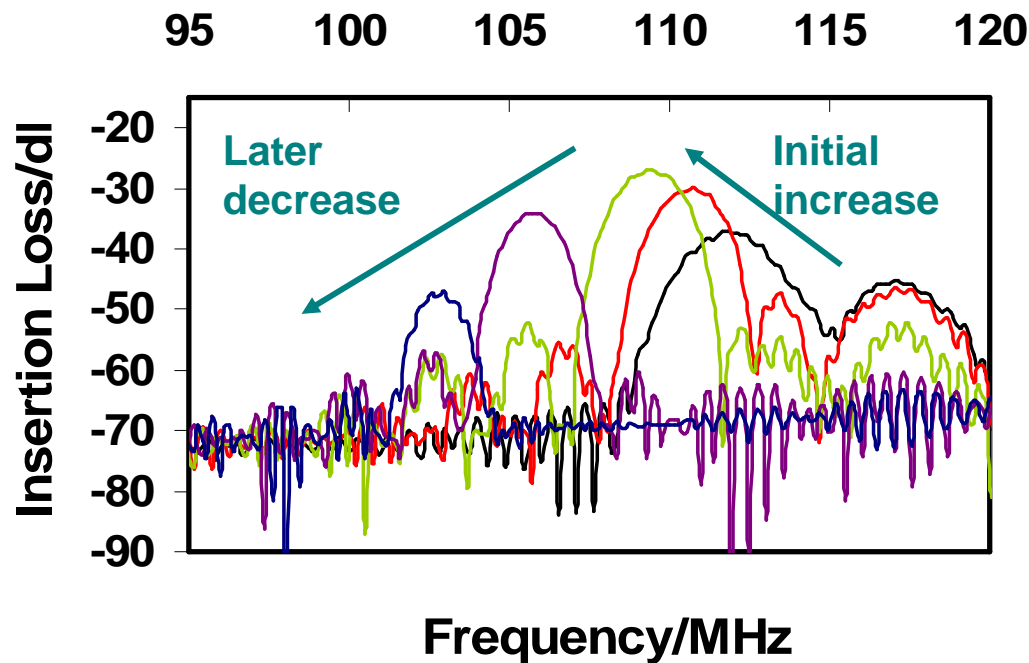
# Multiple Love Wave Modes

- **Spectra**

Thick guiding layers  
Photoresist layers  
Quartz substrate (SSBW)

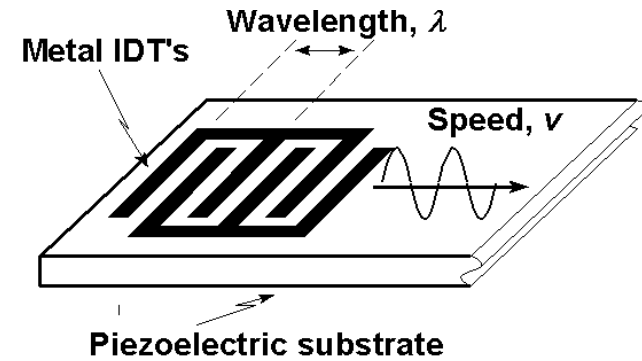
- **Experimental Results**

Points = results for devices  
110/330 and 309 MHz  
Lines = theory

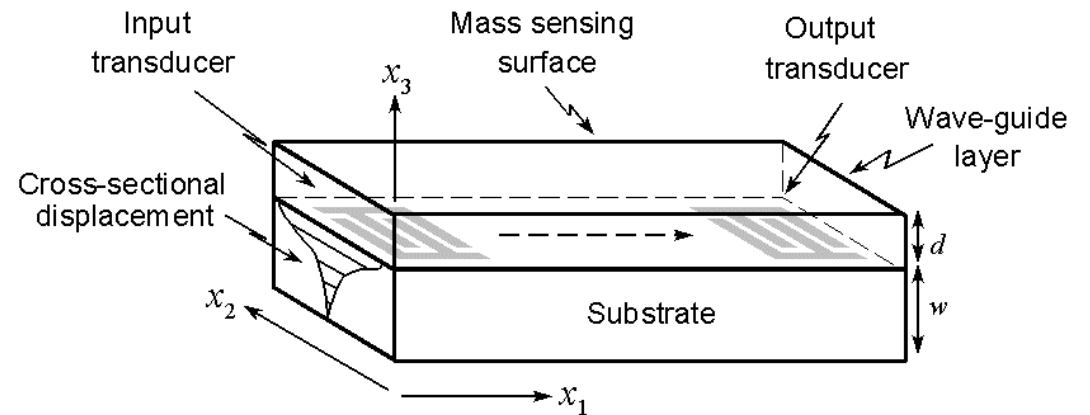


# Love Waves v SH-APMs

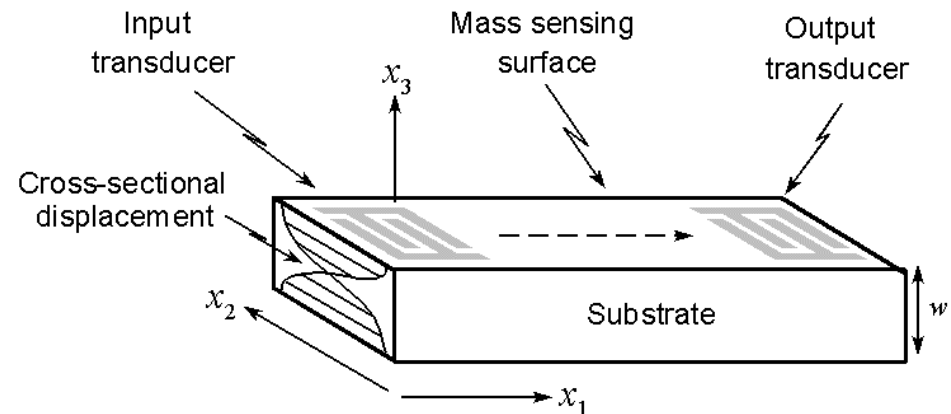
- Surface Acoustic Wave (SAW)



- Love Wave  
Layer guided SH-SAW  
with  $v_l < v_s$

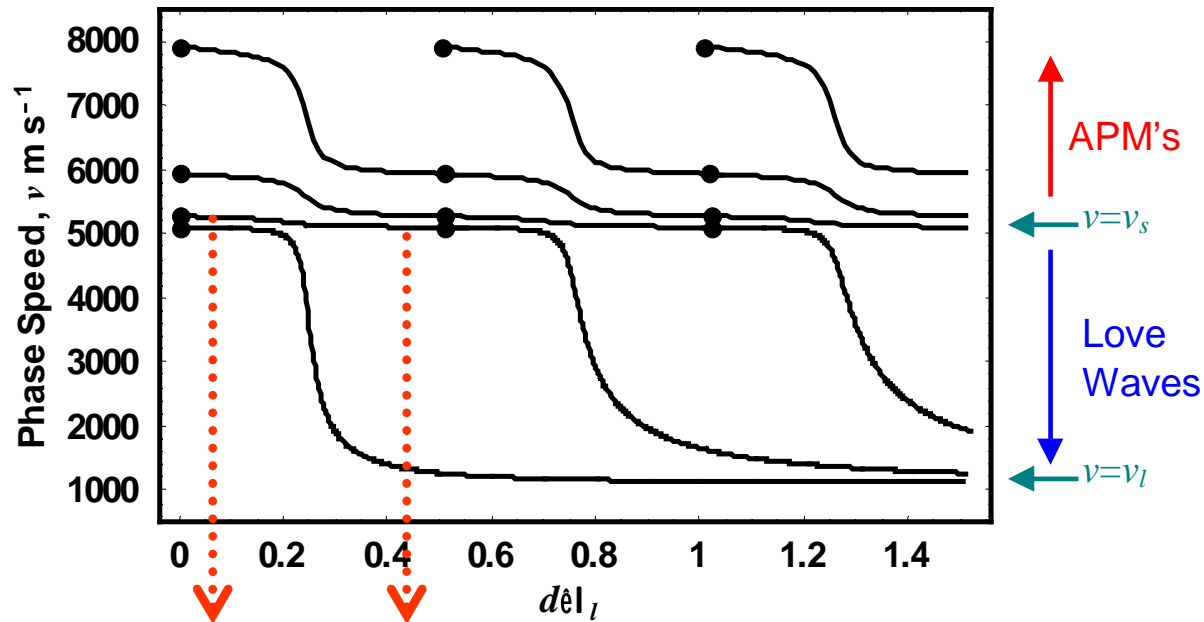


- SH-APM  
Substrate resonance



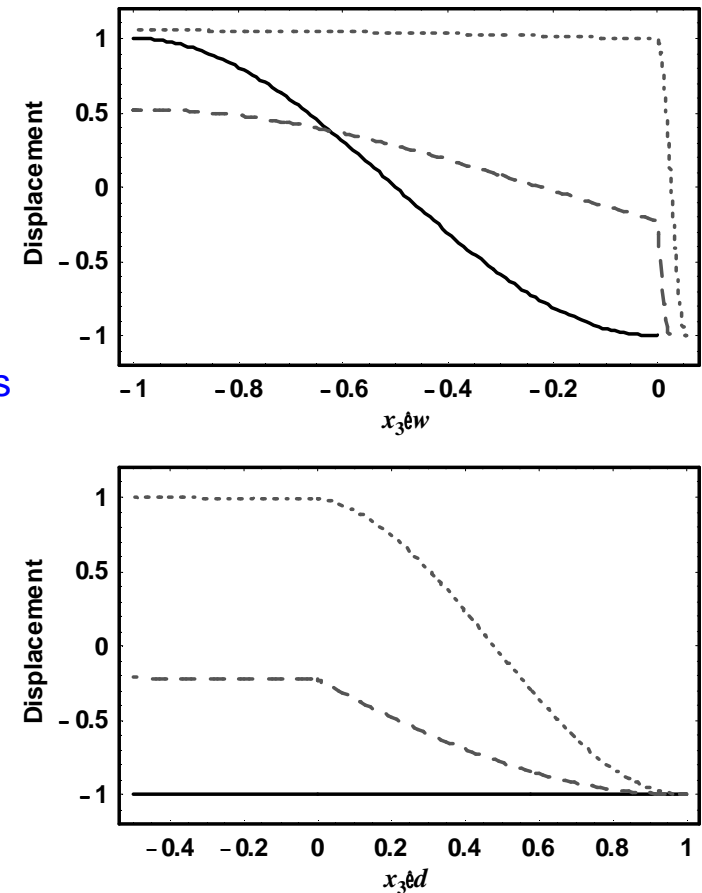
# Layer-Guided SH-APMs

## Dispersion Curve



Points = Anti-node moving from substrate to layer

## Evolution of 1st SH-APM



Solid  $\rightarrow$  dashed  
with increasing guiding

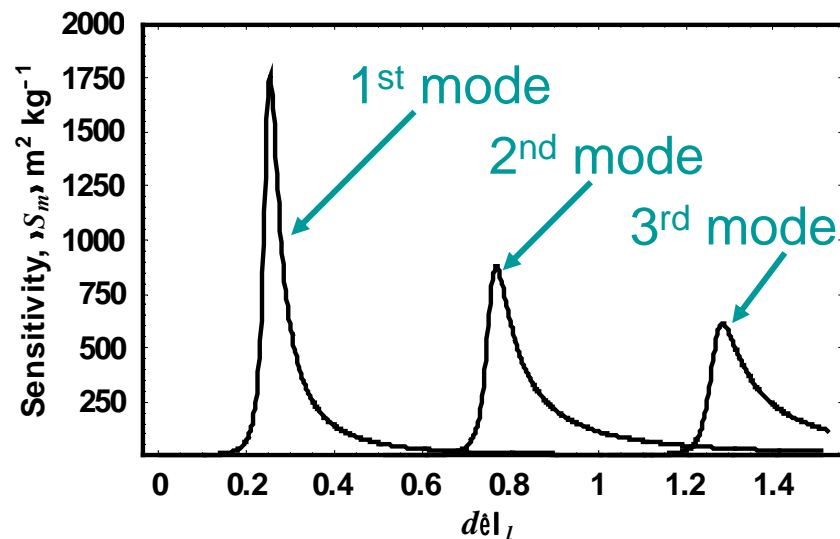
# Phase Speed Mass Sensitivity

$$S_m = \lim_{\Delta m \rightarrow 0} \frac{1}{\Delta m} \left( \frac{\Delta v}{v_o} \right) \approx \frac{f_o}{\rho_l |v_l|} \left( \frac{d \log_e v}{dz} \right)_{z_0}$$

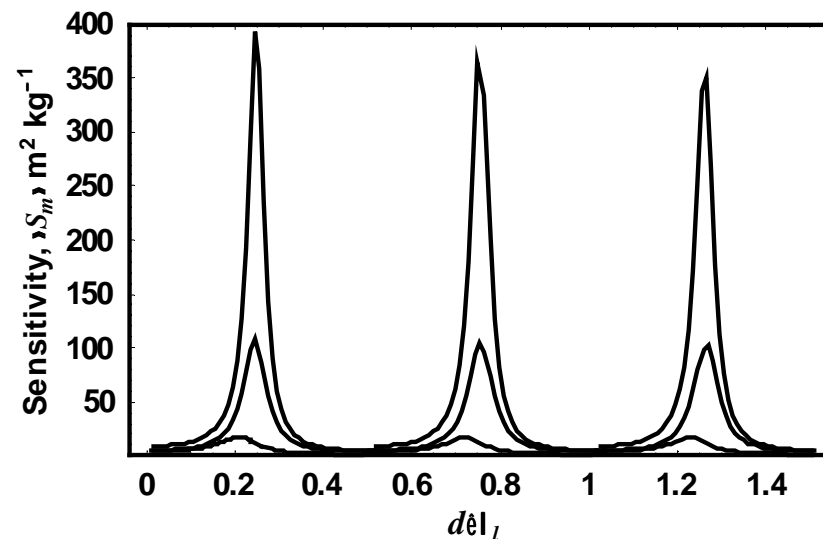
$\Delta m$  is mass per unit area being sensed,  $z = df/v_l$  is the normalized thickness

sensitivity is slope of dispersion curve

## Love Waves



## Layer-Guided SH-APMs



# Generalized Sauerbrey-Kanazawa

## Generalized Sauerbrey Equation – Love waves/SH-APMS

Complex velocity shift

$$\frac{\Delta v}{v_o} \approx \left( \frac{1 - v_f^2/v_o^2}{1 - v_l^2/v_o^2} \right) \left( \frac{d \log_e v}{dz} \right)_{z=z_o} \left( \frac{\tan(T_f^o h)}{T_f^o h} \right) \frac{\omega \rho_f h}{2\pi v_l^\infty \rho_l}$$

Complex slope factor  
from polymer waveguide

Care Needed

1. Slope depends on  $\omega$
2. IL response possible

$\tan x/x$  factor gives mass/liquid loading limits

$$\left( \frac{\tan(T_f^o h)}{T_f^o h} \right) \rightarrow \begin{cases} 1 & h \rightarrow 0 & \text{solid limit} \\ \frac{\sqrt{-2j}}{2h(1 - v_f^2/v_o^2)^{1/2}} \sqrt{\frac{2\eta_f}{\omega \rho_f}} & h \rightarrow \infty \text{ and } \omega\tau \rightarrow 0 & \text{liquid limit} \end{cases}$$

# Generalized Sauerbrey-Kanazawa

## Generalized Sauerbrey Equation - QCM

Complex velocity shift

$$\frac{\Delta\omega}{\omega_o} \approx \left( \frac{d \log_e \omega}{dz} \right)_{z=z_o} \left( \frac{\tan(T_f^o h)}{T_f^o h} \right) \frac{\omega \rho_f h}{2\pi v_l^\infty \rho_l}$$

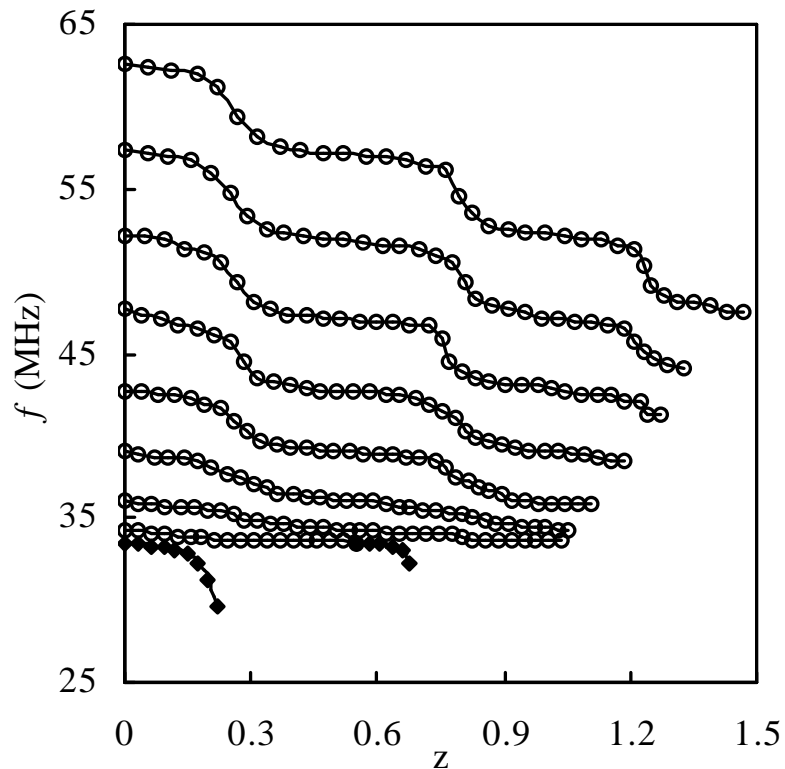
Changes to Love wave/SH-APM case

tanx/x factor gives mass/liquid loading limits

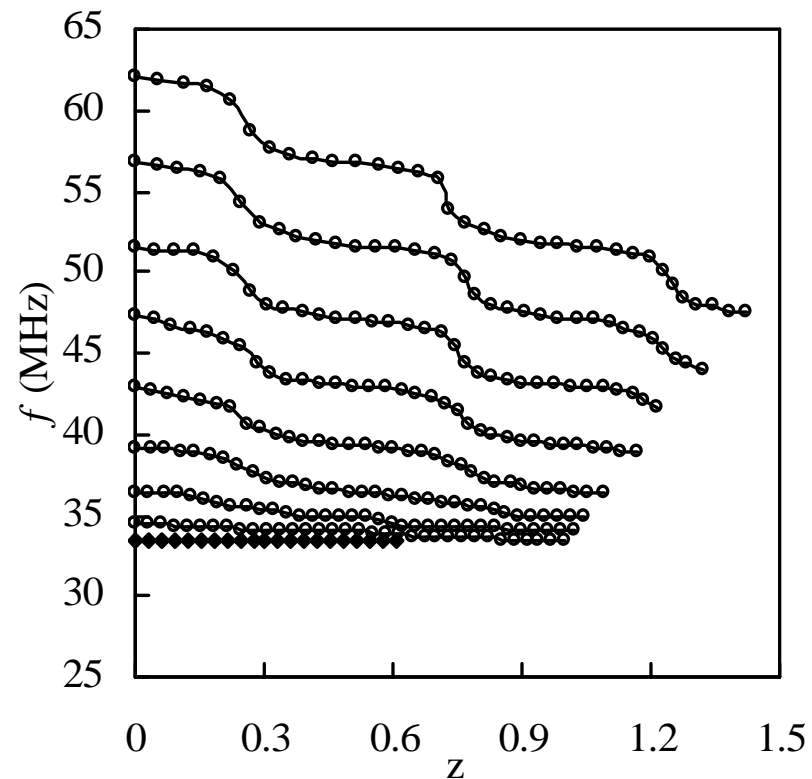
$$\left( \frac{\tan(T_f^o h)}{T_f^o h} \right) \rightarrow \begin{cases} 1 & h \rightarrow 0 & \text{solid limit} \\ \frac{\sqrt{-2j}}{2h} \sqrt{\frac{2\eta_f}{\omega \rho_f}} & h \rightarrow \infty \text{ and } \omega\tau \rightarrow 0 & \text{liquid limit} \end{cases}$$

# Experimental Results for SH-APMs

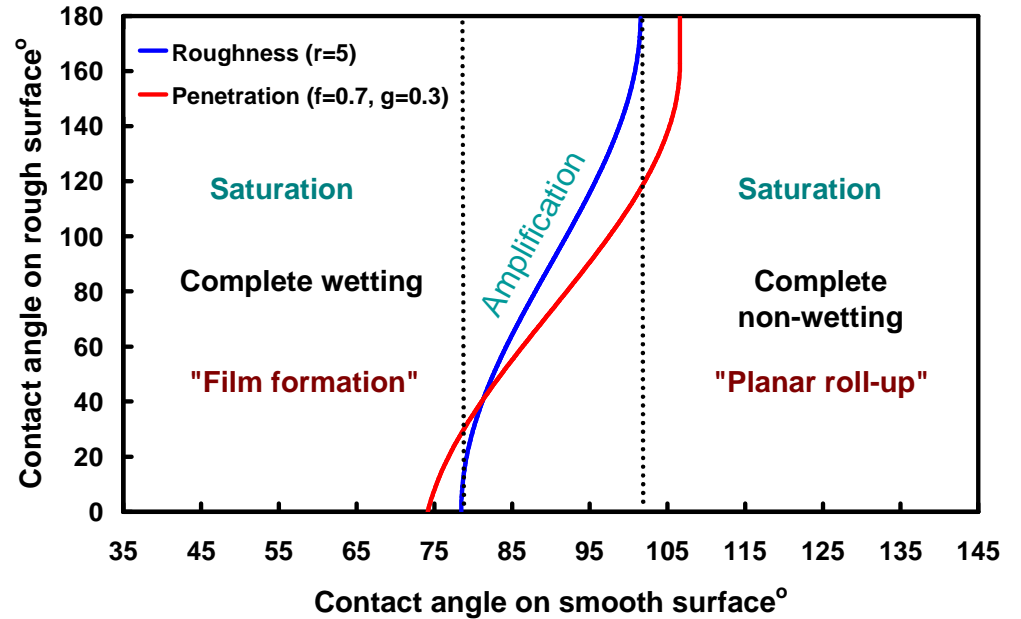
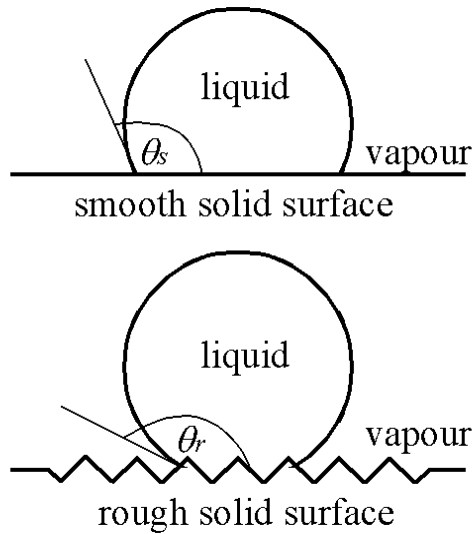
- **IDT Face Coated**  
Love wave and SH-APM  
both sensitive



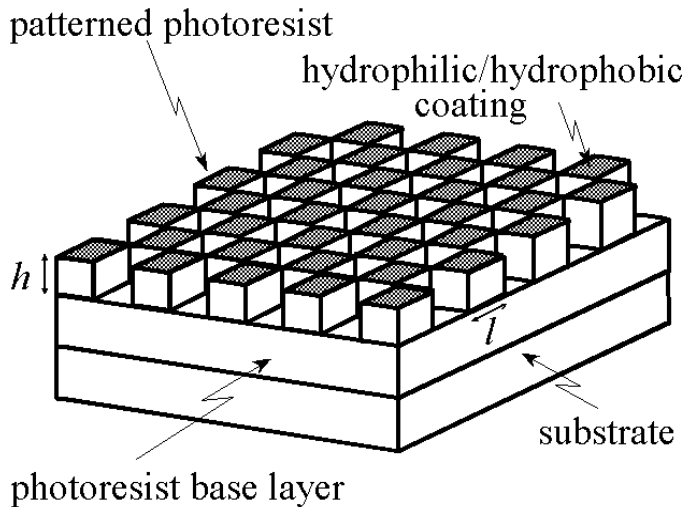
- **Opposing Face to IDTs**  
SH-APM changes  
Love wave insensitive



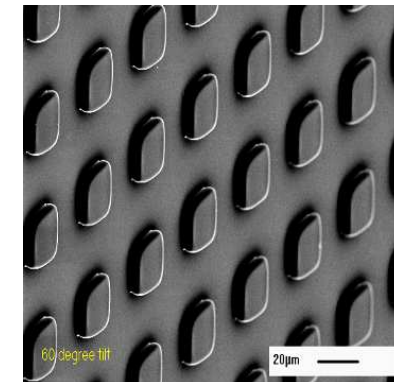
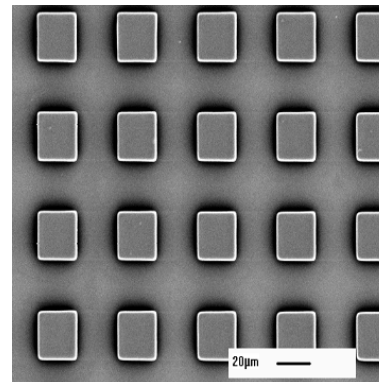
# Rough/Structured Surfaces & Hydrophobicity



## Lithographic Surface



## SEM Images



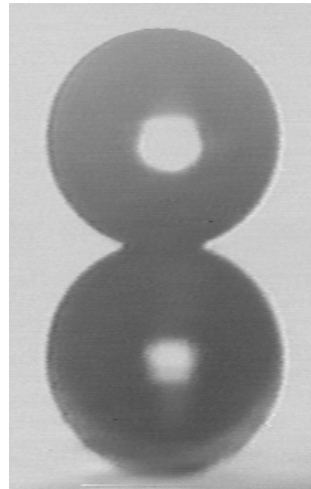
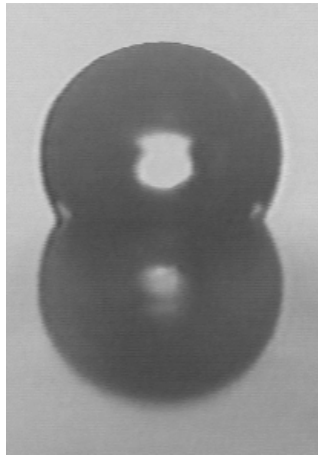
# Super-Hydrophobicity

- Contact Angle

Side view images

Identical chemical functionality

Different topography

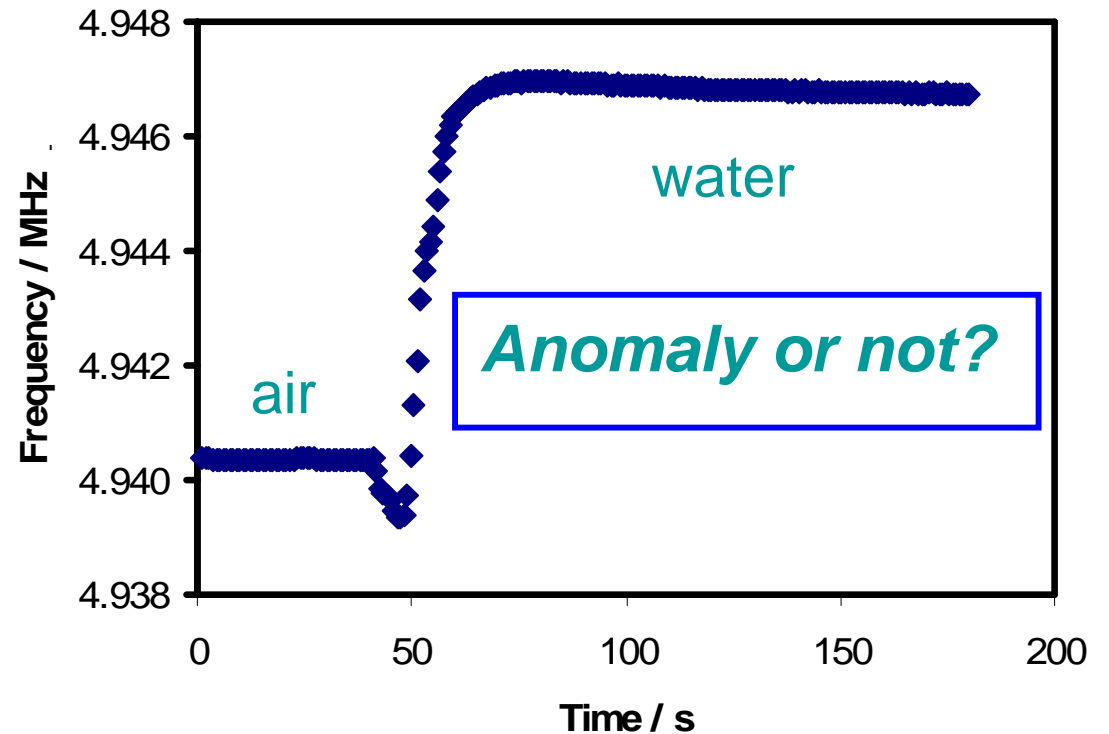


- Effect on QCM?

Response in air

versus

response in water



# Summary

## Acoustic Waves are

- Highly sensitive to interfacial properties
- Operate *in-situ* in gas/liquid phase
- Understood for
  - Uniform mass films
  - Simple liquids
  - Uniform viscoelastic films

## Acoustic Waves are not

Intrinsically species selective  
Understood for many situations

---

The End

---

# Acknowledgements

## Collaborators at Nottingham Trent

### Academics

Dr Mike Newton  
Dr Carl Percival  
Prof. Krylov  
Mr Mike Rowan  
Dr Alan Braithwaite  
Dr Carole Perry

### PDRAs/PhDs

<i>Dr Fabrice Martin</i>	All experimental
Dr Simon Stanley	QCM/MIPs & SAWs for particulates
Dr John Cowen	SAWs and wetting (Now at L'boro)
<i>Dr Markus Banerjee</i>	SAWs and wetting MIPs
Dr Neil Shirtcliffe	Superhydrophobic surfaces
<i>Ms Sanaa Aqil</i> + Mr Edward Harding (Student)	

## External Collaborators

Dr Electra Gizeli/Dr Kathryn Melzak	Institute of Biotechnology, Cambridge University
Dr Ralf Lücklum/Prof. Peter Hauptmann	IPE, Magdeburg, Germany
Dr Wayne Hayes	Reading University, UK
Prof. Yildirim Erbil	Istanbul, Turkey
Dr Brendan Carroll	Unilever plc

## Funding Bodies

EPSRC GR/L82090, GR/R36718 , GR/R01284      BBSRC 301/E11140  
The Royal Society-DAAD, Nuffield Foundation, The British Council-TUBITAK/EU COST  
EPSRC for funding and Dr Cernosek and Dr Casalnuovo for hosting this visit



# Acoustic Waves - Comparisons

- Types of Wave

  - Thickness shear mode

    - Quartz crystal microbalance (QCM)

  - Surface Acoustic Waves (SAWs)

    - Rayleigh waves, Love waves, Surface transverse waves (STWs), Lamb waves/Flexural plate waves (FPWs)

  - Acoustic Plate Modes

    - Shear horizontally polarised SAWs (SH-SAWs)

    - Surface skimming bulk waves (SSBW)

<u>Mode</u>	<u>Rel. Sens.</u>	<u>Complexity</u>	<u>Robustness</u>	<u>Gas/Liquid</u>
QCM	Low	Low/Xtal	Med	g+l
SAW	High	Med/metal on Xtal	High	g
Love	High	Med/film+metal+Xtal	High	g+l
STW	High	Med/metal on Xtal	High	g+l
Lamb	High	High/membrane	Low	g+l
APM	Med	Med/metal on Xtal	Med	g+l

# Acoustic Waves Devices - Parameters

- QCM v SAW

QCM

Simple, off-the-shelf, 5 to 10 MHz, fragile

SAWs

Flexibility by design, MHz to GHz, robust

- Basic Characteristics

Higher frequencies

Higher sensitivity

Smaller  $\lambda$ , smaller devices

- Typical SAW Parameters

Frequency and wavelength

MHz  $\rightarrow$  GHz    400  $\mu\text{m}$   $\rightarrow$  4  $\mu\text{m}$

Rapid response

in-situ and better than 10 Hz

Sensitive

13 Hz per  $\text{ng cm}^{-2}$  at 100 MHz

Size, mass and cost

mm/cm, low and  $<$  \$1

Power consumption

low

Temp. stability

depends on crystal cut

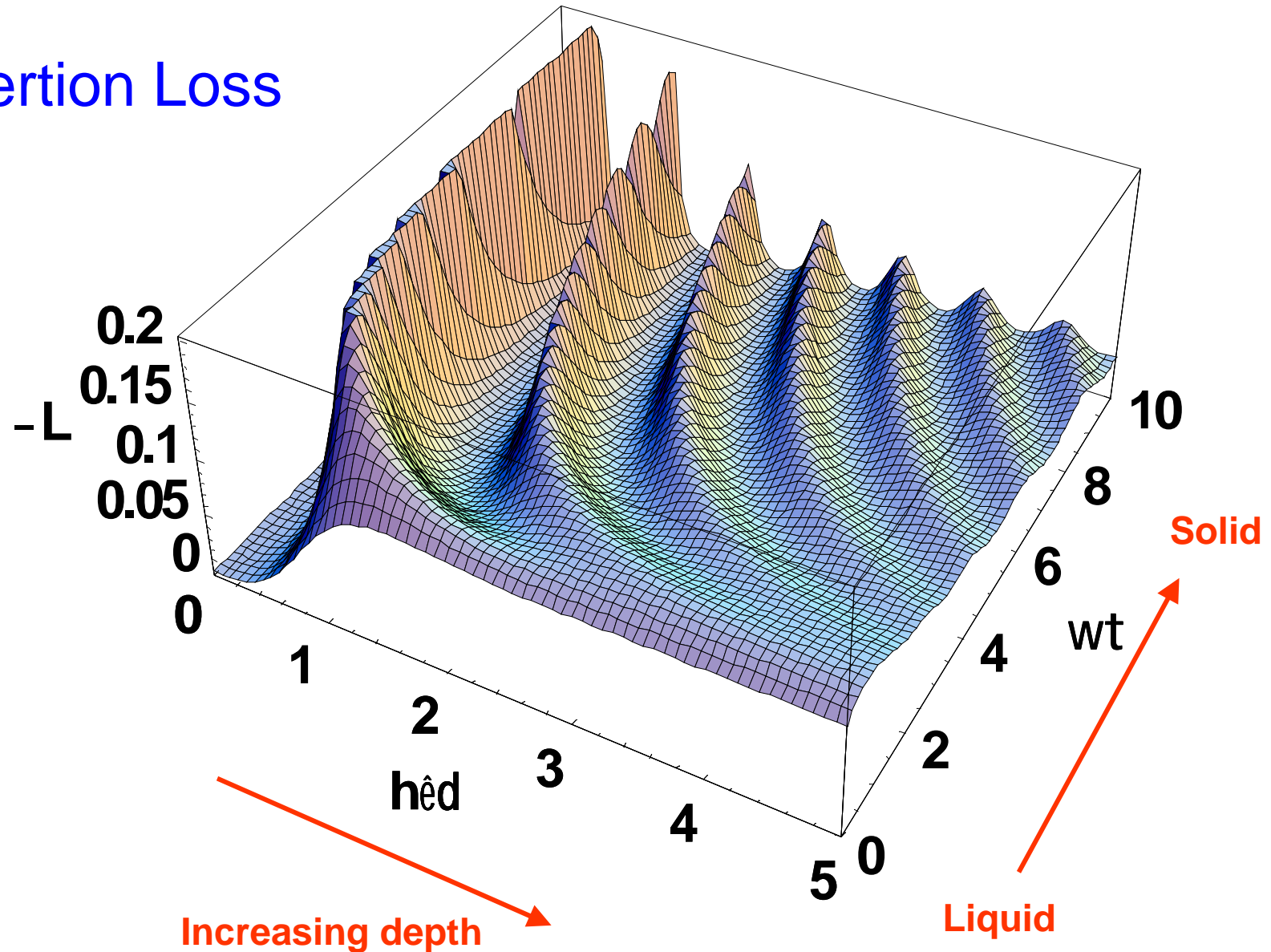
- Problems?

Selectivity and reproducibility

poor and depends on coating

# Viscoelastic Layer on QCM/SAW - Theory

Insertion Loss



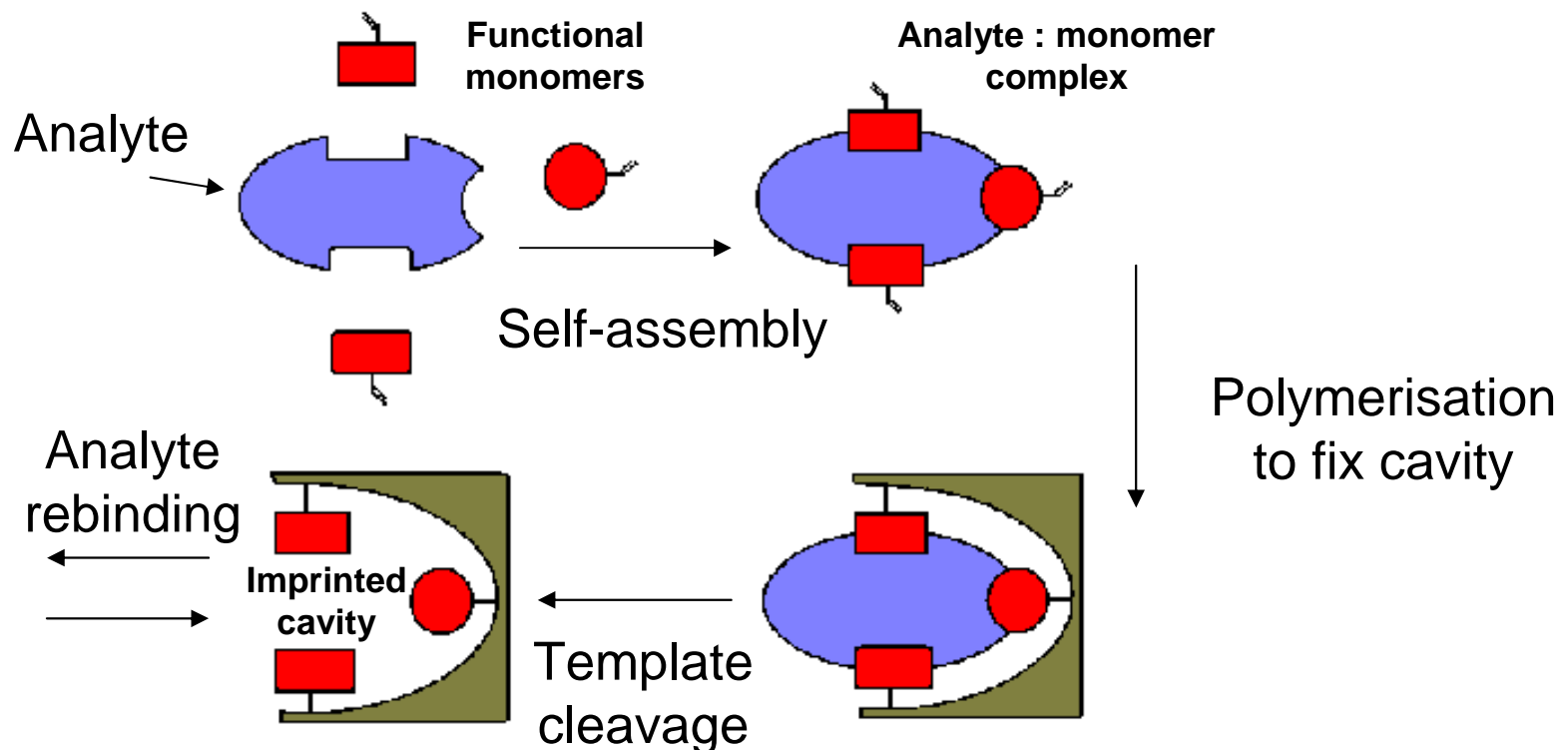
# MIPs as Recognition Elements

- **Non-Covalent Approach**

Self-assemble functional monomers around template molecule

Add cross-linker and 'fix' assembly by polymerisation

Remove non-covalently bound template via solvent



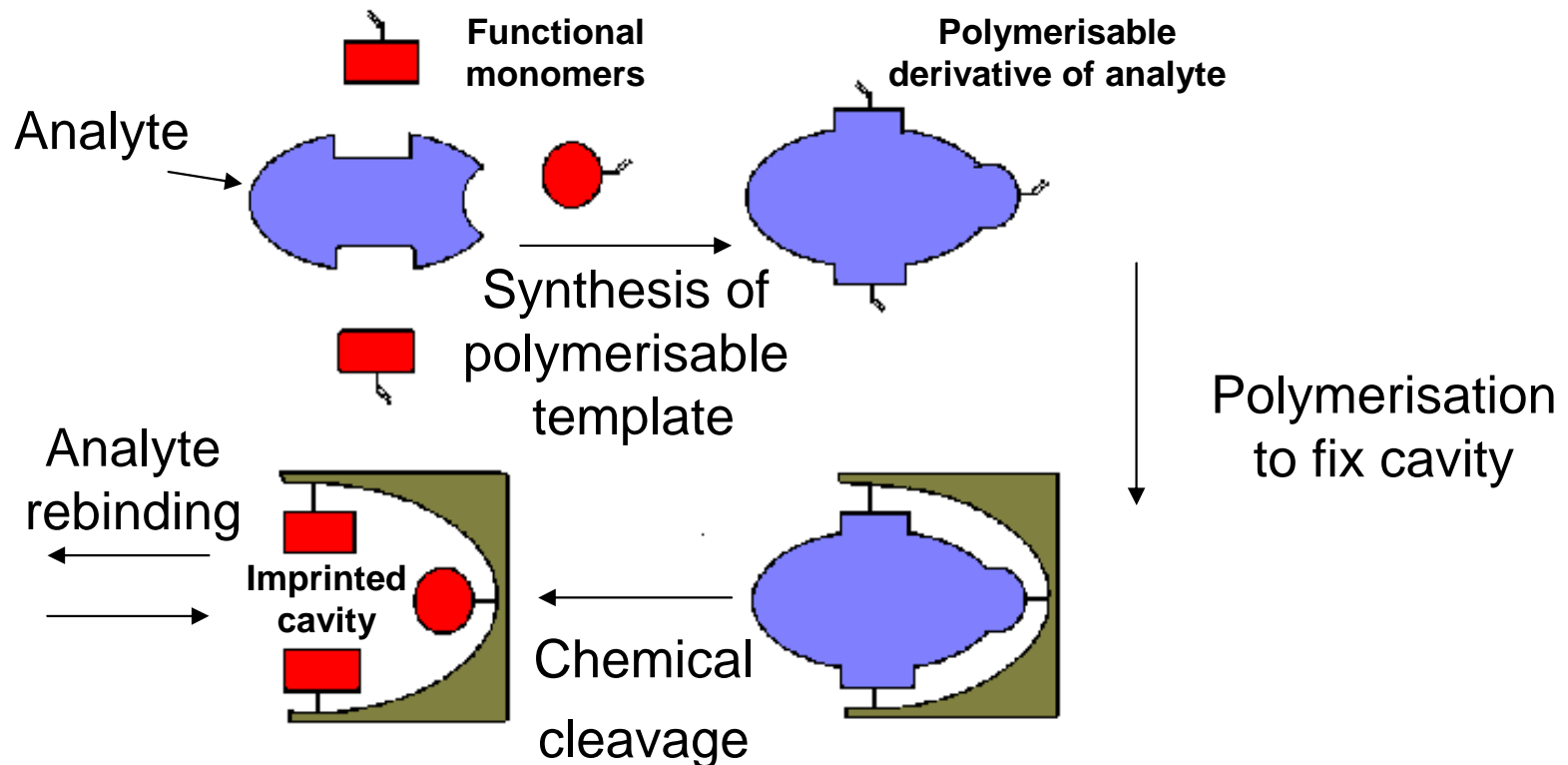
# MIPs as Recognition Elements

- **Covalent Approach**

Convert template into a polymerisable derivative

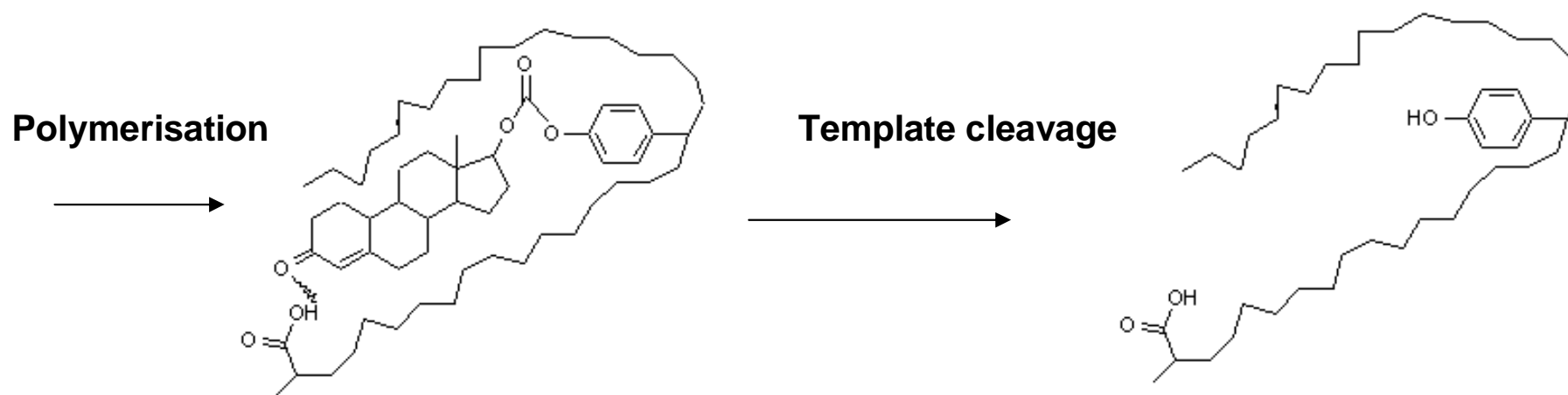
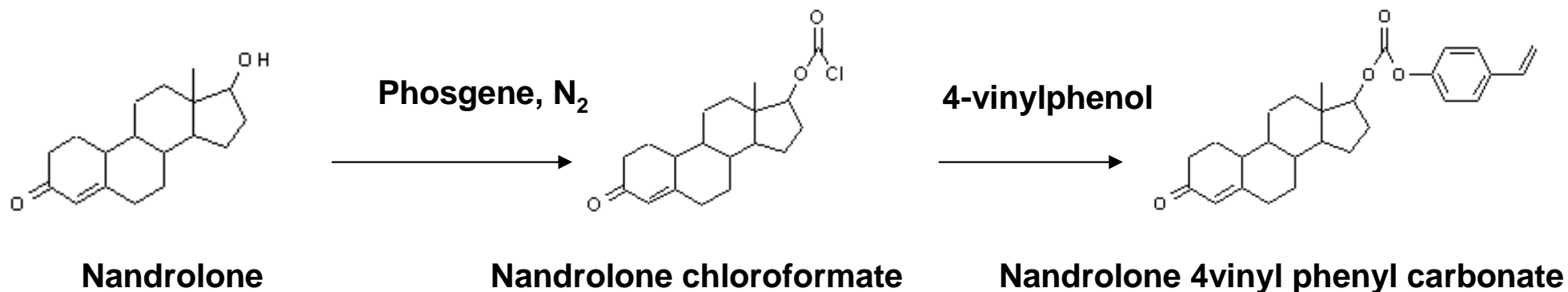
Co-polymerise with a cross-linker

Resin covalently incorporates the template



# Synthesis of Nandrolone MIP

- Covalent Approach (Scheme 1)



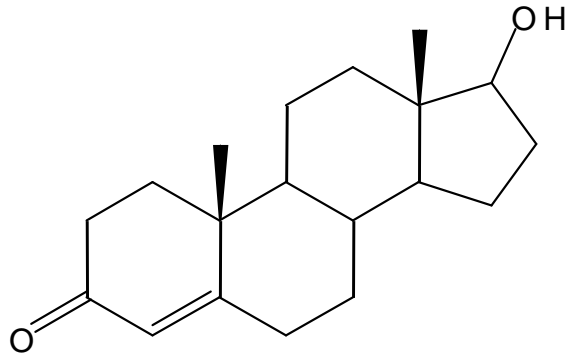
Gives non-covalent recognition sites

# Selectivity Between Steroids

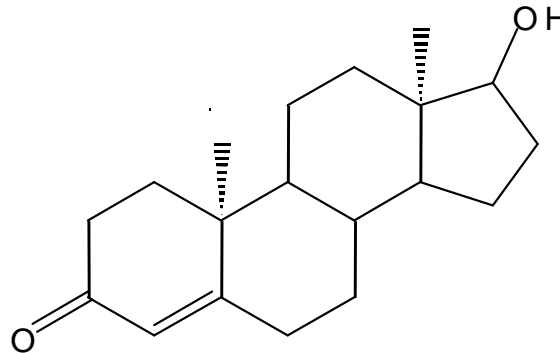
- Future Extension of Scheme 1

Can be applied to any steroid containing an OH moiety

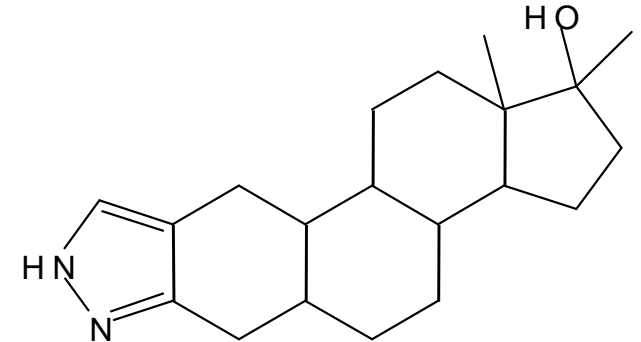
- Steroids of Interest



**Testosterone**



**Epitestosterone**



**Stanozolol**

- Selectivity between Stereoisomers

Stereoisomers

testosterone and epitestosterone

*preliminary work shows can distinguish them*

Natural ratio is 1.5:1

steroid abuse disturbs this ratio