Acoustic Waves for Gas and Liquid Phase Sensing

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

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

- Surface (Rayleigh) wave
  
  $v_p = 2000 - 6000 \text{ m s}^{-1}$

Basic Sensor Devices

- QCM
- SAW

Rayleigh Wave

Lamb Wave (FPW)

Love Wave

Acoustic Plate Mode

STW (Surface Transverse Wave)

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 \( \Delta f \propto f^2 \Delta m/A \)
• **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 \( \delta = \left( \frac{\eta}{\pi f \rho} \right)^{1/2} \)

  Sense mass in penetration depth
  Kanazawa \( \Rightarrow \Delta f \propto \sqrt{(\eta \rho)} f^{3/2} \)

  For water \( \delta \sim 250 \text{ nm} \) (at 5 MHz)
Devices

QCMs
- Quartz (IQD) Blank/ with Contacts 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

From PTU sonde
From SAW

Ascent, July 1999 from Gap; close up of 600 to 200 hPa shows clouds recorded by the SAW hygrometer and faster response of SAW device compared to the PTU sonde.
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

**Krypton 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

Liquid to solid monolayer transition point
NTU Based Acoustic Wave Research
Overview

• Experimental
  QCMs
  MIPs for steroids, terpenes & amino acids, SAMs for PAHs
  Surface texture & hydrophobicity
  SAWs
  Electrostatic precipitation of atmospheric particulates
  Spreading oils and Rayleigh-SAWs
  Love waves for biosensing
  Multiple modes and layer-guided SH-APMs

• 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)

Nandrolone → Nandrolone chloroformate → Nandrolone 4vinyl phenyl carbonate

Polymerisation Template cleavage

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

![Graph showing frequency decrease for different hormones](image)
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

[Diagram showing the system design with flow inlet, filter, EP-SAW, and frequency monitor]
Particulate Response with Bias

- **Test Device Configuration**
  
  LiNbO$_3$ - Rayleigh-SAW, $\lambda \sim 45$ $\mu$m
  86 MHz & 253 MHz
  Test particulates via a mono-disperse $\sim (2.0\pm0.1)$ $\mu$m NaCl aerosol

- **Preliminary Results**

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

![Diagram of test setup](image)
Our Historical Development
Dynamic Wetting and SAWs

Concept of the Experiment

Schematic of Experiment

Interferometry

SAW Reflection

SAW propagation direction

Amplitude/arb. units

Time/sec

318 342 366 391 409

330 357 360 400 409
Viscoelastic Layer on QCM/SAW - Theory

Frequency Shift

Increasing depth

Solid

Liquid
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

![Graph showing insertion loss and phase speed vs. frequency](image-url)
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

Evolution of 1st SH-APM

Points = Anti-node moving from substrate to layer

Solid → dashed with increasing guiding
Phase Speed Mass Sensitivity

\[ S_m = \lim_{\Delta m \to 0} \frac{1}{\Delta m} \left( \frac{\Delta v}{v_o} \right) \approx \frac{f_o}{\rho l v_l} \left( \frac{d \log_e v}{dz} \right) z_0 \]

\( \Delta m \) 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**

![Graph showing Love Waves and Layer-Guided SH-APMs with labeled modes](image-url)
Generalized Sauerbrey-Kanazawa

Generalized Sauerbrey Equation – Love waves/SH-APMS

Complex velocity shift

\[
\frac{\Delta v}{v_o} \approx \left(1 - \frac{v_f^2}{v_o^2}\right) \left(\frac{d \log \epsilon}{dz}\right) \left(\frac{\tan(T_f^o h)}{T_f^o h}\right) \frac{\omega \rho_f h}{2 \pi \nu^{\infty}_l \rho_l}
\]

Complex slope factor from polymer waveguide

\[
\tan \frac{x}{x} \text{ factor gives mass/liquid loading limits}
\]

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

Care Needed
1. Slope depends on \( \omega \)
2. IL response possible

\( \omega \Delta m/A \)

(\( \rho \eta \omega \)^{1/2})
Generalized Sauerbrey-Kanazawa

Generalized Sauerbrey Equation - QCM

Complex velocity shift

\[
\frac{\Delta \omega}{\omega_o} \approx \left( \frac{d \log_e \omega}{dz} \right)_{z=z_f} \left( \frac{\tan(T_f^o h)}{T_f^o h} \right) \frac{\omega \rho_f h}{2\pi_1^\infty \rho_1}
\]

Changes to Love wave/SH-APM case

tan\(x/x\) factor gives mass/liquid loading limits

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

solid limit

liquid limit
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

- patterned photoresist
- hydrophilic/hydrophobic coating
- photoresist base layer

SEM Images

- Roughness ($r=5$)
- Penetration ($f=0.7$, $g=0.3$)

Contact angle on smooth surface $^\circ$

- Saturation
- Complete wetting
- "Film formation"
- Complete non-wetting
- "Planar roll-up"

Contact angle on rough surface $^\circ$

- Amplification
- Saturation

Penetration ($f=0.7$, $g=0.3$)
Super-Hydrophobicity

- **Contact Angle**
  - Side view images
  - Identical chemical functionality
  - Different topography

- **Effect on QCM?**
  - Response in air
  - versus
  - response in water

![Anomaly or not?](image)

**Graph**

<table>
<thead>
<tr>
<th>Time / s</th>
<th>Frequency / MHz</th>
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<tr>
<td>0</td>
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<tr>
<td>50</td>
<td>4.940</td>
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<tr>
<td>100</td>
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<tr>
<td>150</td>
<td>4.944</td>
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<tr>
<td>200</td>
<td>4.946</td>
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**Legend**

- **Air**
- **Water**

**Graph**

- Frequency vs. Time
- Anomaly or not?
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

<table>
<thead>
<tr>
<th>Academics</th>
<th>PDRAs/PhDs</th>
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<tbody>
<tr>
<td>Dr Mike Newton</td>
<td>Dr Fabrice Martin All experimental</td>
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<tr>
<td>Dr Carl Percival</td>
<td>Dr Simon Stanley QCM/MIPs &amp; SAWs for particulates</td>
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<tr>
<td>Prof. Krylov</td>
<td>Dr John Cowen SAWs and wetting (Now at L’boro)</td>
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<tr>
<td>Mr Mike Rowan</td>
<td>Dr Markus Banerjee SAWs and wetting</td>
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<tr>
<td>Dr Alan Braithwaite</td>
<td>Dr Neil Shirtcliffe MIPs</td>
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<tr>
<td>Dr Carole Perry</td>
<td>Ms Sanaa Aqil + Mr Edward Harding (Student)</td>
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External Collaborators

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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)

<table>
<thead>
<tr>
<th>Mode</th>
<th>Rel. Sens.</th>
<th>Complexity</th>
<th>Robustness</th>
<th>Gas/Liquid</th>
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<td>Low</td>
<td>Low/Xtal</td>
<td>Med</td>
<td>g+l</td>
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<td>SAW</td>
<td>High</td>
<td>Med/metal on Xtal</td>
<td>High</td>
<td>g</td>
</tr>
<tr>
<td>Love</td>
<td>High</td>
<td>Med/film+metal+Xtal</td>
<td>High</td>
<td>g+l</td>
</tr>
<tr>
<td>STW</td>
<td>High</td>
<td>Med/metal on Xtal</td>
<td>High</td>
<td>g+l</td>
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<tr>
<td>Lamb</td>
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<td>APM</td>
<td>Med</td>
<td>Med/metal on Xtal</td>
<td>Med</td>
<td>g+l</td>
</tr>
</tbody>
</table>
Acoustic Waves Devices - Parameters

- **QCM v SAW**
  - **QCM**
    - Simple, off-the-shelf, 5 to 10 MH, 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 $\mu$m $\rightarrow$ 4 $\mu$m
  - Rapid response
    - in-situ and better than 10 Hz
  - Sensitive
    - 13 Hz per 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

Increasing depth

Liquid

Solid
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)

Nandrolone $\xrightarrow{\text{Phosgene, } N_2} \text{Nandrolone chloroformate} \xrightarrow{4\text{-vinylphenol}} \text{Nandrolone 4vinyl phenyl carbonate}

Polymerisation $\rightarrow$ Template cleavage

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](image)

![Epitestosterone](image)

![Stanazolol](image)

• **Selectivity between Stereoisomers**

  Stereoisomers: 
  - Testosterone and epitestosterone

  *Preliminary work shows can distinguish them*

  Natural ratio is 1.5:1, steroid abuse disturbs this ratio