Acoustic Wave Sensors: Modes, Responses and Hydrophobicity

Professor Glen McHale

School of Science & Technology

MicroNanoacoustics Workshop, Prato, Italy

www.naturesraincoats.org

September 23rd-24th 2009
Overview

1. Basics of Acoustic Wave Sensors
   - Acoustic waves: Modes and devices
   - Sensing principles: Solids and liquids

2. Layer-Guided Acoustic Waves
   - Love waves & acoustic plate modes
   - Layer-guided devices: Operating points and sensitivity

3. Sensor Research Examples
   - Steroids: Molecularly imprinted polymers
   - Cancer vaccines: Peptide binding

4. Current Acoustics Research
   - VetAI: Sperm motility
   - Green solvents: Ionic liquids and microfluidics
   - Wetting: Hydrophobicity and slip on topographically structured surfaces
Basics of Acoustic Waves
Acoustic Waves

QCM versus SAW

QCM – frequency determined by thickness
SAW – frequency determined by fingers
Acoustic Wave Modes

Delay Lines

<table>
<thead>
<tr>
<th>Mode</th>
<th>Rel. Sens.</th>
<th>Complexity</th>
<th>Robustness</th>
<th>Gas/Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>QCM</td>
<td>Low</td>
<td>Low/Xtal</td>
<td>Med</td>
<td>g+l</td>
</tr>
<tr>
<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>
</tr>
<tr>
<td>Lamb</td>
<td>High</td>
<td>High/membrane</td>
<td>Low</td>
<td>g+l</td>
</tr>
<tr>
<td>APM</td>
<td>Med</td>
<td>Med/metal on Xtal</td>
<td>Med</td>
<td>g+l</td>
</tr>
</tbody>
</table>
QCM/QCR Sensing Principles

Thickensh Shear Mode Vibration

QCM has a sharp resonance
Frequency given by quartz thickness, \( w \)

\[ v_s = f \lambda \quad \Rightarrow \quad f = \frac{2v_s}{w} \]

Mass Loading or Immersion

QCR resonant frequency reduces due to mass
Resonance broadens due to polymer/liquid

Sauerbrey equation \( \Rightarrow \) \( \Delta f \propto -f^2 \Delta m/A \)
Kanazawa & Gordon \( \Rightarrow \) \( \Delta f \propto -\sqrt{(\eta \rho)} f^{3/2} \)

1. Increasing mass or viscosity-density product decreases resonant frequency
2. Increasing viscosity-density product (or polymer) broadens resonance

Liquids and Penetration Depth

Shear Mode Vibration
- Entrains liquid
- Liquid oscillation decays
- Penetration depth
  \[ \delta = \left( \frac{\eta}{\pi f \rho} \right)^{1/2} \]

Liquid Sensing
- Sense liquid mass (via viscosity-density product) within penetration depth

<table>
<thead>
<tr>
<th>Method</th>
<th>Frequency</th>
<th>Penetration Depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>QCM</td>
<td>5 MHz</td>
<td>( \delta \sim 250 \text{ nm} )</td>
</tr>
<tr>
<td>SAW</td>
<td>500 MHz</td>
<td>( \delta \sim 25 \text{ nm} )</td>
</tr>
</tbody>
</table>

1. Penetration depth gives sensing zone which decreases with frequency
2. Penetration depth/sensing zone increases with viscosity
Layer-Guided Acoustic Waves
Love Waves versus SH-APMs

Love Wave

Layer guided SH-SAW with $v_i < v_s$
Surface localised wave
Increased sensitivity

SH-APM

“QCM with propagation”
Substrate resonance
Sensing via both faces

Increased sensitivity versus isolation between sensing face and transduction

24 September 2009  
Generalized Love Waves – Operating Point

Phase Speed, \( v \), m s\(^{-1} \)

del (guiding layer thickness)

\[ \nu > \nu_s \]: Plate modes = Switch in order of resonance induced by layer

\[ \nu < \nu_s \]: Love wave = Shear mode in substrate-to-shear mode in layer transition

Increased mass/liquid sensitivity related to slope of dispersion curve

Phase Speed Mass Sensitivity

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

\( \Delta m \) is mass per unit area being sensed, \( z = df/v_i \) is the normalized thickness

"Rigid" mass \( \Rightarrow \) Mass sensitivity is slope of dispersion curve

Love Waves

Layer-Guided SH-APMs
Experimental Data for Layer-Guided SH-APMs

25 MHz surface skimming bulk wave (SSBW)
Propagation orthogonal to x-axis of thinned (200 mm) ST-Q substrate

**IDT Face Coated**

- Love wave and SH-APM are both sensitive
- x-axis is $d/\lambda$ with $\lambda=$IDT period

**Opposing Face to IDTs Coated**

- SH-APM changes
- Love wave insensitive
- x-axis is $d/\lambda$ with $\lambda=$IDT period

---

Polymer Waveguide on Polymer Substrate

Complex velocity shift

\[ \frac{\Delta v}{v_o} \approx \left( \frac{1-v_f^2/v_o^2}{1-v_l^2/v_o^2} \right) \left( \frac{d \log_e v}{dz} \right) \bigg|_{z=z_0} \left( \frac{\tan(T_f^0 h)}{T_f^0 h} \right) \frac{\omega \rho_f h}{2 \pi v_l^\infty \rho_l} \]

Complex slope factor from polymer waveguide

\( \omega \Delta m/A \) and \((\rho \eta \omega)^{1/2}\)

tanx/x factor gives mass/liquid loading limits

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

Sauerbrey/ solid limit

Kanazawa & Gordon/liquid limit

Sensor Research Examples

(Selected) Past Work
Example 1: Steroids and MIPs

Target Applications (*Liquid Phase*)

Recognition/selectivity via molecularly imprinted polymers (MIPs)
Applications: monoterpenes, amino acids, *topical steroids*
Tailor made enantioseparation materials

MIP - Polymer Type Artificial Receptor

Selectivity to Nandrolone

QCM Coating
- Spin coated/cast layer
- Covalent imprinting strategy

Response to Replicates
- One-shot screening
- Test data for 5 crystals

Example 2: Vaccines - Peptides and T-Cells

1. Infection/virus broken into peptide fragments and presented on cell surface
2. Cytotoxic T-cells attach to peptides and “read” peptide sequence
3. If foreign, cell is killed by release of a cytotoxic chemical
4. Major histocompatibility complex (MHC) antigens are responsible for the expression of peptides on the infected cell
5. Vaccine introduces peptide to the T-cell – Aim is to find suitable peptides
Peptides and T-Cells

1. Infection/virus broken into peptide fragments and presented on cell surface
2. Cytotoxic T-cells attach to peptides and “read” peptide sequence
3. If foreign, cell is killed by release of a cytotoxic chemical
4. Major histocompatibility complex (MHC) antigens are responsible for the expression of peptides on the infected cell
5. Vaccine introduces peptide to the T-cell – Aim is to find suitable peptides

Sensor Strategy

Make this the acoustic wave sensor
Recognition layer is MHC protein
Detect peptide specific binding
Screen for suitable peptides (from the 1000’s that exist) with specificity and strong affinity for the MHC

Current State-of-Art

Cellular peptide-MHC assays → yes/no and not real-time

Sensitive, real-time and non-cellular based assay would assist vaccine development
Flow Cell with Love Wave Screening Device

$\beta_{2m}$ protein binds to A2 and folds to create peptide specific binding cleft.
Acoustic Wave Research

Current Sensor Work
Project 1: Sperm Motility

Veterinary Artificial Insemination (VetAI)
Sperm Quality Assessment & Detection Device (SQuADD)
Time of flight/swim
5 MHz QCM (or use other AWS device)
Frequency drop relative to reference
Crystal pre-coated with sperm ‘sticky’ material

Experimental Sequence
Stabilisation of signal in PBS
Addition of sperm (arrow)
Time of arrival data – swim speed

Project 2: Ionic Liquids Chip

Determining Physical Properties

Room temperature ionic liquids (RTIL’s)
Green because non-volatile
Millions of simple IL’s, billions of binary ILs, ...
Designer solvents
Poorly characterised

QCM

Can measure density-viscosity product, but can also determine whether Newtonian via coupled frequency shift-bandwidth increase

$$\Delta f = -\Delta B/2$$

Data

Polydimethylsiloxane oil - known non-Newtonian at higher molecular weights (ooo)
Two ionic liquids $[\text{C}_4\text{mim}]\text{[OTf]}$ (□□□) and $[\text{C}_4\text{mim}]\text{[NTf}_2\text{]}$ (△△△)

Chip Version – Dilutions of Ionic Liquids

Experiment

Sample: 30 µl with 10 µl in contact with QCM
QCM: 14 mm diameter, rough surface, 10 MHz operated at 3rd harmonic (30 MHz)
Flow-rate: 0.06 µl/s
Liquids: Glycerol/water and [C₄mim][NTf₂]/methanol
Also looked at smooth QCMs and pure ILs

\[ y = 1.0813x + 0.9974 \]
\[ R^2 = 0.9968 \]

Traditionally measured (viscosity-density product)^\frac{1}{2}, \text{kg m}^{-2} \text{s}^{-\frac{1}{2}}

Lab on a chip measured (viscosity-density product)^\frac{1}{2}, \text{kg m}^{-2} \text{s}^{-\frac{1}{2}}

\[ y = 1.0813x + 0.9974 \]
\[ R^2 = 0.9968 \]
Separating Viscosity from Density

Original Concept (Martin et al)
Dual QCM: Smooth and trap surfaces
Frequency shifts allow separation of viscosity from density
Our traps are fabricated using SU-8
Various ionic liquids used
Currently off-chip results

<table>
<thead>
<tr>
<th>Trap</th>
<th>Width  $\mu$m</th>
<th>Separation $\mu$m</th>
<th>Effective Height $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.7</td>
<td>30.4</td>
<td>0.838</td>
</tr>
<tr>
<td>2</td>
<td>24.1</td>
<td>34.5</td>
<td>2.118</td>
</tr>
<tr>
<td>3</td>
<td>43.3</td>
<td>52.5</td>
<td>1.818</td>
</tr>
<tr>
<td>4</td>
<td>70.5</td>
<td>84.0</td>
<td>1.419</td>
</tr>
<tr>
<td>5</td>
<td>108.0</td>
<td>97.0</td>
<td>1.277</td>
</tr>
</tbody>
</table>
Acoustic Wave Research

Wetting and Acoustics Work
Foam heated (and cooled) prior to droplet deposition.

Hydrophobic grains

Optional PTFE

water

metal contact

substrate

Superhydrophobic tube

Normal tube

Foam heated (and cooled) prior to droplet deposition

Normal tube

Superhydrophobic tube

24 September 2009
Old Work: SAWs and Stripes of Oil

Determining Physical Properties

170 MHz Rayleigh SAW
Pulse mode
PDMS oils (10 000-100 000 cSt)
Attenuation and reflection of SAW
Simultaneous interferometry for shape
Old Work: Attenuation and Reflections

Attenuation Data:

Reflection Data:

Current Work: Superhydrophobicity

Immersed Superhydrophobic Surfaces

Provided design of features correct, penetration of water can be resisted
A silvery sheen can be seen when immersed – due to surface retained layer of air.

Hydrophobicity and Acoustics

What might happen when an acoustic wave device has a hydrophobic, or a structured hydrophobic or even a superhydrophobic surface?
Usual Hydrodynamic View of Acoustic Response

Mathematical Formulation

Wave equation for substrate and solid layer or Navier-Stokes equations for liquid
define substrate and layer/fluid displacements
Match solutions at boundary (substrate-air, substrate-layer or substrate-liquid)
Provides dispersion equation and solution gives resonances

No-Slip Boundary Condition

Solid-Air $\Rightarrow q_s(z=0)=q_f(z=0)$ substrate & layer displacements
  match at all times
  i.e. $v_s(z=0)=v_f(z=0)$ speeds at wall match

Solid-Water $\Rightarrow v_s(z=0)=v_f(z=0)$ speeds at wall match - fluid
  speed extrapolated from bulk

References
The Effect of Wall Slip: Theory

Flow Profile

With slip length, $b$

![Diagram showing flow profile with slip length $b$.]

Equations

Match speeds

$$v_s(z = 0) = v_f(z = -b)$$

Expand

$$v_w - v_f(z = 0) = -b \left( \frac{\partial v_f}{\partial z} \right)_{z=0}$$

Force exerted on wall divided by viscosity

Slip length, $b$, models effective position of interface

Negative $b$ implies effective interface moves to liquid side of boundary

Slip length is a mechanism for modelling an effective average boundary and/or taking into account liquid-solid interfacial forces

24 September 2009


Effective Sauerbrey “Trapped Liquid Mass”

Equations of Motion

Solve with slip boundary condition for acoustic impedance
Consider in terms of slip length and interpret solution for small \( b \)

Newtonian Liquid

Kanazawa & Gordon result for no-slip modified by “slip” correction using \( b/\delta \)

\[
\left( \frac{\Delta \omega}{\omega} \right)_{slip} \approx \left( \frac{\Delta \omega}{\omega} \right)_{no\ slip} \left( 1 - \frac{2b}{\delta} \right)
\]

Negative Slip Length

Define a liquid mass as \( \Delta m_f = b \rho_f \)

\[
\left( \frac{\Delta \omega}{\omega} \right)_{additional} \approx \left( -\frac{2b}{\delta} \right) \left( \frac{\Delta \omega}{\omega} \right)_{no\ slip} = \frac{\omega \Delta m_f}{\pi \sqrt{\mu_s \rho_s}}
\]

\textit{Kanazawa & Gordon viscosity-density product contribution + trapped “Sauerbrey-like liquid mass”, but this assumes all locations are equal, i.e. complete liquid penetration.}

24 September 2009

Implicit Assumptions: Acoustic Reflection View

Simple Cavities and Standing Waves

- **Solid-Air** $\Rightarrow$ Uniform and strong reflection
- **Solid-Water** $\Rightarrow$ Partial reflection at an effective plane within penetration depth

Cavity length increases: $f_\downarrow$
- Reflection remains strong

Cavity length increases: $f_\downarrow$
- Reflection becomes partial: $B_\uparrow$

Assumes reflection from all locations along the surface are of equal strength

---

Effect of Topography and Hydrophobicity?

Structured Cavities and Standing Waves

Air contact ⇒ Equally strong reflections from peaks and troughs of surface

Water contact ⇒ Changes cavity length and strength of reflection defined by peaks

Deposit solid (or penetrating liquid)

Skating form of superhydrophobicity offers possibility of new liquid phase responses

Extreme Superhydrophobic Case

Water immersion \Rightarrow Water skates across surface features and pressure (or other force) is needed to force capillary penetration

**Superhydrophobic**

Coupling to liquid is at vanishingly small number of points

**Conceptually**

Crystal does not sense the liquid. No significant changes in frequency or bandwidth i.e. $f_\downarrow$ and $B_\uparrow << K&G$ values

**Wenzel/Penetrating**

Coupling across troughs. Effective cavity length increases and reflection weakened, i.e. $f_\downarrow$ and $B_\uparrow$

*QCM behaves as if decoupled from the liquid, unless liquid penetrates into structure*

24 September 2009

QCM with Microposts: “Skating” Transition

Hydrophobised 18 µm micro-posts. Solid-line is before pressure applied. Dotted curves is after pressure is applied. Visually confirmed water ingress after pressure applied.
Micro-Post Surfaces – Water/Glycerol Mixtures

Bare (non-hydrophobised) and Hydrophobised (0-100%)

Data parallel to K&G line
Newtonian-like + offset

Above 80% glycerol

Unusual?
Compressional waves?

Unusual?
Data close to origin

5µm = □□□
10µm = ◇◇◇
15µm = △△△
18µm = ○○○

Filled symbols = hydrophobised

Kanazawa & Gordon Theory = - - - -

Hydrophobisation of posts changes type of response – all data generally closer to origin

24 September 2009

SiO$_2$ Surfaces: Viscosity-Density

**Frequency**

- $\delta > 350$ nm
- Data for $(\eta\rho)^{1/2} = 2.3, 3.02$ and 4.2 kg m$^{-2}$ s$^{-1/2}$ taken on a later day

**Bandwidth**

- $\delta > 350$ nm
- Data for $(\eta\rho)^{1/2} = 2.3, 3.02$ and 4.2 kg m$^{-2}$ s$^{-1/2}$ taken on a later day

Blank at 25 °C = △△△
Hydrophobic crystal at 20°C = ▲▲▲

a1 (Super?)hydrophobic SiO$_2$ = ◆◆◆◆ at 20 °C
b1 Superhydrophobic SiO$_2$ = ●●●● at 20 °C

---

*a1:* most data points show reduction below K&G levels, later data are at K&G levels

*b1:* data has stronger decoupling trend – consistent with contact angle data/mobile drop

---

24 September 2009

Conclusions

1. Acoustic Wave Devices
   - Many modes for liquid and gas phase operation
   - Well established as effective sensors in simple systems

2. Current Research on Sensors
   - Sperm motility using simple swim time and effective “mass”
   - Lab-on-a-Chip for ionic liquids + traps to separate viscosity

3. Hydrophobic Surfaces
   - Response depends on combination of topography and hydrophobicity
   - “Slippy” superhydrophobic surfaces should decouple acoustic response
   - Skating-to-penetrating transition could be used as a sensor principle

The End
Acknowledgements

Collaborators

Academics
Dr Mike Newton (NTU), Prof. Mike Thompson (Toronto), Dr Electra Gizeli and Dr Kathryn Melzak (Cambridge/Crete), Dr Ralf Lucklum (Magdeburg), Prof. Chris Hardacre (QUB), Prof. Ray Allen and Dr Jordan MacInnes (Sheffield), Prof. Bob Rees (NTU), Prof. Toni Dodi (ANRI/NTU), Dr David Hughes (NTU), Dr Carl Percival (Manch)

PDRA’s
Dr Neil Shirtcliffe, Dr Simon Stanley, Dr Carl Evans, Dr Paul Roach + QUB + Sheffield

PhD’s
Dr Fabrice Martin. Mr Shaun Atherton, Ms Nicola Doy, Ms Sanaa Aqil, Mr Steve Elliott + QUB + Sheffield +....

Funding Bodies

EPSRC funding for acoustic, surface wetting and drag reduction research projects
Dstl via EPSRC/MOD JGS for support of wetting research
EU COST Actions D19 and P21
Lachesis Venture Fund for VetAI development

Group website and reprints: http://www.naturesraincoats.org/