COST

EPSRC
Engineering and Physical Sciences
Research Council

NOTTINGHAM
TRENT UNIVERSITY

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

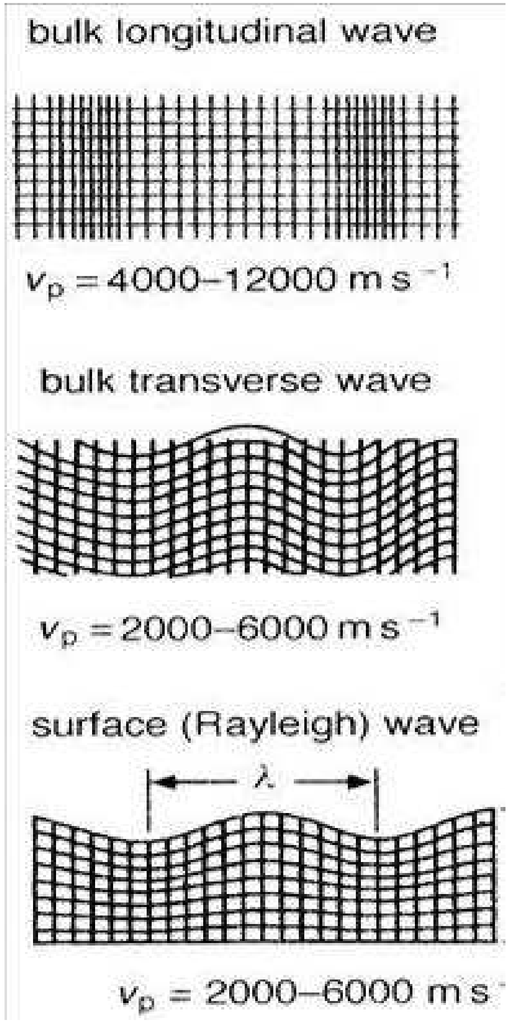
Overview

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

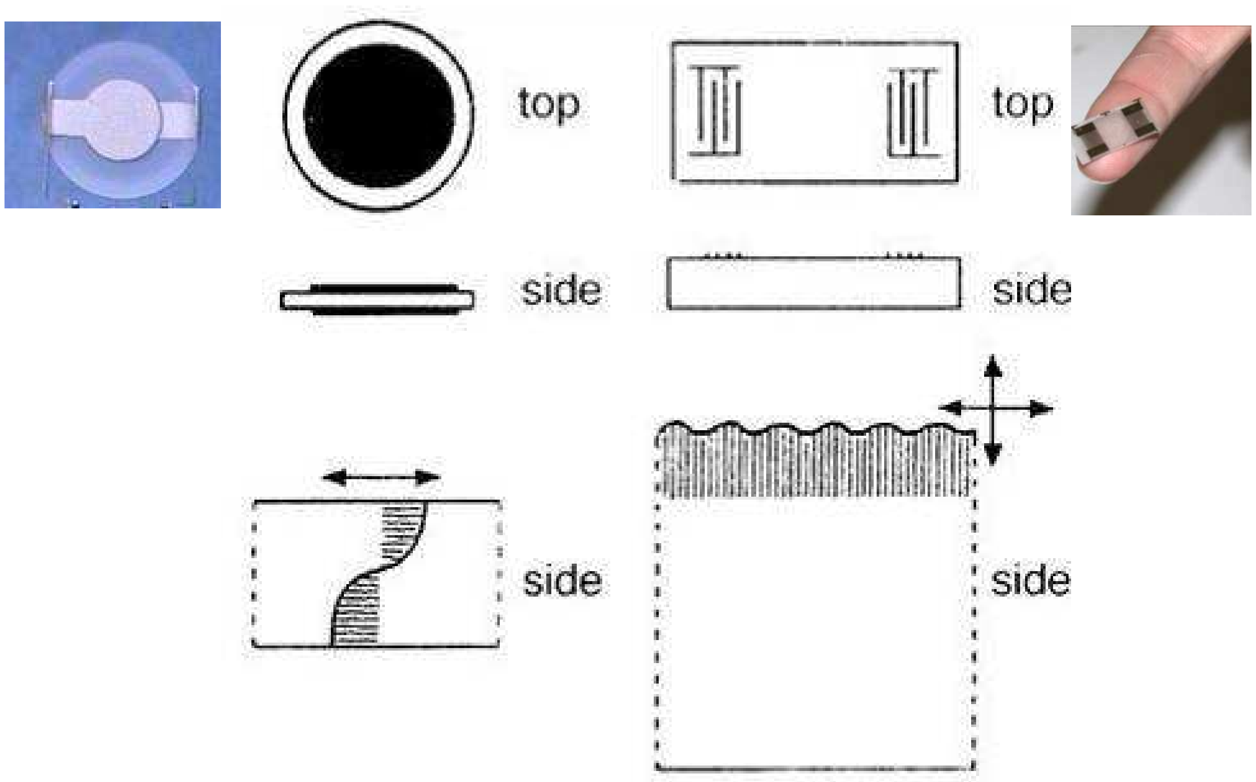
Basics of Acoustic Waves

Acoustic Waves

Acoustic Waves



QCM versus SAW

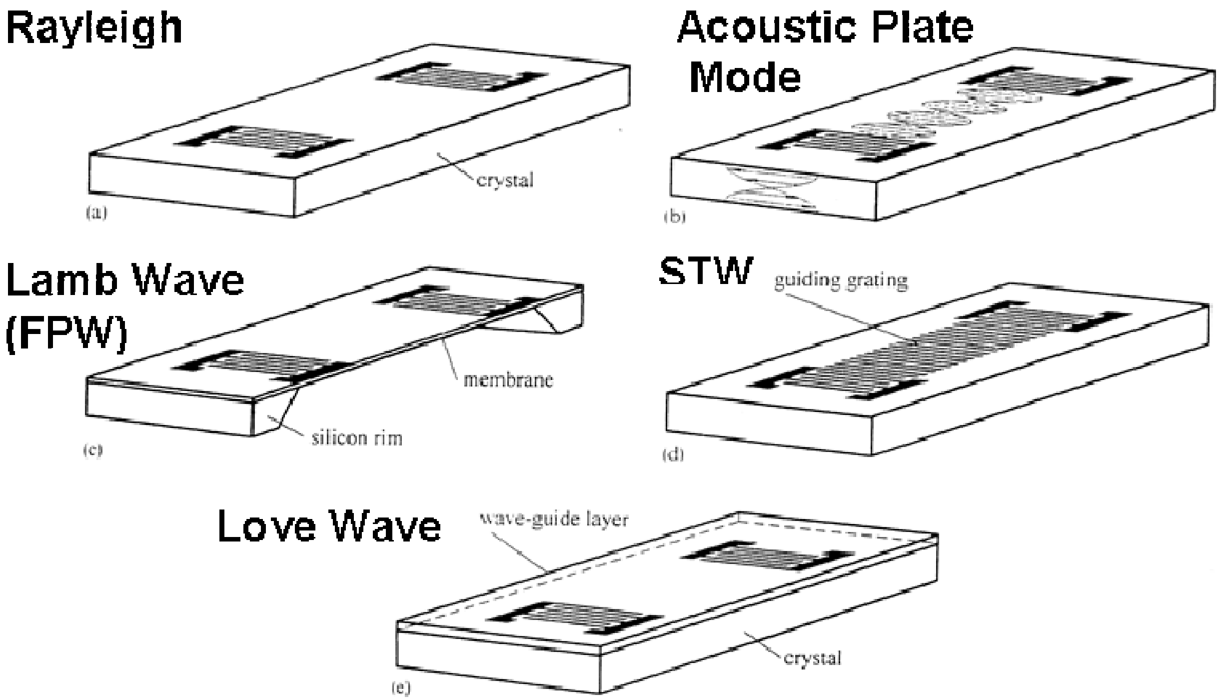


QCM – frequency determined by thickness

SAW – frequency determined by fingers

Acoustic Wave Modes

Delay Lines



Mode	Rel. Sens.	Complexity	Robustness	Gas/Liquid
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

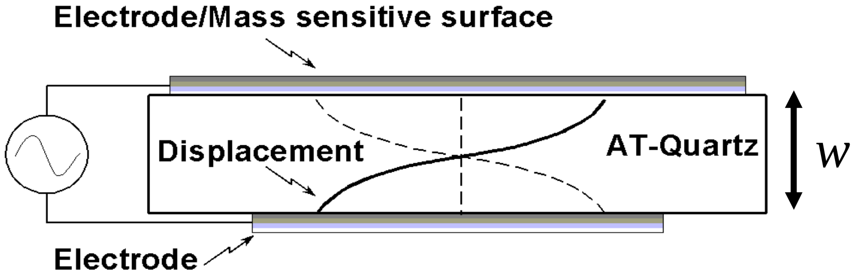
QCM/QCR Sensing Principles

Thickness Shear Mode Vibration

QCM has a sharp resonance

Frequency given by quartz thickness, w

$$v_s = f\lambda \quad \Rightarrow \quad f = 2v_s/w$$



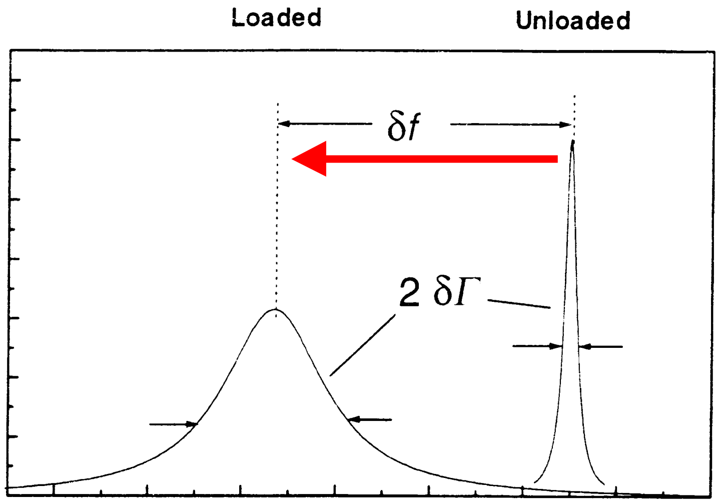
Mass Loading or Immersion

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

Sauerbrey, G., Z. Phys. 155 (1959) 206-222. Bruckenstein, S; Shay, M., Electrochim. Acta 30 (1985) 1295-1300. Kanazawa, K.K.; Gordon, J.G., Anal. Chim. Acta 175 (1985) 99-105.

Liquids and Penetration Depth

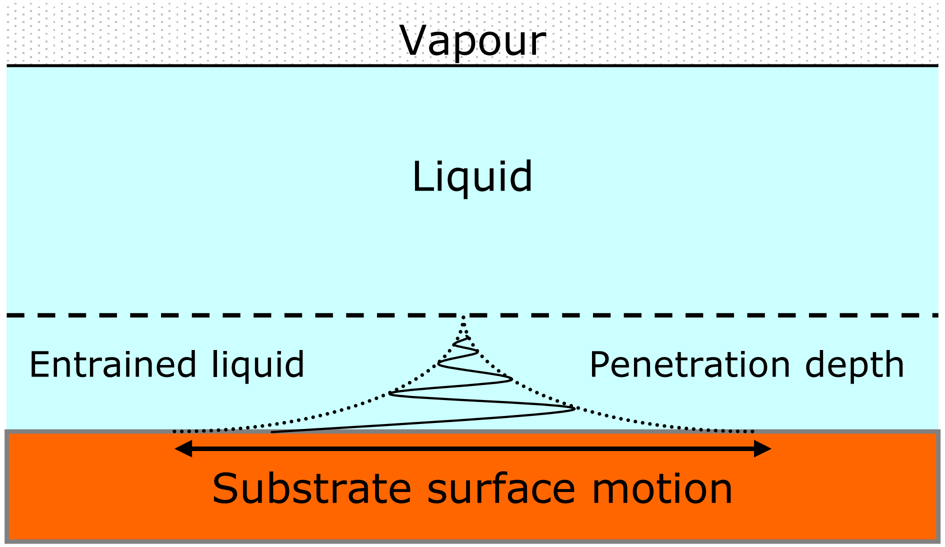
Shear Mode Vibration

Entrains liquid

Liquid oscillation decays

Penetration depth

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



Liquid Sensing

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

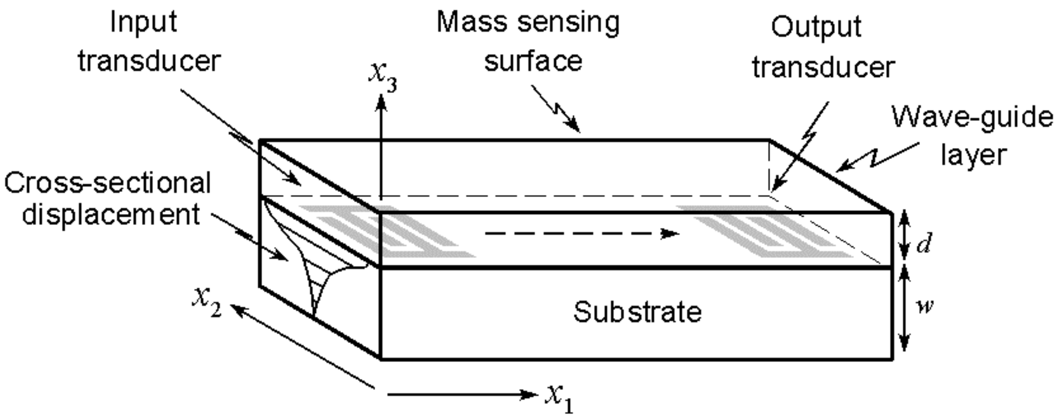
	QCM		SAW	
For water:	5 MHz	$\delta \sim 250$ nm	500 MHz	$\delta \sim 25$ nm

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

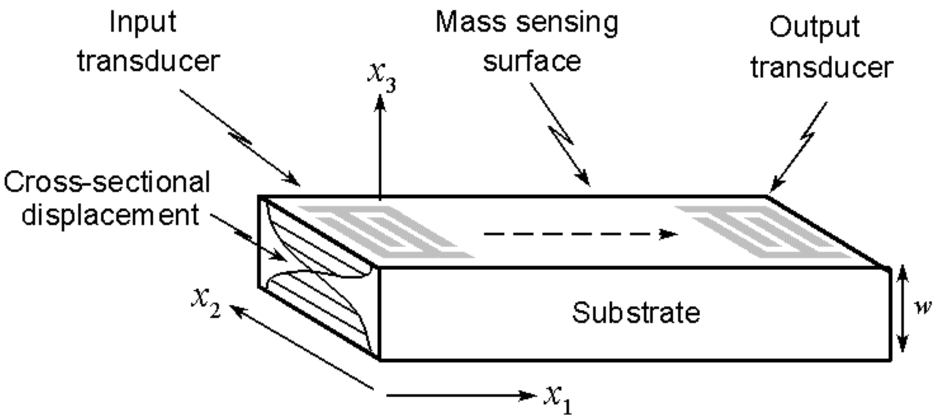


Layer guided SH-SAW with $v_l < v_s$

Surface localised wave

Increased sensitivity

SH-APM



"QCM with propagation"

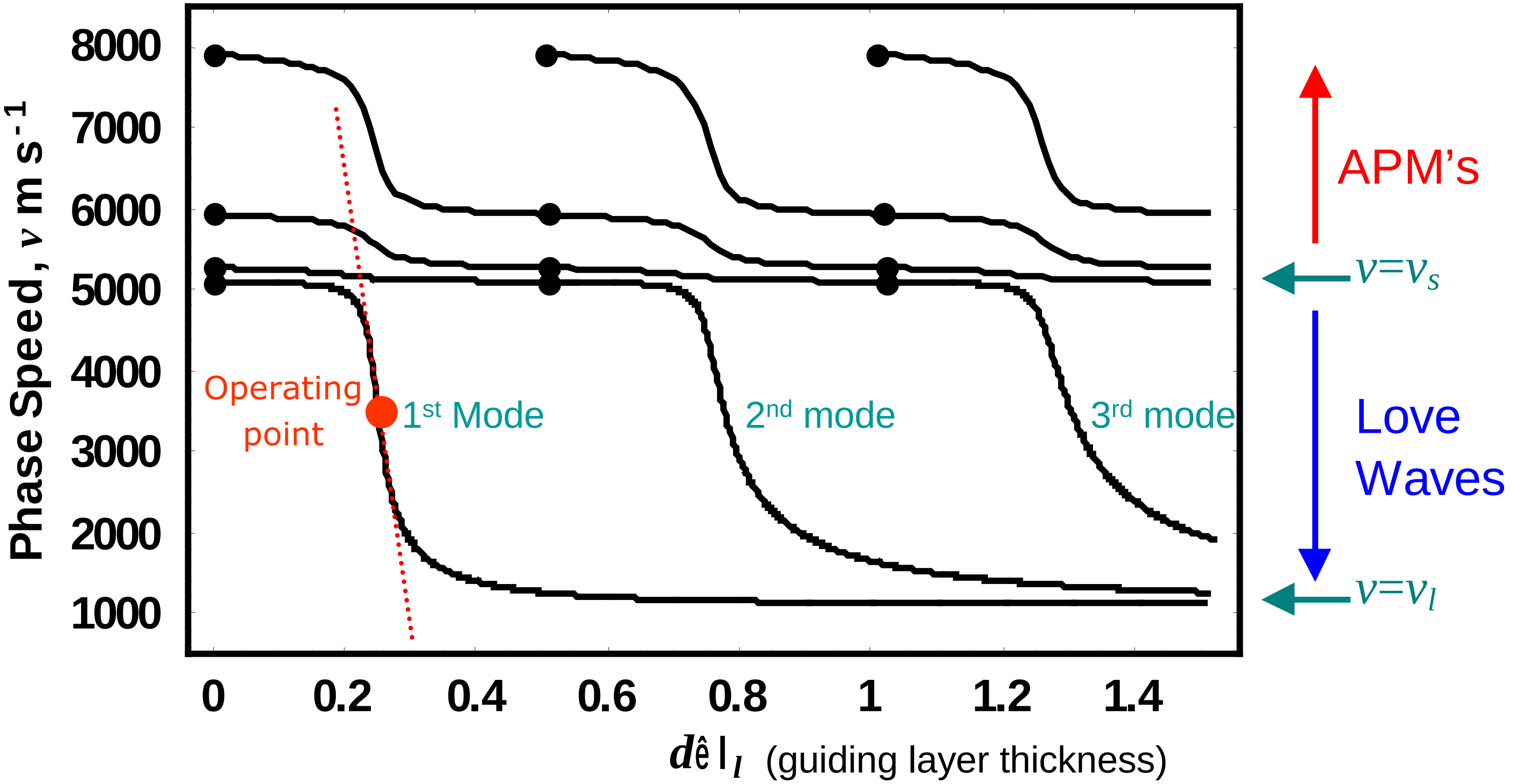
Substrate resonance

Sensing via both faces

Increased sensitivity versus isolation between sensing face and transduction

McHale, *et al, J. Appl. Phys.*, 2003, **93**, 675-690; *MST*, 2003, **14**, 1847-1853.

Generalized Love Waves – Operating Point



$v>v_{s:}$ Plate modes = Switch in order of resonance induced by layer

$v<v_{s:}$ Love wave = Shear mode in substrate-to-shear mode in layer transition

Increased mass/liquid sensitivity related to slope of dispersion curve

McHale, *et al, J. Appl. Phys.*., 2002, **91**, 5735-5744; 9701-9710.

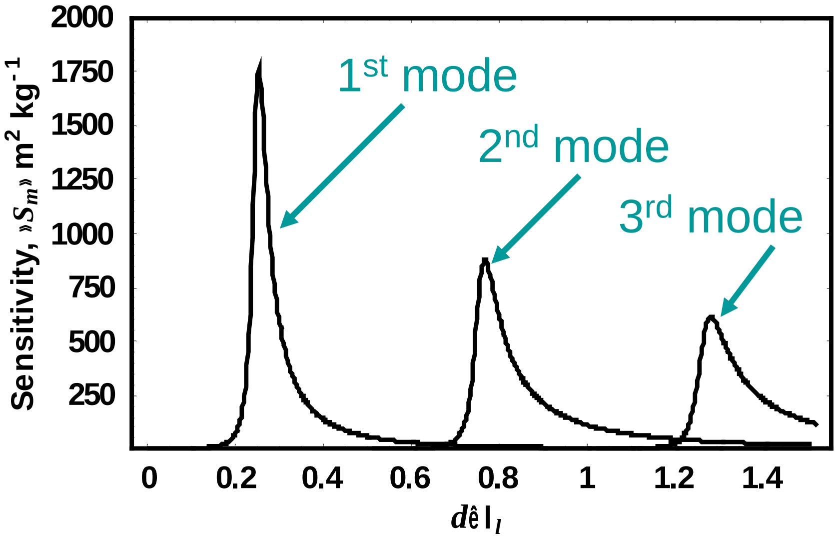
Phase Speed Mass Sensitivity

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

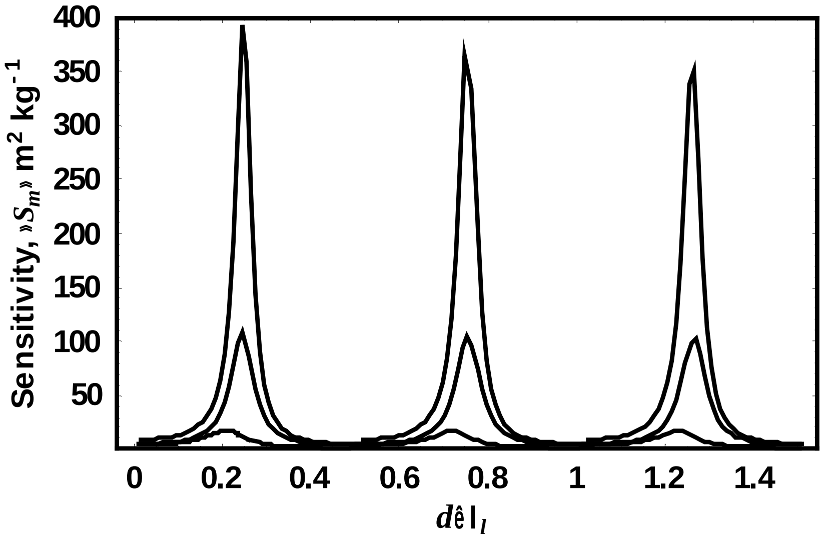
Δm is mass per unit area being sensed, $z=df/v_l$ is the normalized thickness

"Rigid" mass ⇒ Mass sensitivity is slope of dispersion curve

Love Waves



Layer-Guided SH-APMs



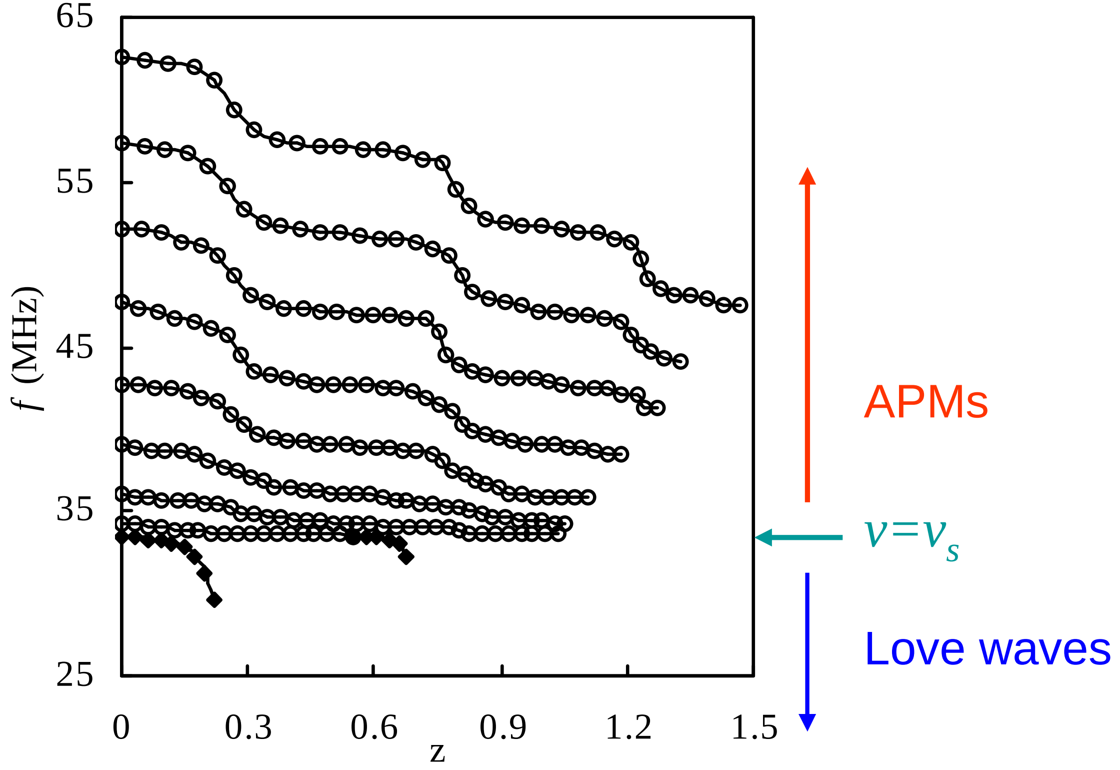
Experimental Data for Layer-Guided SH-APMs

25 MHz surface skimming bulk wave (SSBW)

Propagation orthogonal to x-axis of thinned (200 mm) ST-Q substrate

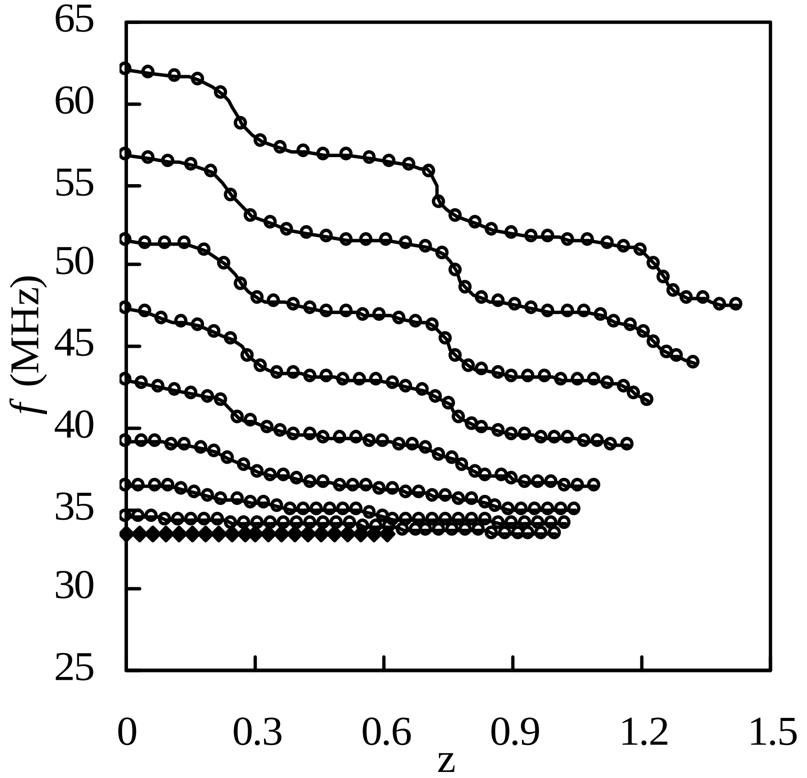
IDT Face Coated

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



Opposing Face to IDTs Coated

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



McHale, *et al*, *Appl. Phys. Lett.*, 2003, **82**, 2181-2183.
Newton, *et al*, *Sens. Act*., 2004, **A109**, 180-185.
F. Martin, PhD Thesis, Nottingham Trent University (2002).

Generalized Sauerbrey/Kanazawa & Gordon

Polymer Waveguide on Polymer Substrate

Complex velocity shift

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

$\omega\Delta m/A$

$(\rho\eta\omega)^{1/2}$

Complex slope factor
from polymer waveguide

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

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

Sauerbrey/
solid limit

Kanazawa &
Gordon/liquid limit

McHale, *et al*, *J. Appl. Phys.*, 2003, **93**, 675-690; *MST*, 2003, **14**, 1847-1853.

Sensor Research Examples

(Selected) Past Work

Example 1: Steroids and MIPs

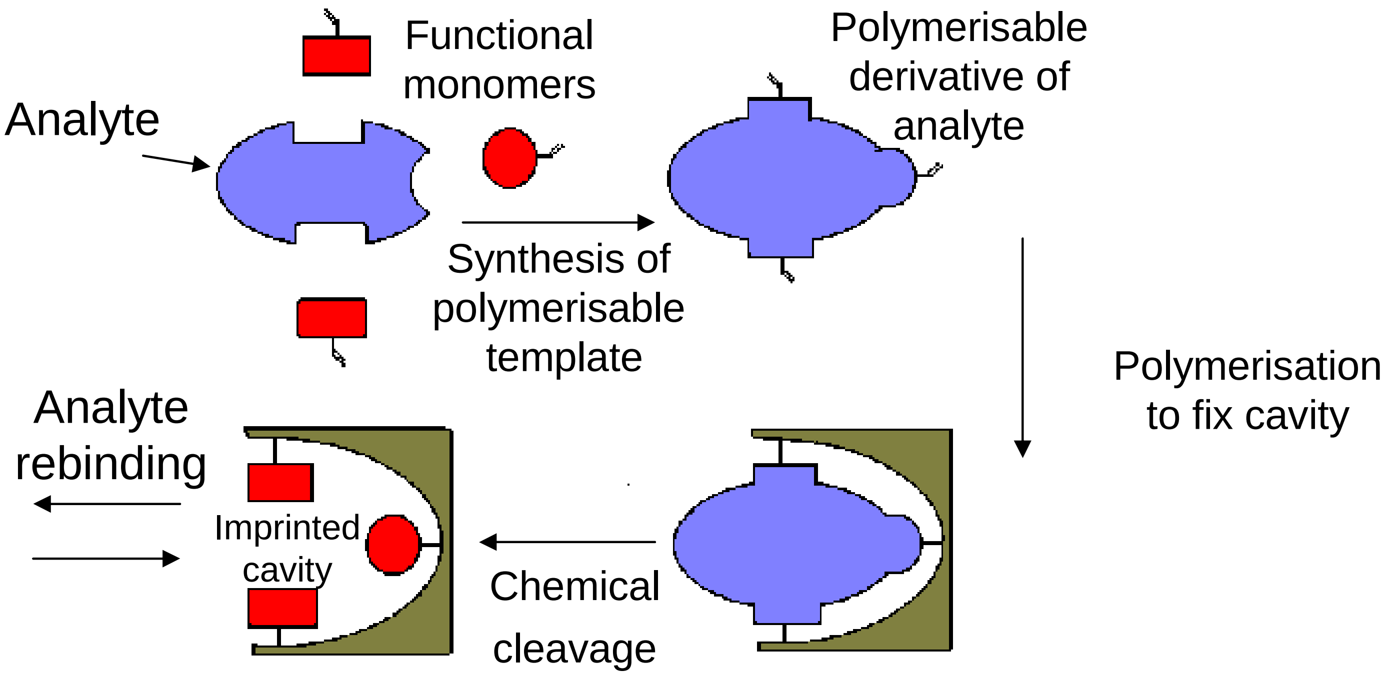
Target Applications (*Liquid Phase*)

Recognition/selectivity via molecularly imprinted polymers (MIPs)

Applications: monoterpenes, amino acids, *topical steroids*

Tailor made enantioseparation materials

MIP - Polymer Type Artificial Receptor



Percival, *et al, Anal. Chem.*, 2001, **73**, 4225 –4228; 2003, **75**, 1573-1577.

Selectivity to Nandrolone

QCM Coating

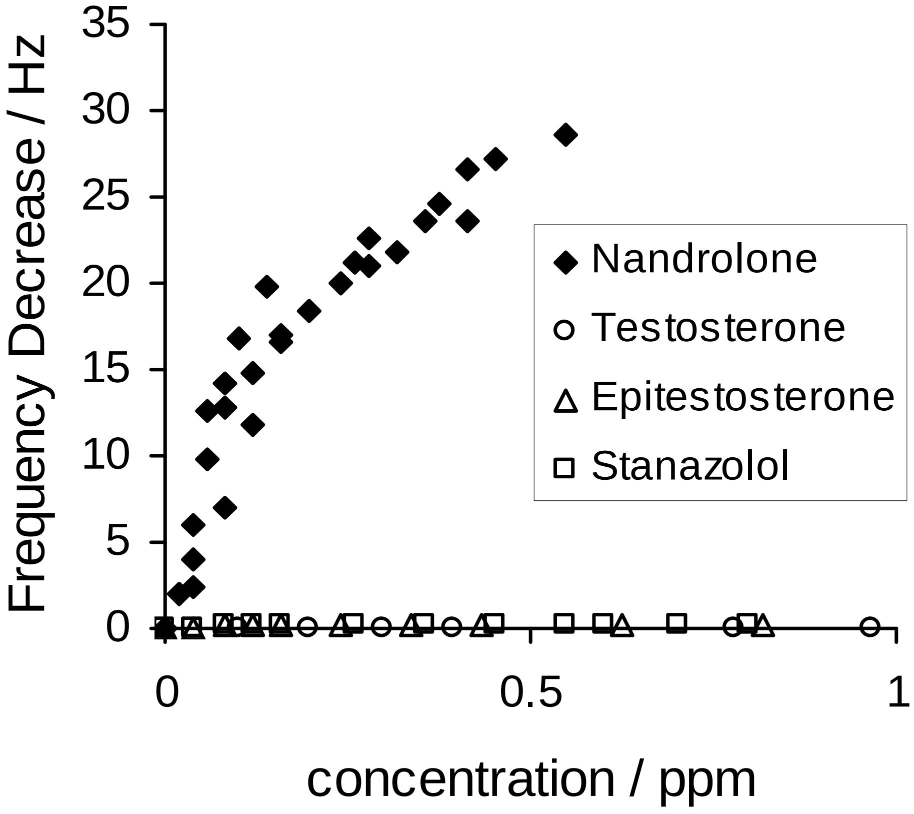
Spin coated/cast layer

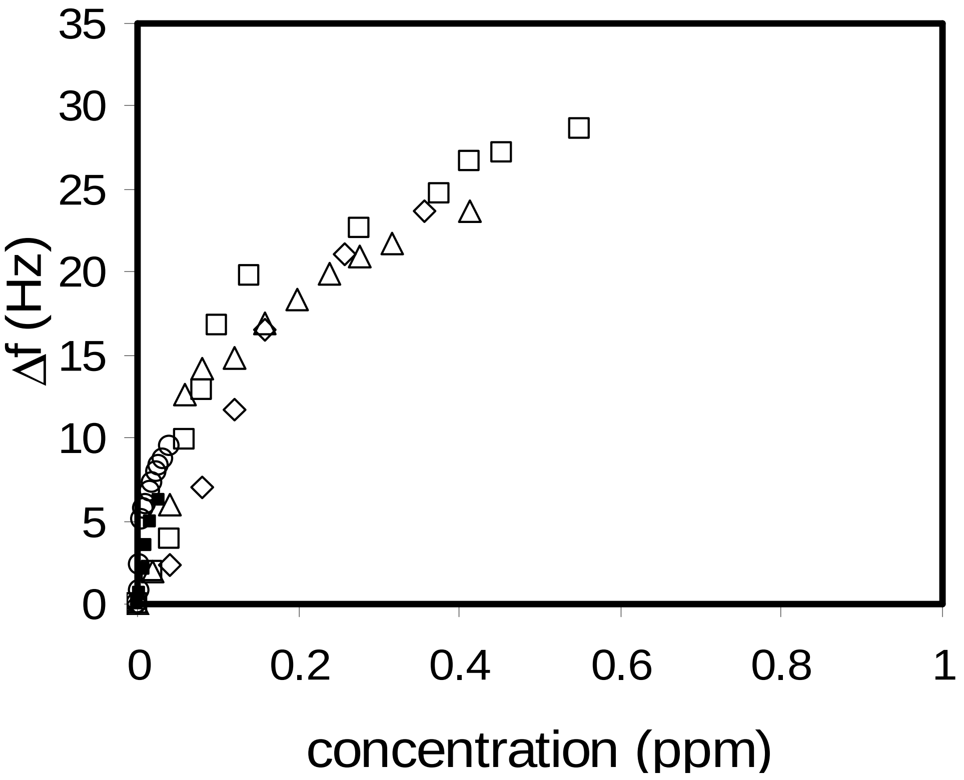
Covalent imprinting strategy

Response to Replicates

One-shot screening

Test data for 5 crystals

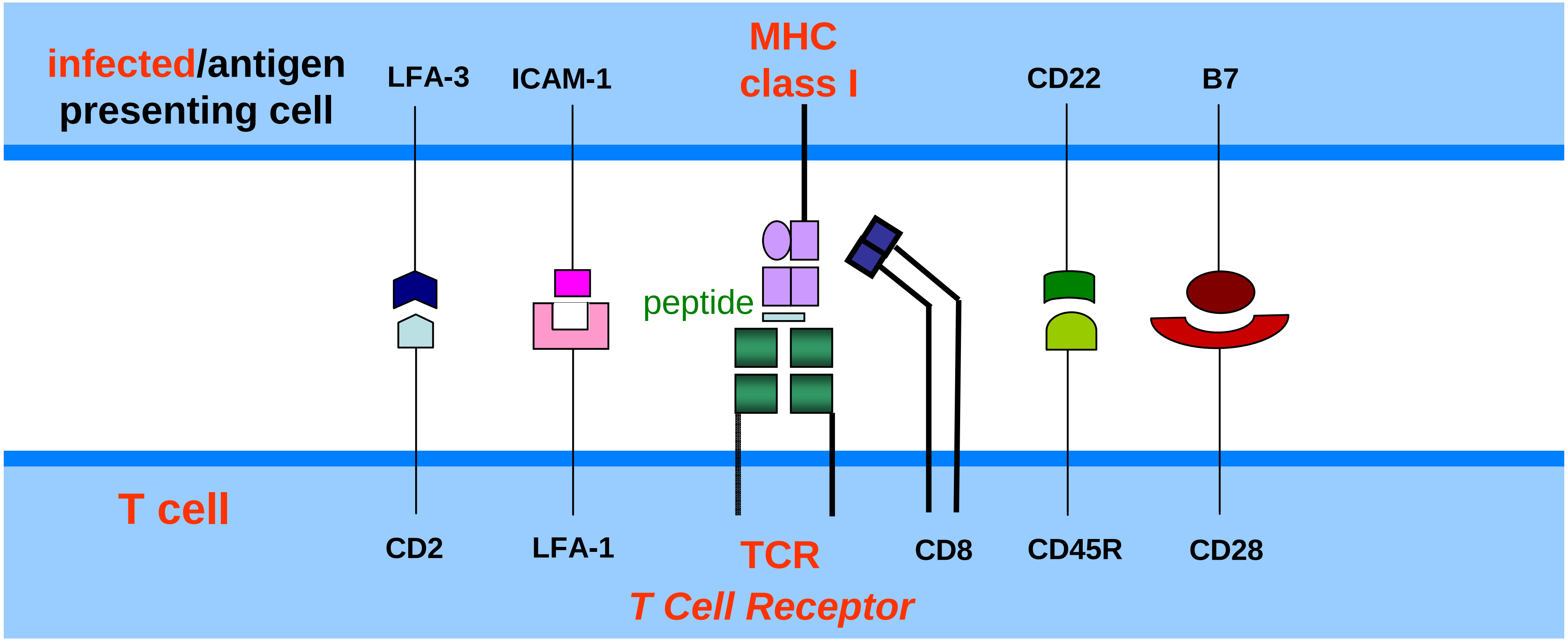




Percival, *et al, Analyst*, 2002, **127**, 1024-1026.

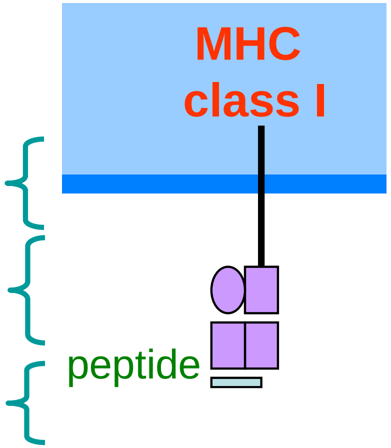
Example 2: Vaccines - Peptides and T-Cells

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 histocompatability 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 histocompatability 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

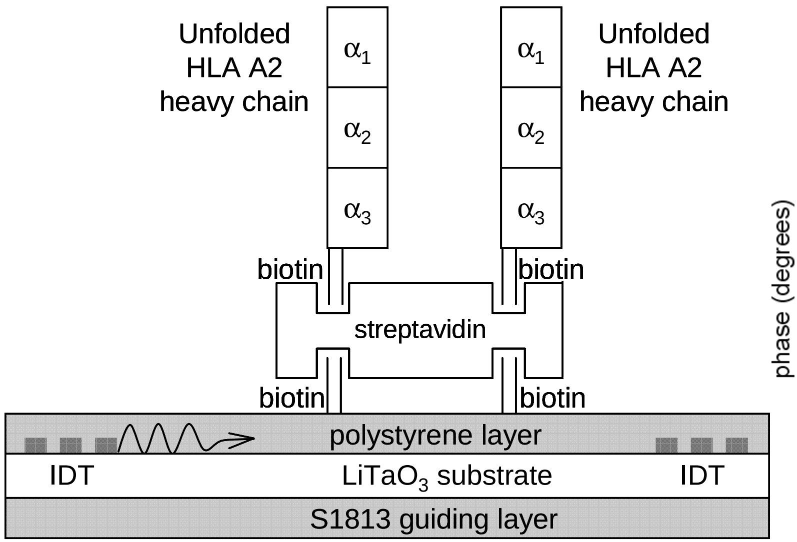
Cellular peptide-MHC assays

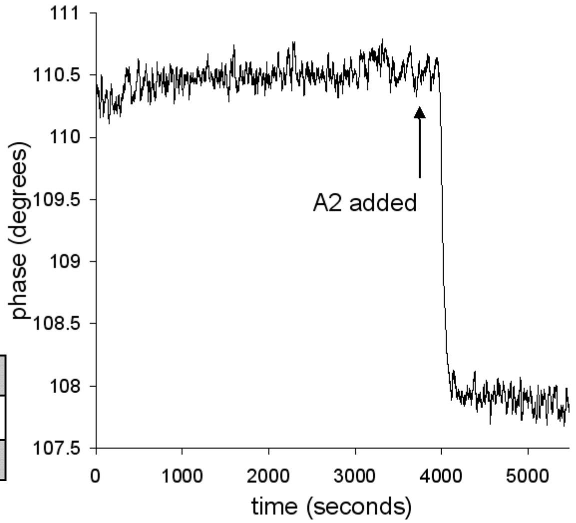
→ yes/no and not real-time

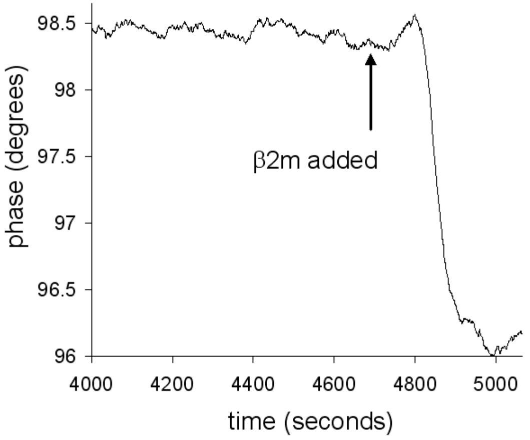
Sensitive, real-time and non-cellular based assay would assist vaccine development

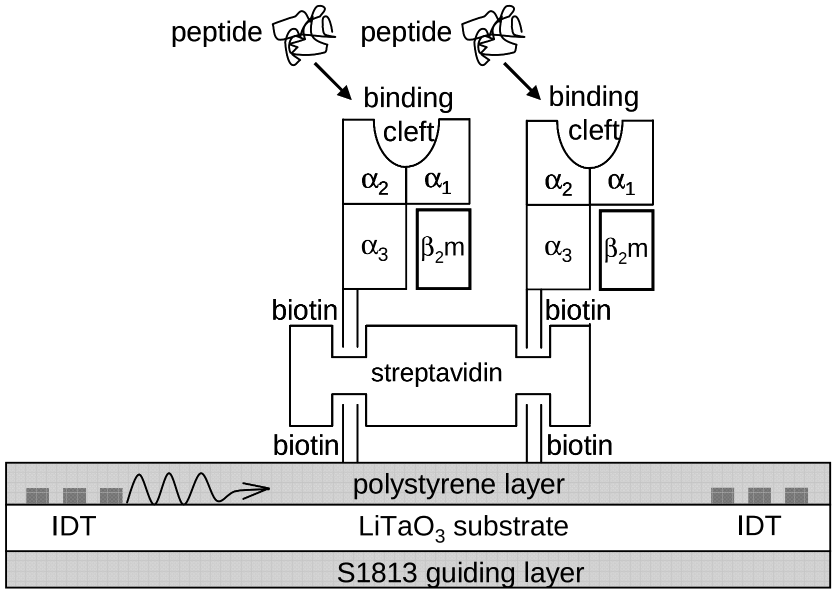
Flow Cell with Love Wave Screening Device

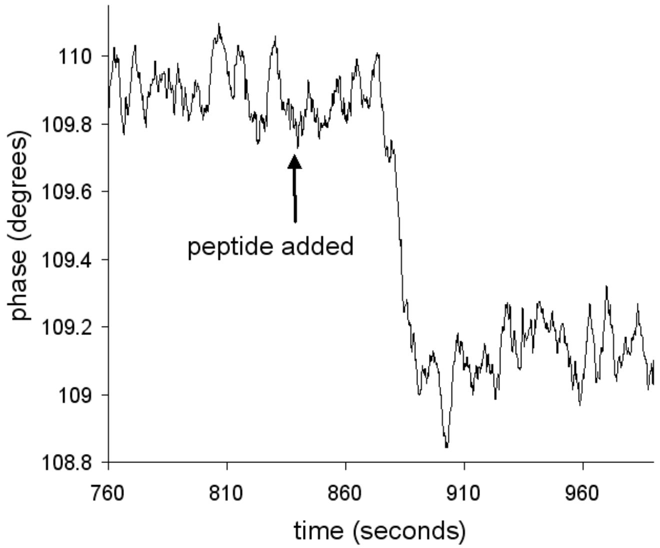
β_{2m} protein binds to A2 and folds to create peptide specific binding cleft











Stanley, *et al, Analyst*, 2006, **136**, 892-894.

Acoustic Wave Research

Current Sensor Work

Project 1: Sperm Motility

Veterinary Artificial Insemination (VetAI)

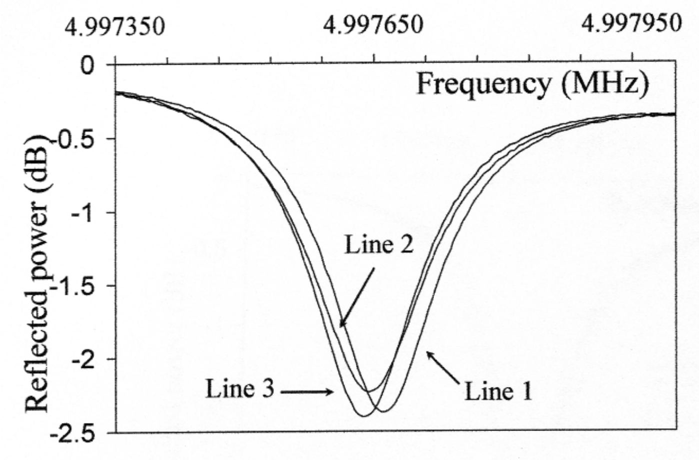
Sperm Quality Assessment & Detection Device (SQuADD)

Time of flight/swim

5 MHz QCM (or use other AWS device)

Frequency drop relative to reference

Crystal pre-coated with sperm ‘sticky’ material

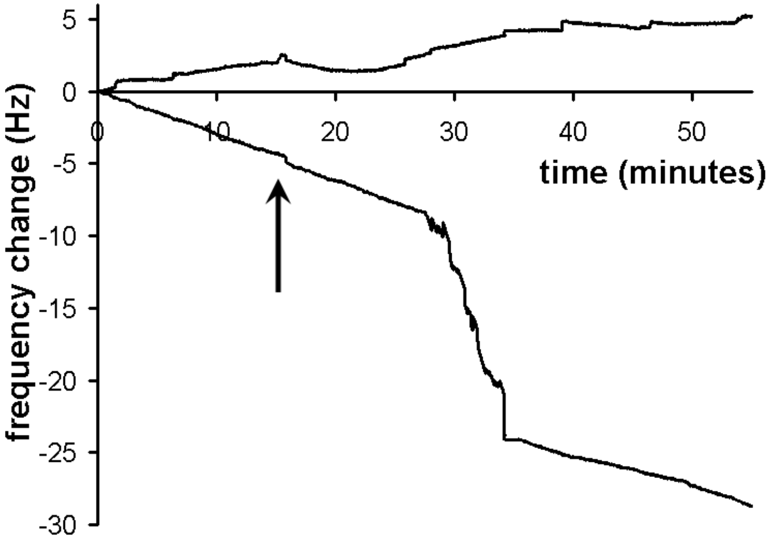


Experimental Sequence

Stabilisation of signal in PBS

Addition of sperm (arrow)

Time of arrival data – swim speed



Hughes, *et al*, *Acoustic wave sperm test kit and assay*, WO2007085839 (2/8/2007)
Newton, *et al, Appl. Phys. Lett.*, 2007, **90**, art. 154103.

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

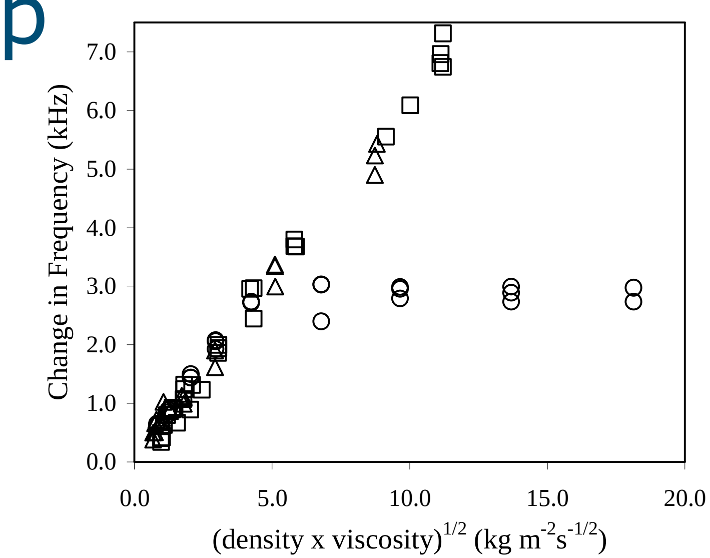
QCM

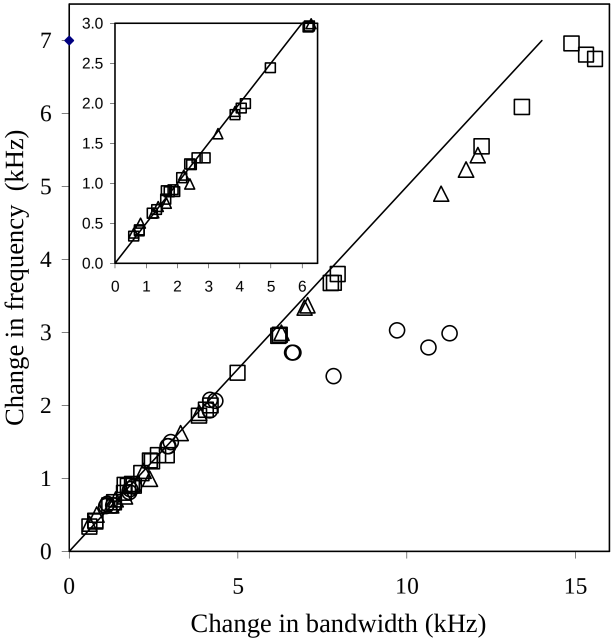
Can measure density-viscosity product, but can also determine whether Newtonian via coupled frequency shift-bandwidth increase

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

Data

Polydimethylsiloxane oil - known non-Newtonian at higher molecular weights (ooo)
Two ionic liquids [C_4mim][OTf] (□□□) and [C_4mim][NTf_2] (ΔΔΔ)





McHale, *et al, Anal. Chem.*, 2008, **80**, 5806-5811.
Ge, *et al, Anal. Chem.*, 2009, **81**, 1628-1637.

Chip Version – Dilutions of Ionic Liquids

Experiment

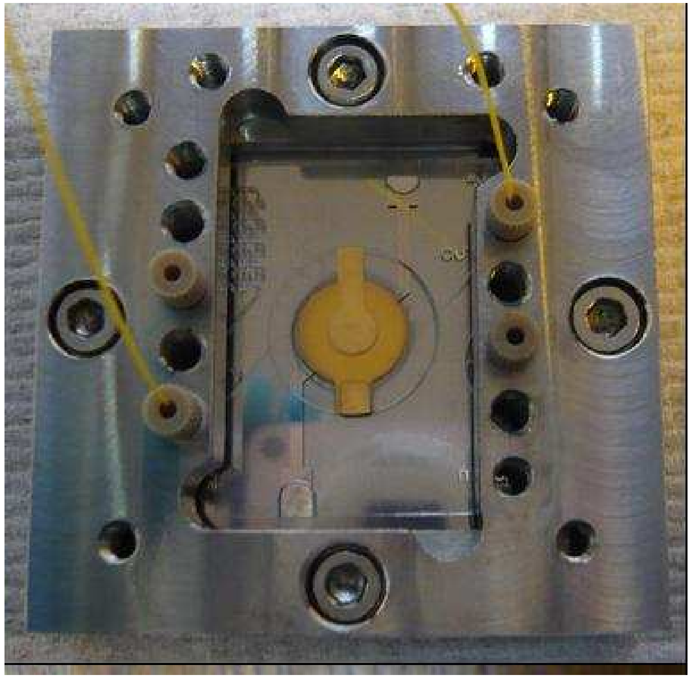
Sample: 30 μl with 10 μl in contact with QCM

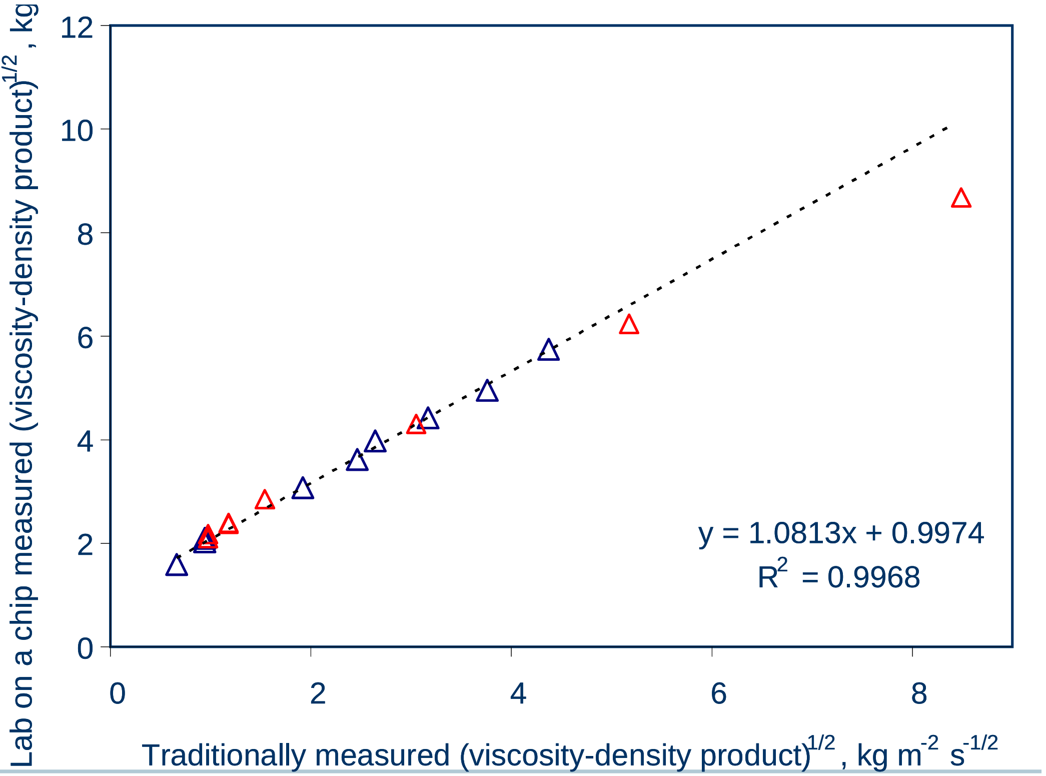
QCM: 14 mm diameter, rough surface, 10 MHz operated at 3rd harmonic (30 MHz)

Flow-rate: 0.06 μl/s

Liquids: Glycerol/water and [C_4mim][NTf_2]/methanol

Also looked at smooth QCMs and pure ILs

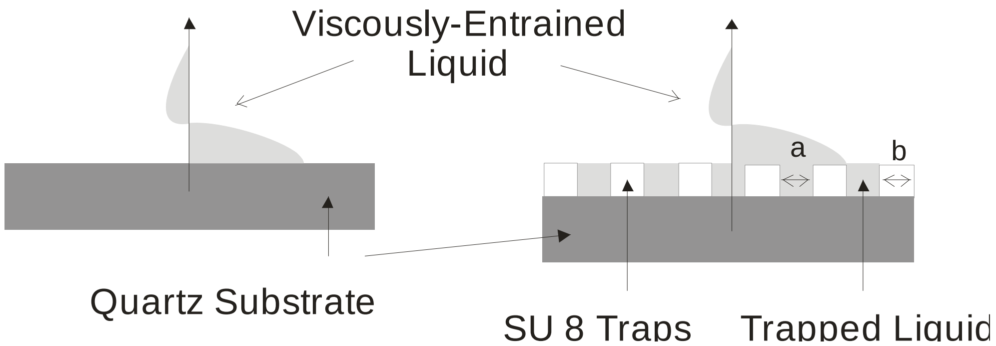




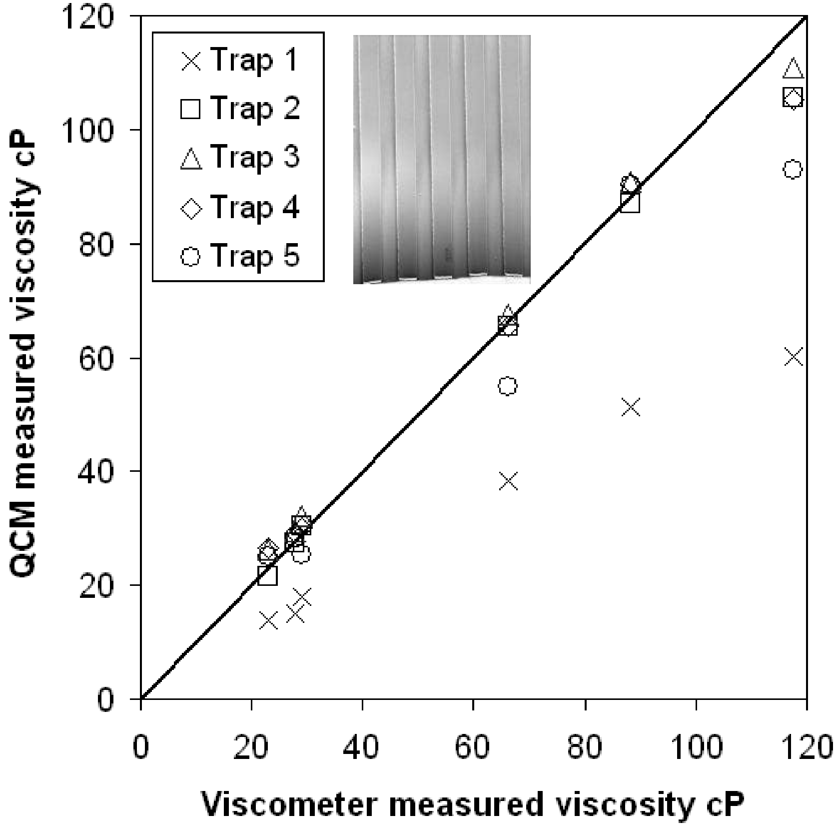
Separating Viscosity from Density

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



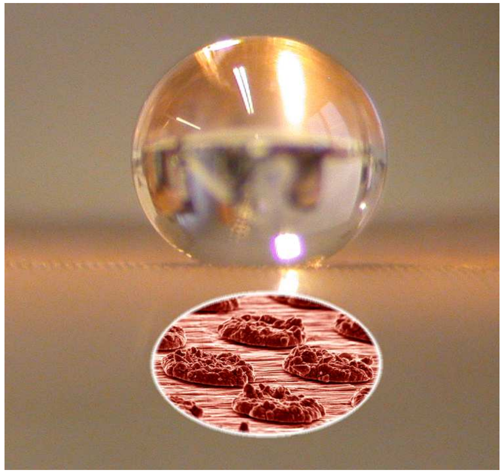
Trap	Width µm	Separation µm	Effective Height µm
1	10.7	30.4	0.838
2	24.1	34.5	2.118
3	43.3	52.5	1.818
4	70.5	84.0	1.419
5	108.0	97.0	1.277

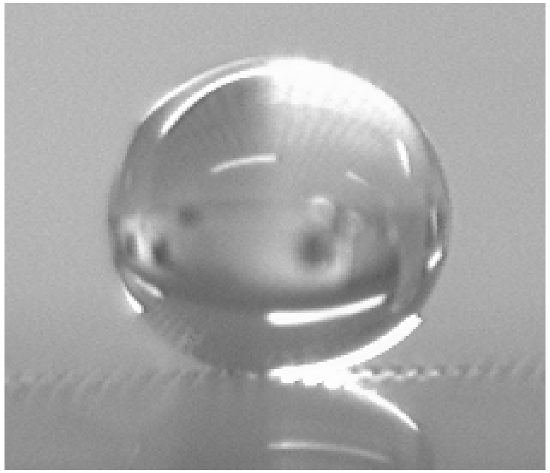


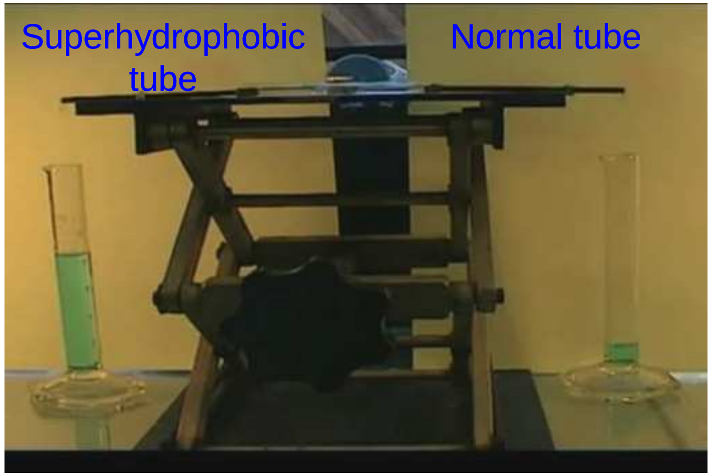
Martin, *et al*, *Sens. Act A*, 1994, 44, 209-218.
Doy, *et al*, *IEEE Sensors Conference* 2009.

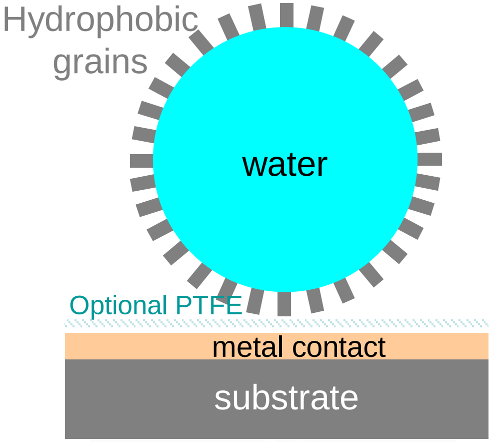
Acoustic Wave Research

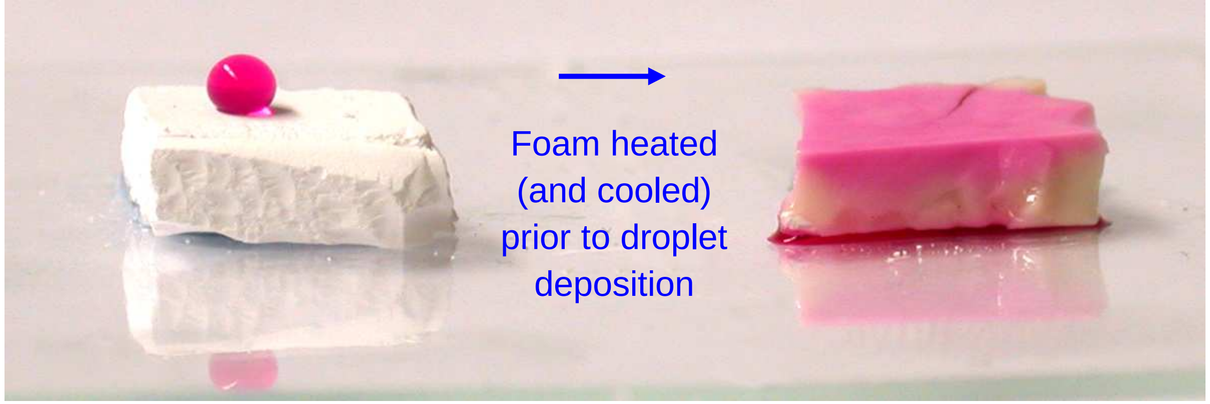
Wetting and Acoustics Work



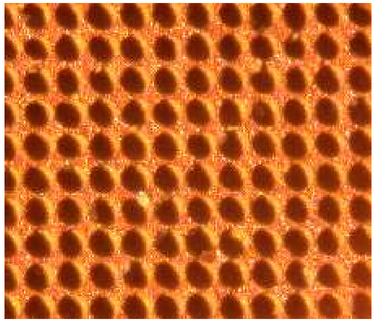


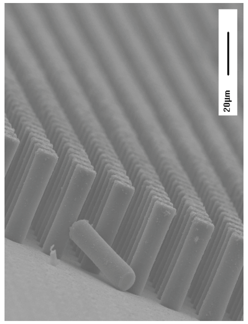


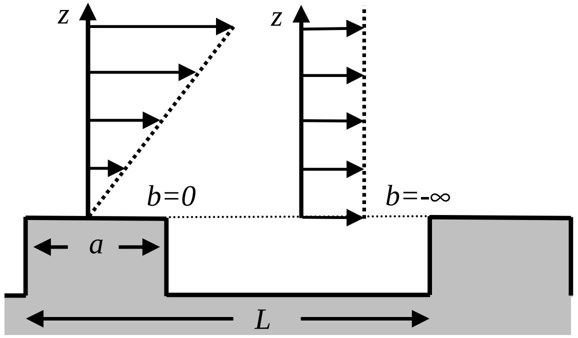




Foam heated (and cooled) prior to droplet deposition







Old Work: SAWs and Stripes of Oil

Determining Physical Properties

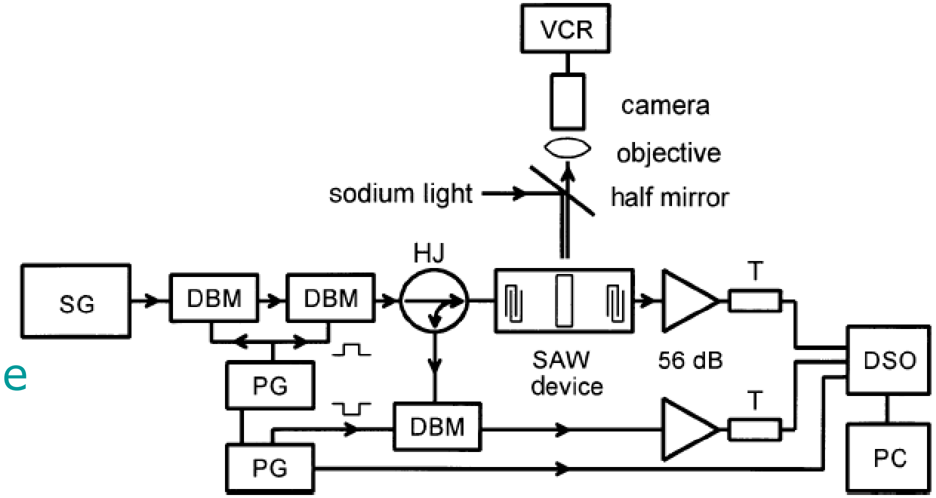
170 MHz Rayleigh SAW

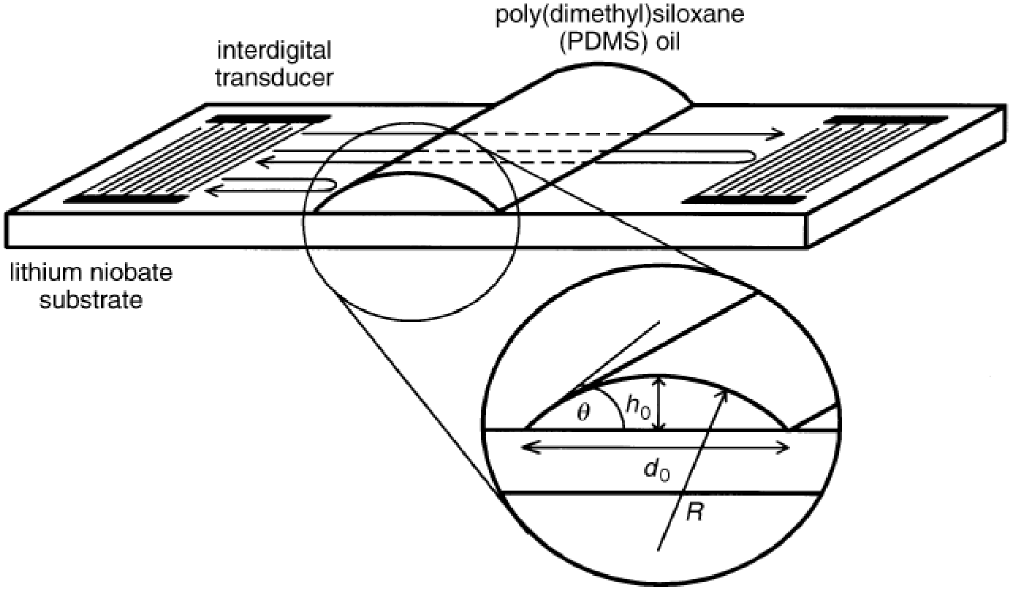
Pulse mode

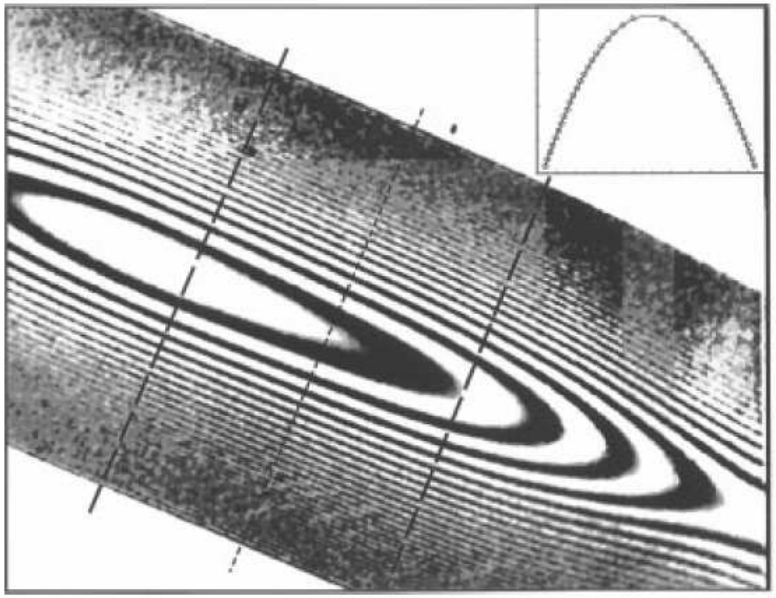
PDMS oils (10 000-100 000 cSt)

Attenuation and reflection of SAW

Simultaneous interferometry for shape



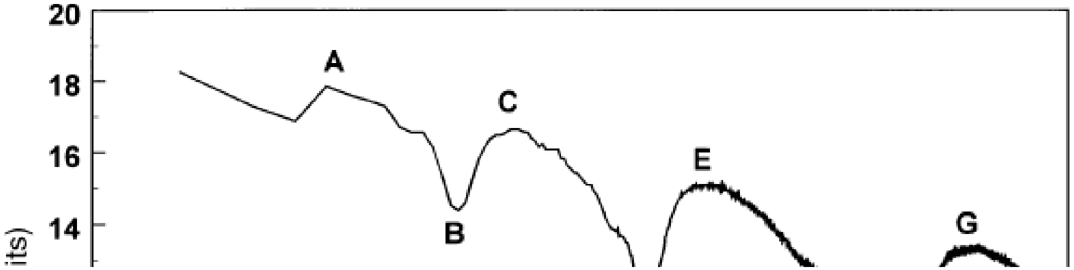




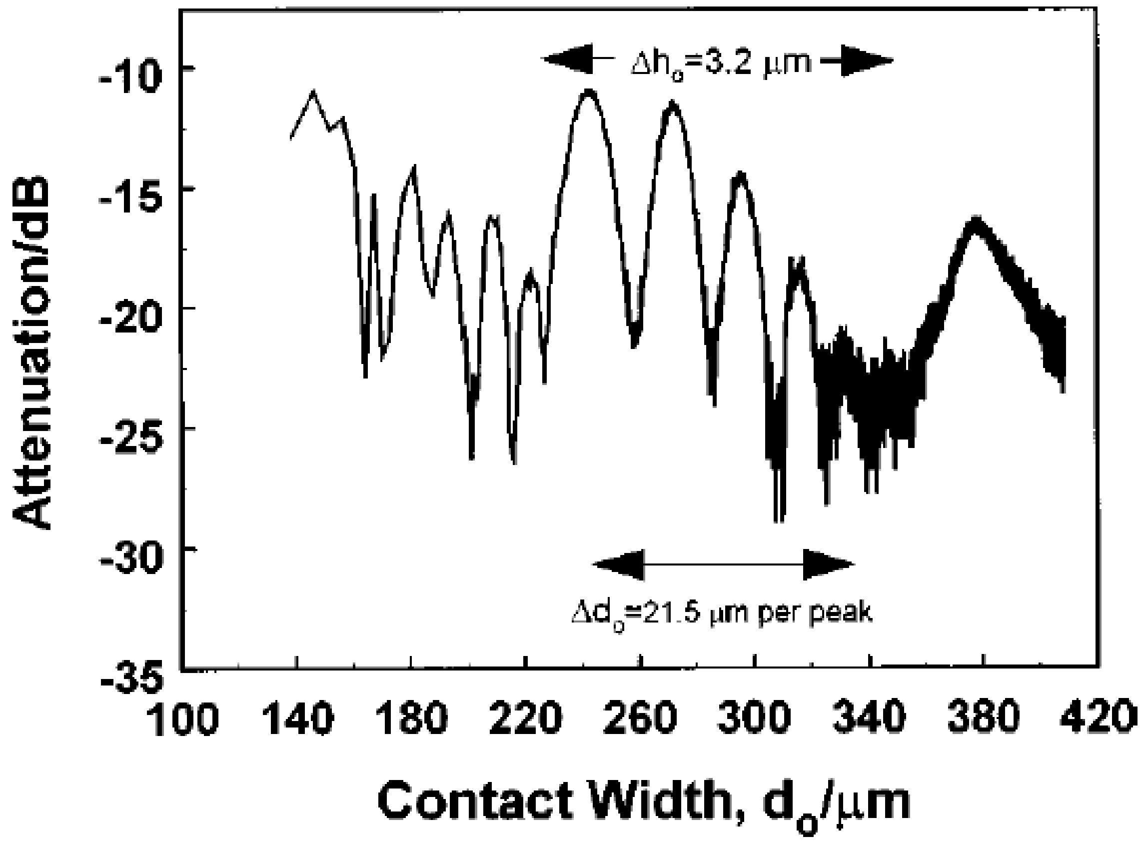
McHale, *et al, Faraday Discuss.*, 1997, **107**, 15-26; Phys. Rev.. B. 1998, ???
McHale, *et al.*, *Appl. Phys. Lett*. 1997, **71**, 3785-3786

Old Work: Attenuation and Reflections

Attenuation Data:



Reflection Data:



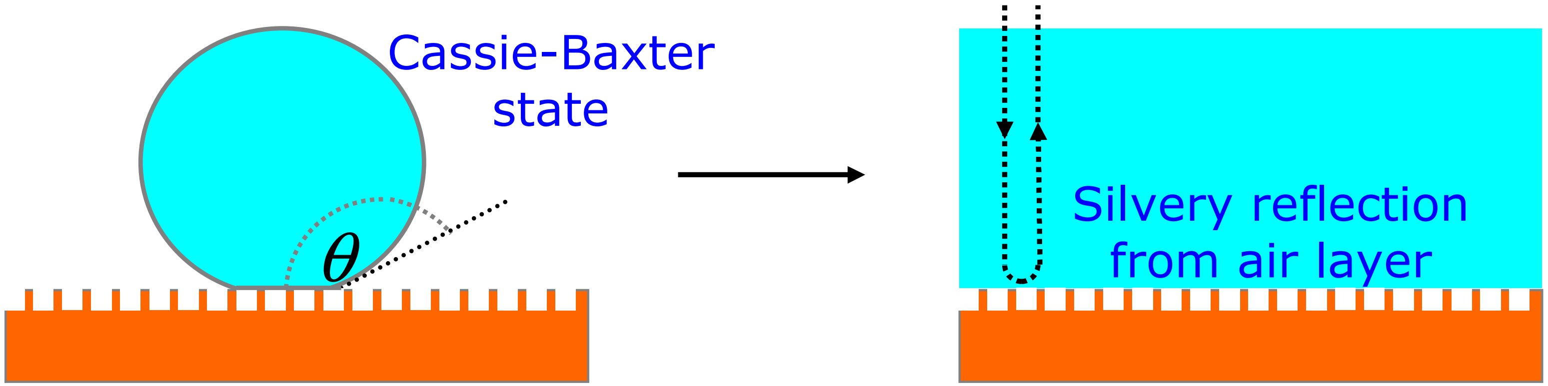
McHale, *et al, Faraday Discuss.*, 1997, **107**, 15-26.
McHale, *et al.*, *Appl. Phys. Lett*. 1997, **71**, 3785-3786

Current Work: Superhydrophobicity

Immersed Superhydrophobic Surfaces

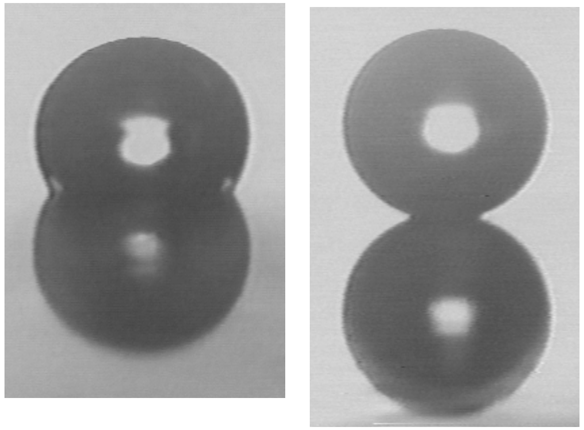
Provided design of features correct, penetration of water can be resisted

A silvery sheen can be seen when immersed – due to surface retained layer of air.



Cassie-Baxter state

Silvery reflection from air layer



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)

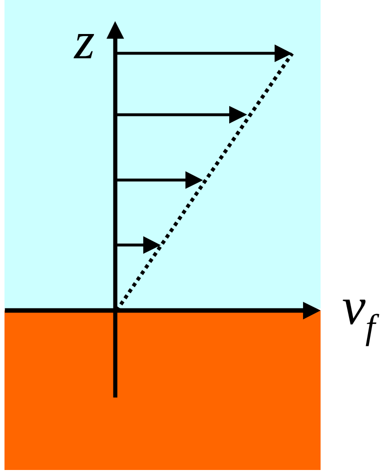
Provides dispersion equation and solution gives resonances

No-Slip Boundary Condition

Solid-Air $\Rightarrow$ $q_s(z=0)=q_l(z=0)$ substrate & layer displacements match at all times

i.e. $v_s(z=0)=v_l(z=0)$ speeds at wall match

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

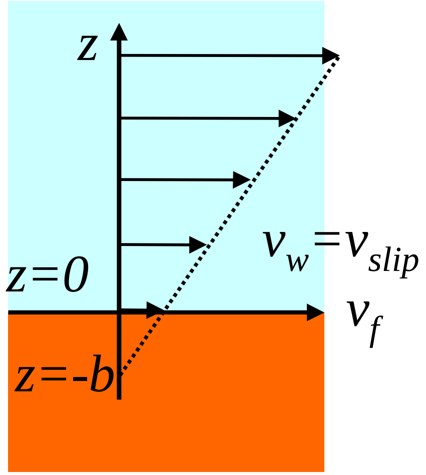


References McHale, G., Meas. Sci. Technol. 14 (2003) 1847-1853. McHale, G., *et al.*, J. Appl. Phys. 93 (2003) 675-690.

The Effect of Wall Slip: Theory

Flow Profile

With slip length, b



Slip length, b, models effective position of interface

Negative b implies effective interface moves to liquid side of boundary

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

McHale, et al., *J. Appl. Phys.*, 2000, **88**, 7304-7312; 2004, **95**, 373-380.
Ellis, J. G., *et al.*, *J. Appl. Phys.*, 2003, **94**, 6201-6207.

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

$$Z_L^{slip} \approx \frac{Z_L^{no\,slip}}{1+\frac{b}{\eta_f} Z_L^{no\,slip}}$$

Newtonian Liquid

Kanazawa & Gordon result for no-slip

modified by "slip" correction using b/δ

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

Slip length to penetration depth ratio

Negative Slip Length

Define a liquid mass as $\Delta m_f = b\rho_f$

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

Kanazawa & Gordon viscosity-density product contribution + trapped "Sauerbrey-like liquid mass" , but this assumes all locations are equal, i.e. complete liquid penetration.

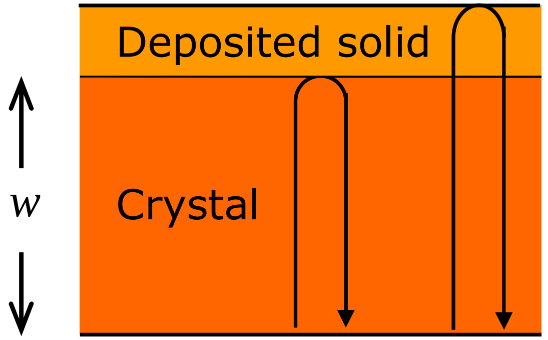
McHale, *et al*, *J. Appl. Phys.*, 2000, **88**, 7304-7312; 2004, **95**, 373-380.

Implicit Assumptions: Acoustic Reflection View

Simple Cavities and Standing Waves

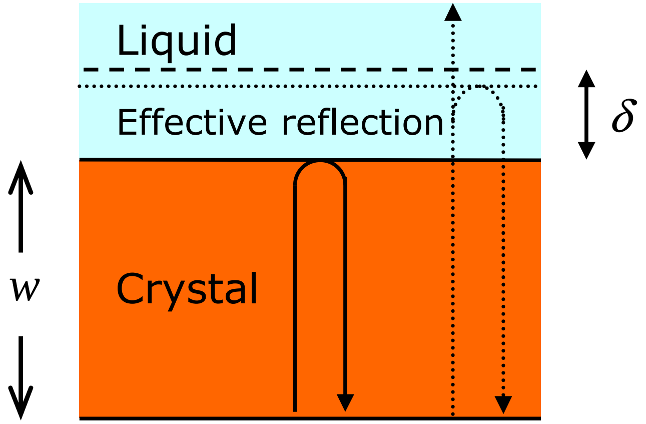
Solid-Air ⇒ Uniform and strong reflection

Solid-Water ⇒ 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

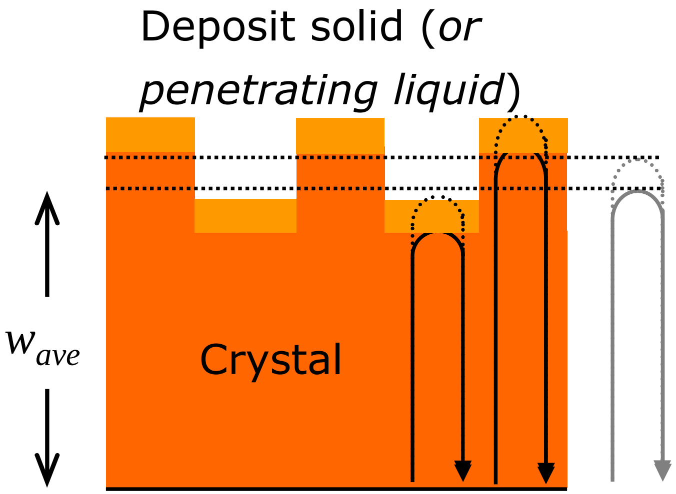
McHale and Newton, *J. Appl. Phys*., 2004, **95**, 373-380.

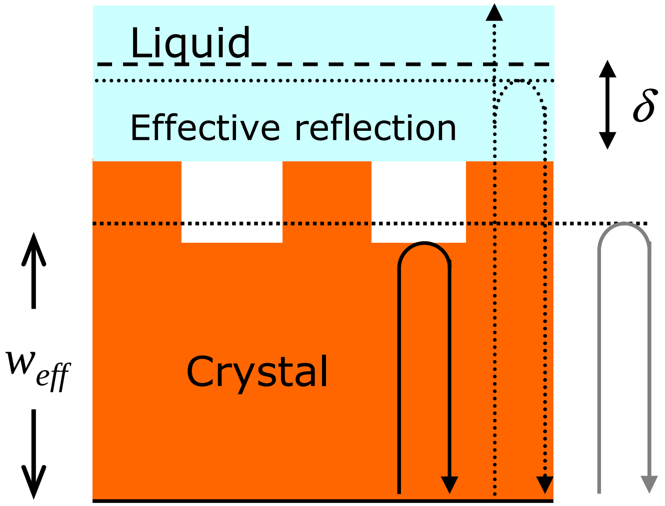
Effect of Topography and Hydrophobicity?

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





Effective cavity length

Peaks and trough increase

cavity lengths equally: $f_{\downarrow}$

Effective cavity length increased? i.e. $f_{\downarrow}$

Or top reflection weakened? If lower

cavity length becomes dominant: $f_{\uparrow}$

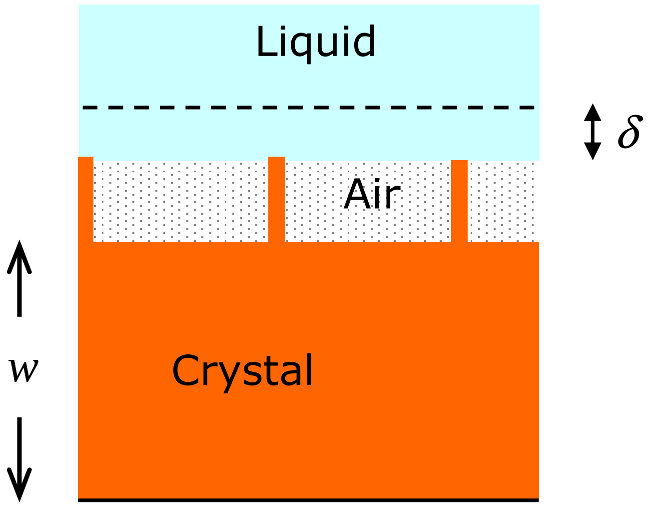
Skating form of superhydrophobicity offers possibility of new liquid phase responses

McHale and Newton, *J. Appl. Phys*., 2004, **95**, 373-380.

Extreme Superhydrophobic Case

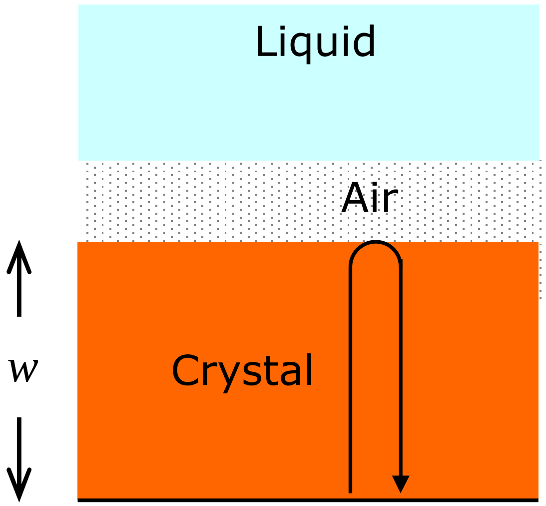
Water immersion ⇒ Water skates across surface features and pressure (or other force) is needed to force capillary penetration

Superhydrophobic



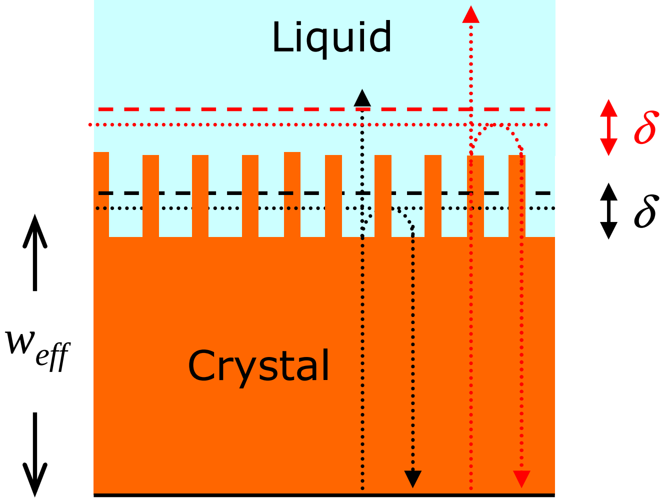
Coupling to liquid is at vanishingly small number of points

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

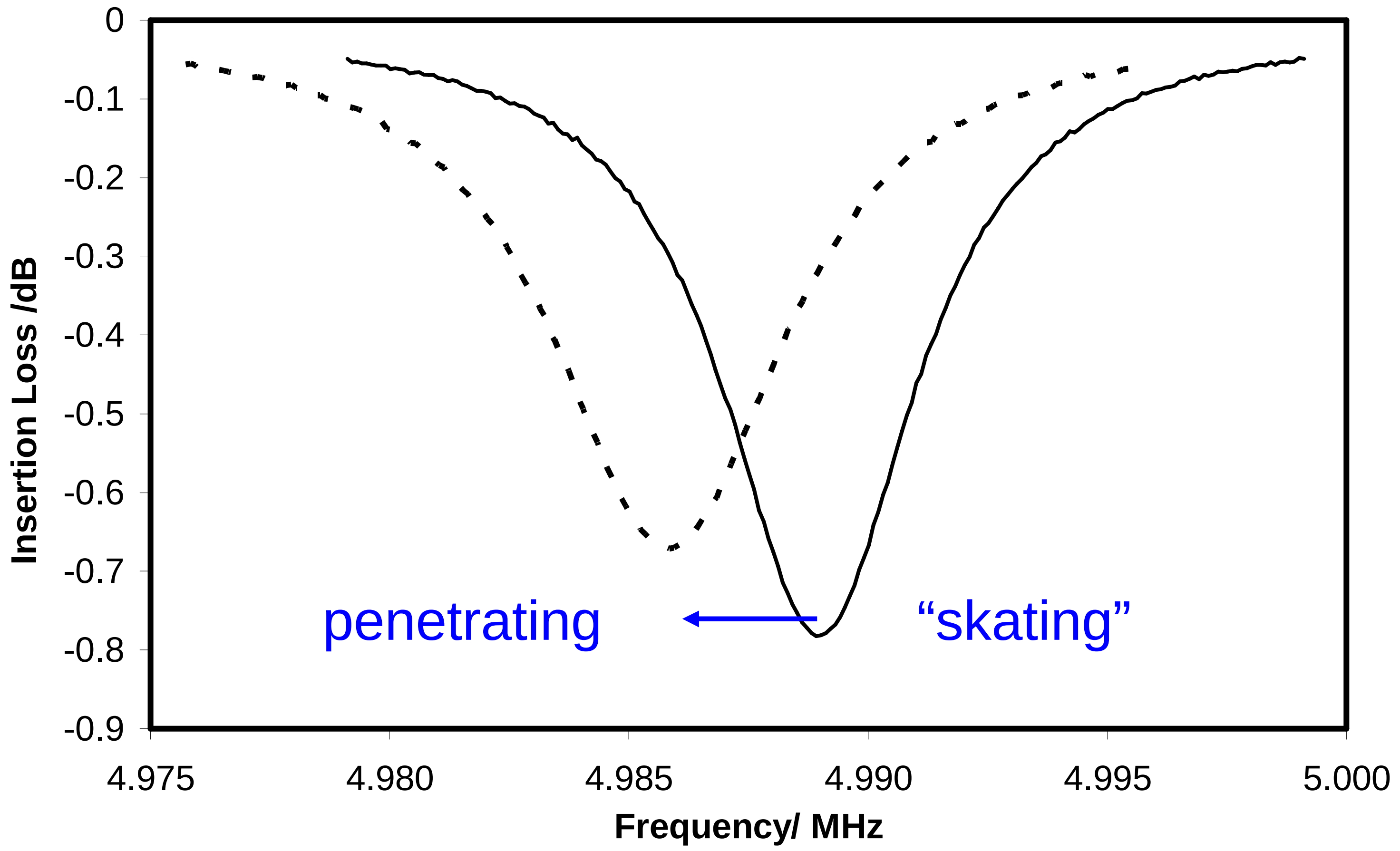


Coupling across troughs. Effective cavity length increases and reflection weakened, i.e. $f_{\downarrow}$ and $B_{\uparrow}$

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

McHale, G.; Newton, M.I., J. Appl. Phys., 2004, **95,** 373-380.

QCM with Microposts: “Skating” Transition

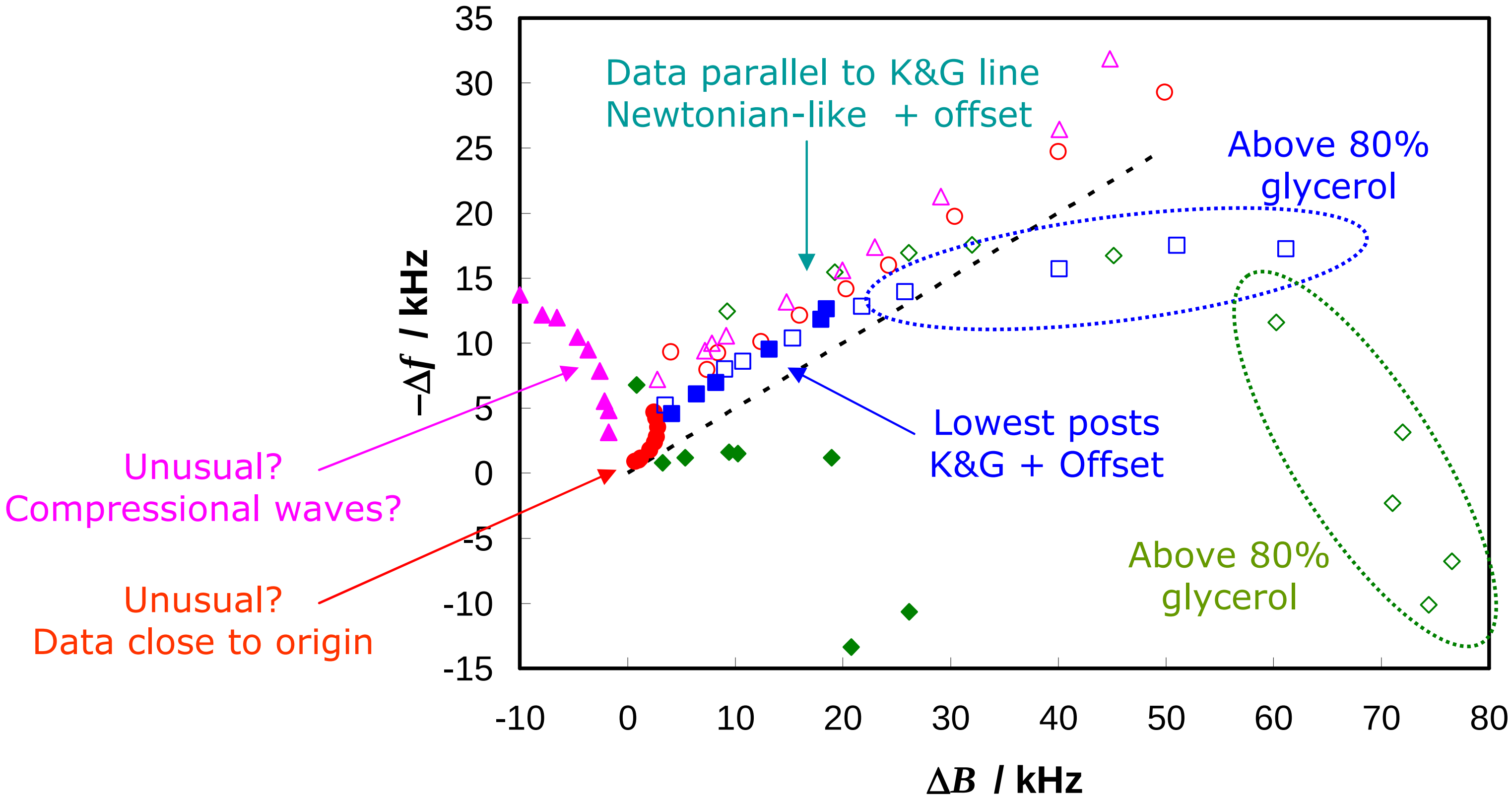


Hydrophobised 18 μm micro-posts. Solid-line is Before pressure applied. Dotted curves is after pressure is applied.

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

Lowest posts
K&G + Offset

Above 80%
glycerol

Unusual?
Compressional waves?

Unusual?
Data close to origin

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

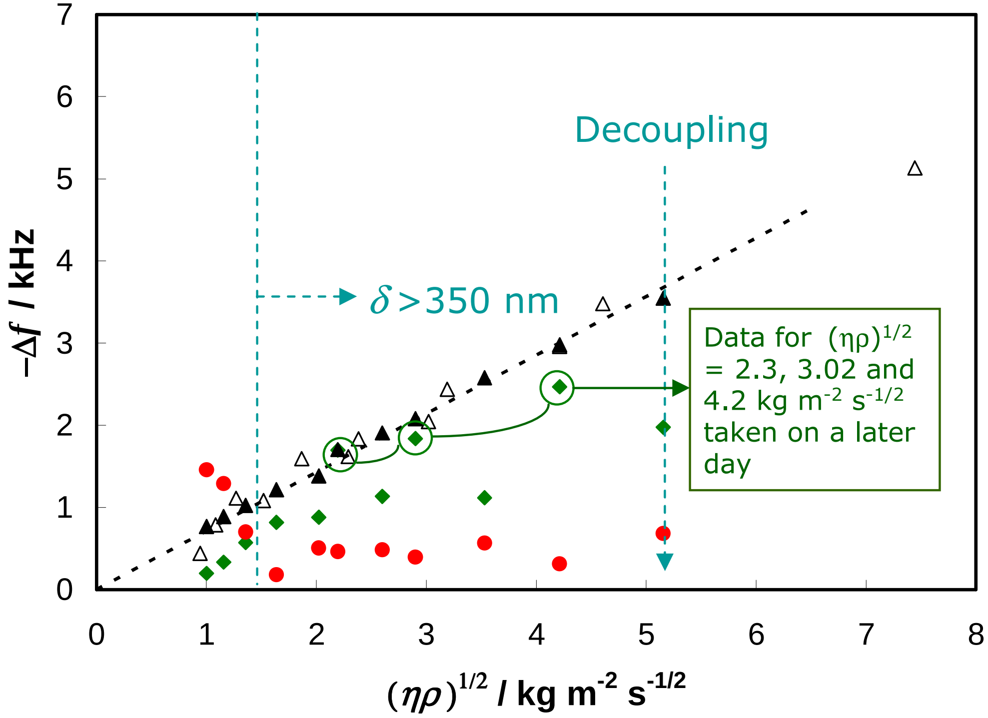
Filled symbols = hydrophobised Kanazawa & Gordon Theory = - - - -

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

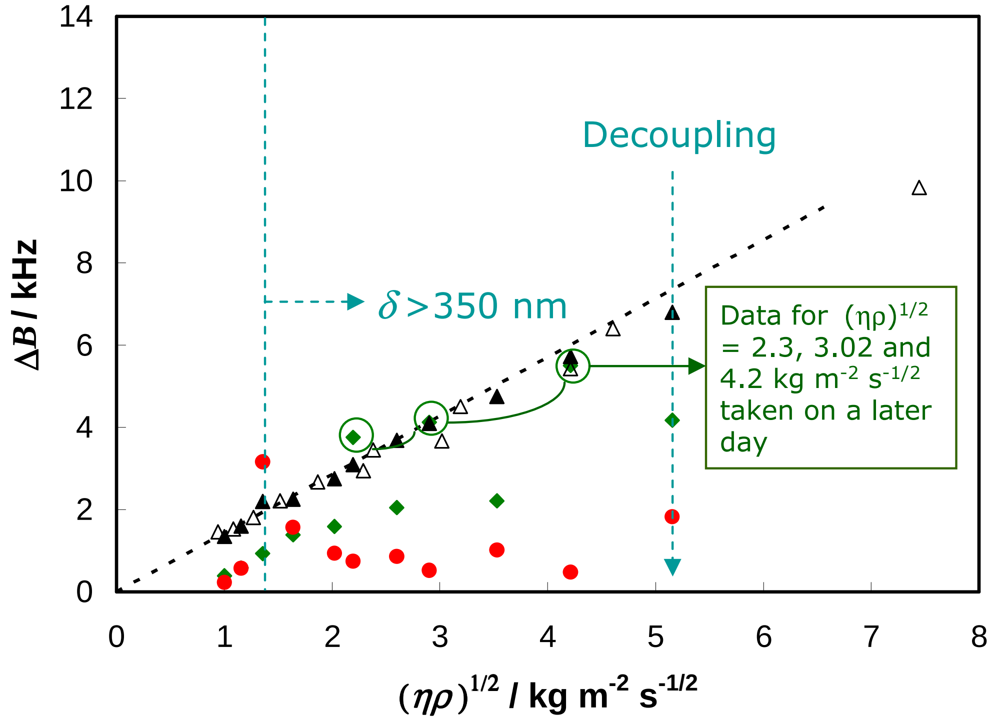
Roach, *et al*., *Langmuir*, 2007, **23**, 9823-9830.
McHale, *et al*., *IEEE-IFC Symp*., 2008, **1-2**, 698-704

SiO_2 Surfaces: Viscosity-Density

Frequency



Bandwidth



Blank at 25 °C = ΔΔΔ

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

Roach, *et al.*, *Langmuir*, 2007, **23**, 9823-9830.
McHale, *et al.*, *IEEE-IFC Symp.*, 2008, **1-2**, 698-704

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