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Sensor response of superhydrophobic quartz crystal resonators

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IEEE FCS, Hawaii 19th-21st May 2008

Overview

1. Superhydrophobic Surfaces
    - Surface tension
    - Topography and wetting
    - Example surfaces
2. Fundamentals of Quartz Crystal Microbalances
    - Gas and liquid phase QCM/QCR responses
    - Hydrodynamics and boundary conditions
    - Acoustic reflections and cavities
3. Superhydrophobic Surfaces on QCMs
    - Theoretical concepts
    - Types of surfaces
    - QCM responses

Superhydrophobic Surfaces

The Natural World

Surface Tension

Surface Tension v Gravity

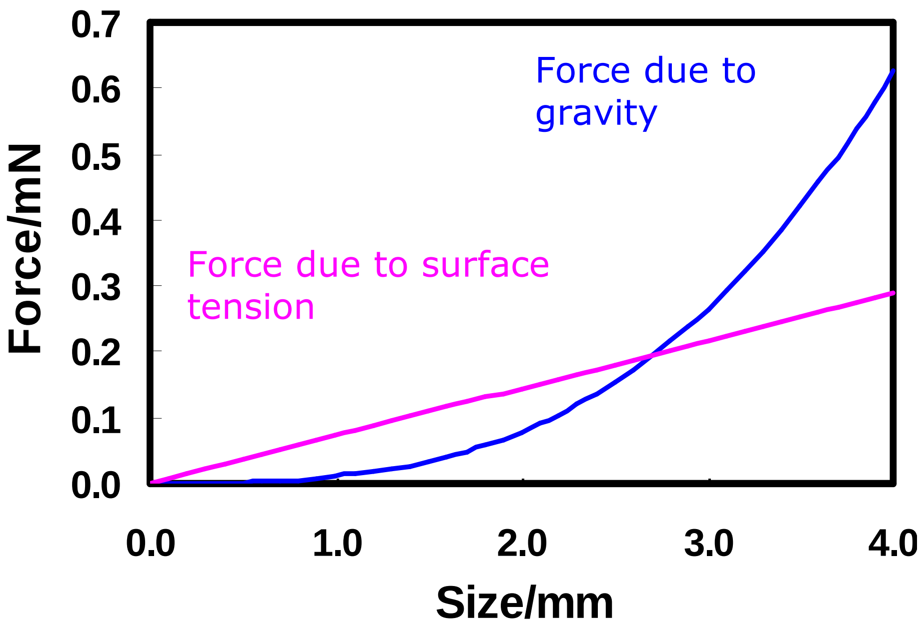
Surface tension forces scale with length, e.g. Force~$R\gamma_{LV}$

Gravity forces scale with length cubed, e.g. Force~$R^3\rho g$

Small sizes $\Rightarrow$ surface tension wins

Small means << capillary length= κ^{-1}=($\gamma_{LV}/\rho g)^{1/2}$ ~ 2.73mm for water

Winners v Losers



Acknowledgement Video: "Microcosmos"

The Sacred Lotus Leaf

Plants

Many leaves are super-water repellent

(i.e. droplets completely ball up and roll off a surface)

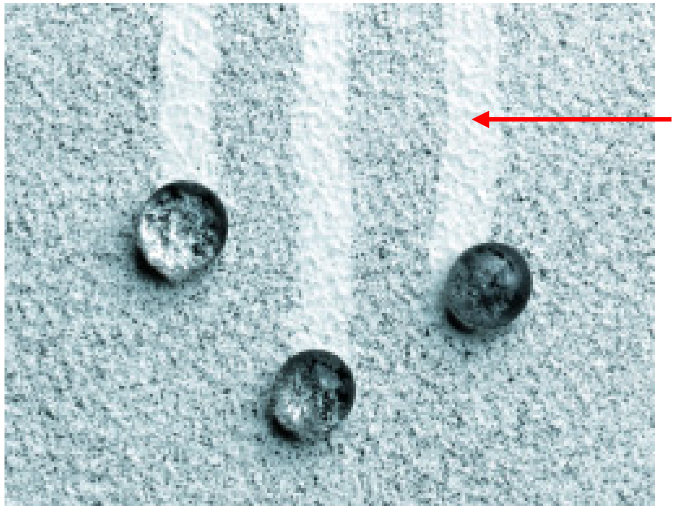
The Lotus plant is known for its purity

Superhydrophobic leaves are self-cleaning

(*under the action of rain*)

SEM of a Lotus Leaf

Self-Cleaning



Dust cleaned away

Acknowledgement Neinhuis and Barthlott

References Neinhuis,C.; Barthlott, W. Ann. Bot., 79 (1997) 667-677; Planta 202 (1997) 1-8.
Onda, T. *et al.*, Langmuir 12 (1996) 2125-2127.

Plants and Leaves

Honeysuckle, Fat Hen, Tulip, Daffodil, Sew thistle (Milkweed), Aquilegia
Nasturtium, Lady’s Mantle, Cabbage/Sprout/Broccoli

Superhydrophobic Surfaces

Man-made Surfaces

Water Repellency (Hydrophobicity)

Surface Chemistry

Terminal group determines whether surface is water hating

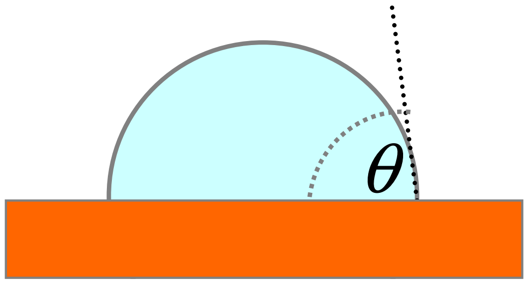
Hydrophobic terminal groups are Fluorine (F) and Methyl (CH_3)

Contact Angles

Characterize hydrophobicity

Water-on-Teflon gives ~ 115°

The best that *chemistry* can do



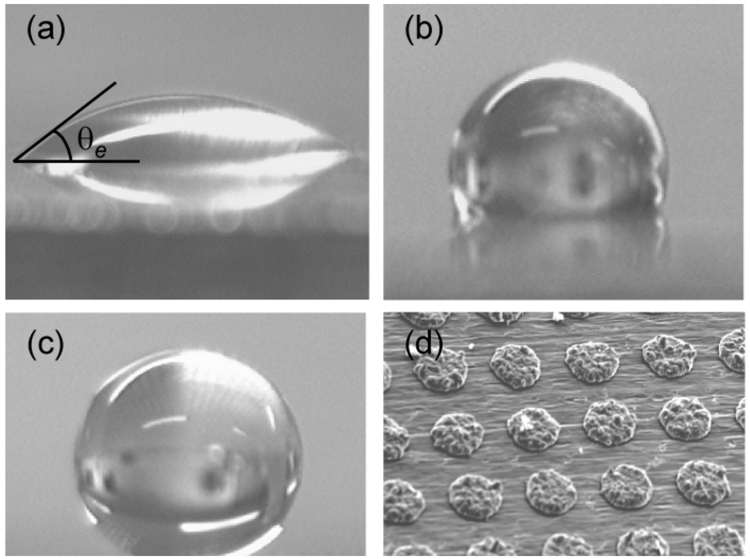
Physical Enhancement

(a) is water-on-copper

(b) is water-on-fluorine coated Cu

(c) is a super-hydrophobic surface

(d) "chocolate-chip-cookie" surface



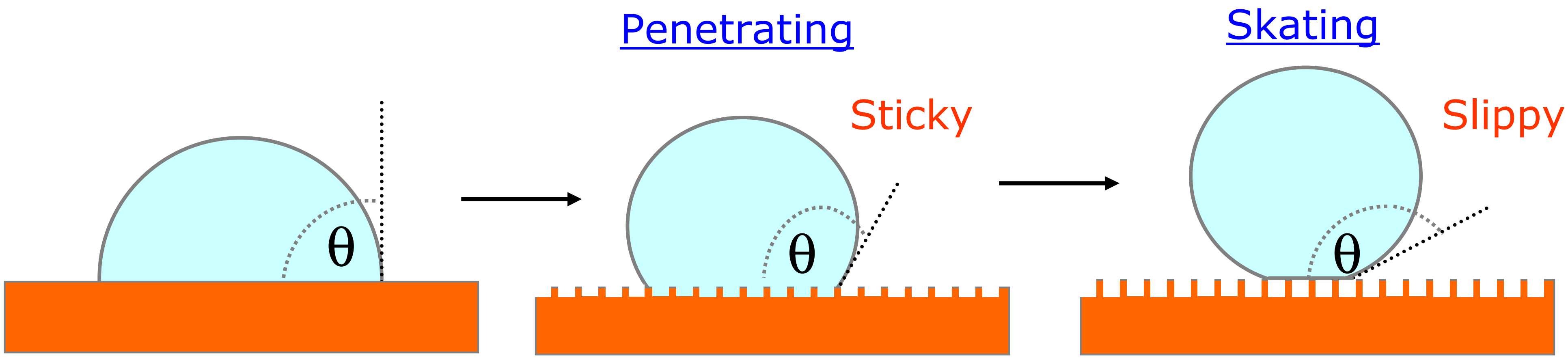
Superhydrophobicity is when θ>150°
and contact angle hysteresis is low

Reference McHale, G. *et al.*, Analyst 129 (2004) 284-287.

Topography & Wetting

Droplets that Skate

What contact angle does a droplet adopt on a “rough” surface?



Young’s Law

$$\cos\theta_e = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$$

Wenzel Equation

$$\cos\theta_{CB} = r\cos\theta_e$$

Cassie-Baxter Equation

$$\cos\theta_{CB} = f_s\cos\theta_e - (1-f_s)$$

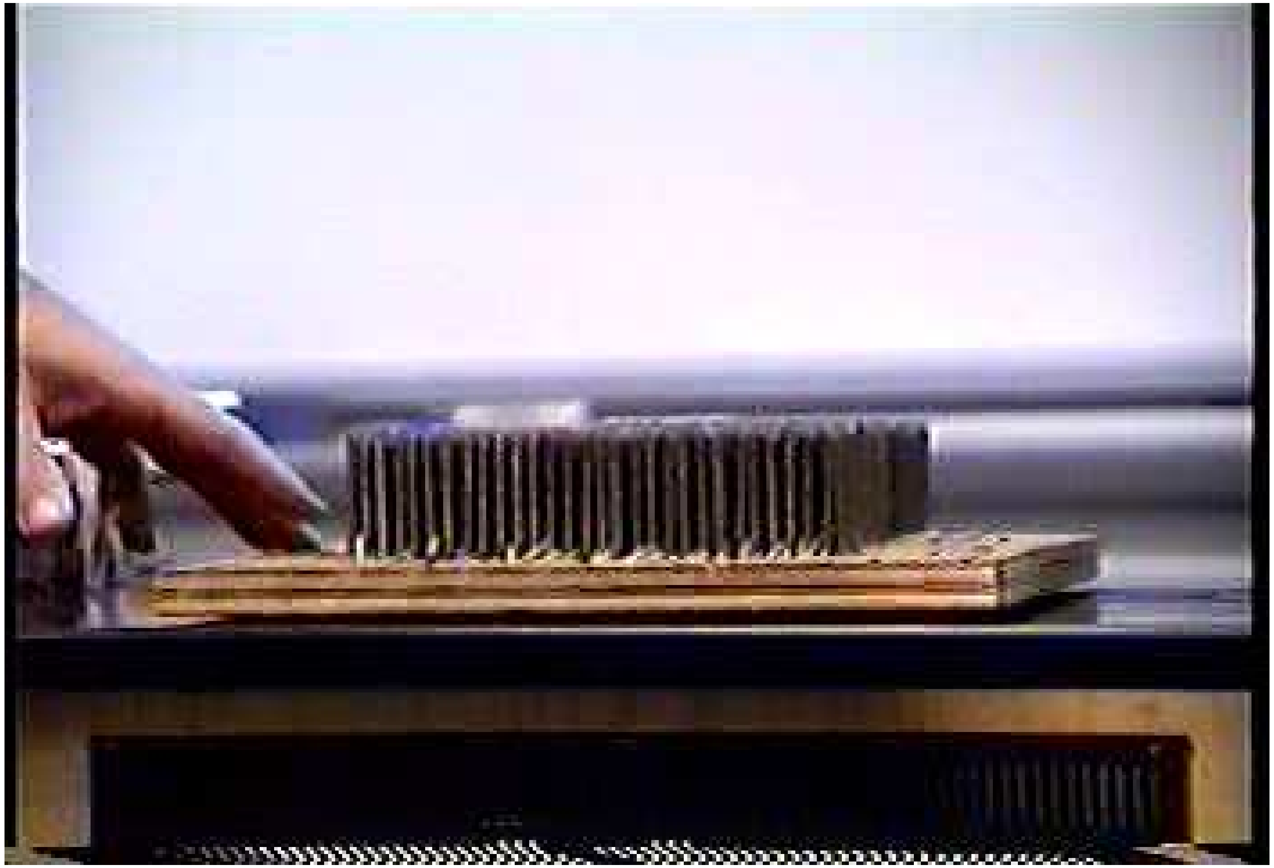
Roughness — r = true area/planar projection

Chemistry — Young’s Law θ_e

Topography — f_s = solid surface fraction

References Cassie, A. B. D.; Baxter, S. Trans. Faraday Soc. 40 (1944) 546-551. Wenzel, R. N. Ind. Eng. Chem. 28 (1936) 988-994; J. Phys. Colloid Chem. 53 (1949) 1466-1467. McHale, G., Langmuir 23 (2007) 8200-8205

Fakir's Carpet - "Bed of Nails" Effect



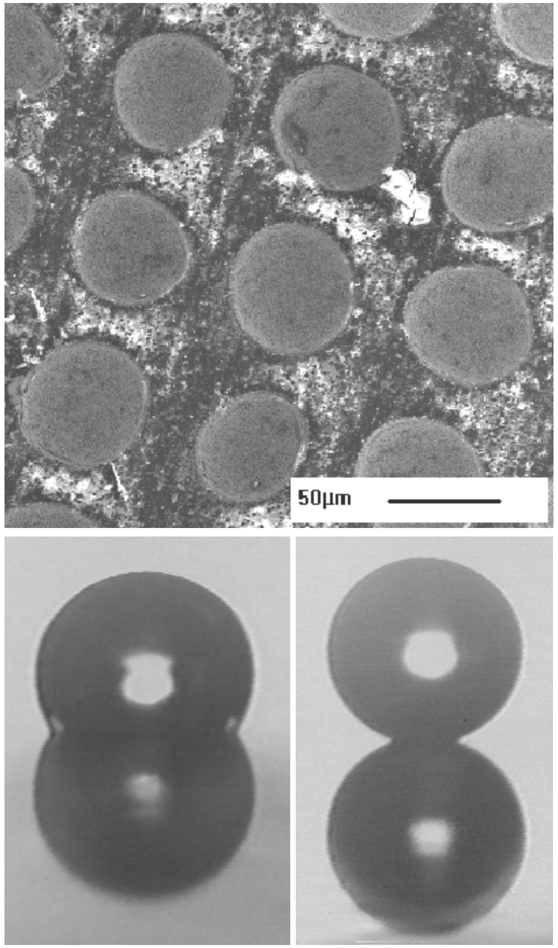
Balloon on a Bed of Nails

But …. liquid skin interacts with solid surfaces and "nails" do not need to be equally separated. A useful analogy, but it is not an exact view.

Acknowledgement Wake Forest University

Superhydrophobicity - Man-Made Examples

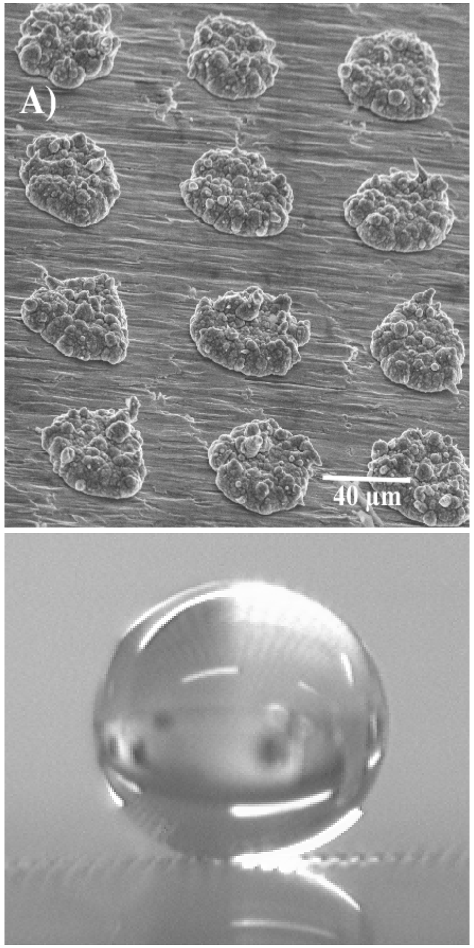
Etched Metal



Flat & hydrophobic

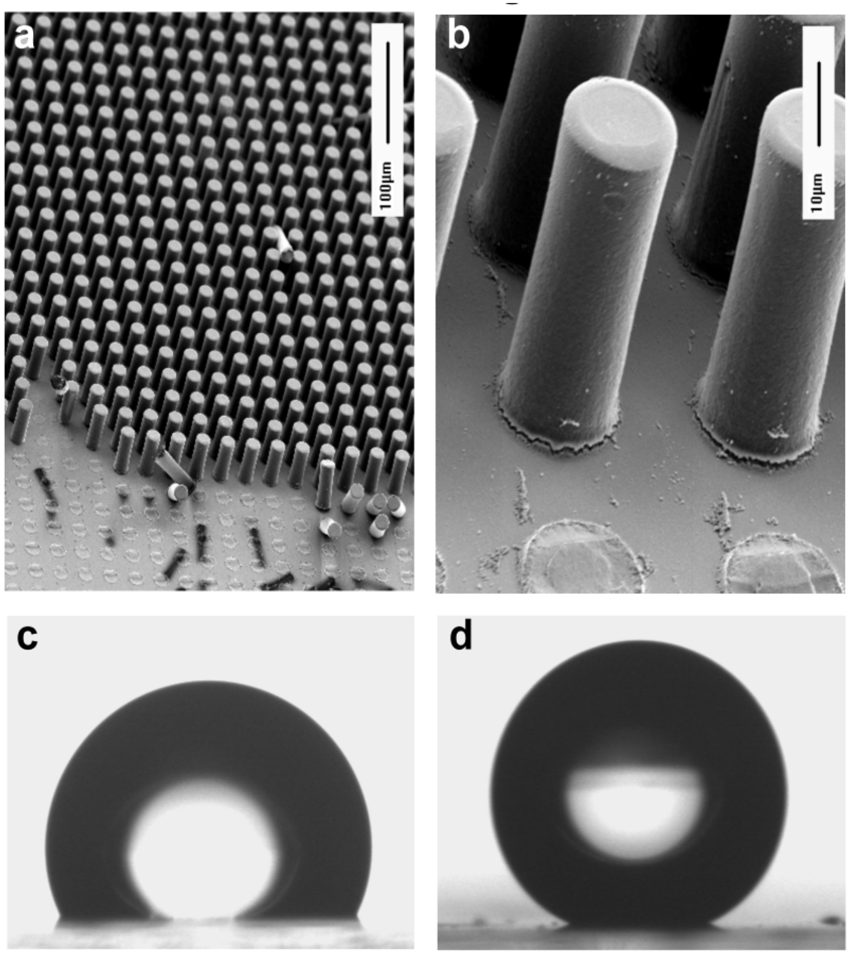
Patterned & hydrophobic

Deposited Metal



Patterned & hydrophobic

Polymer Microposts

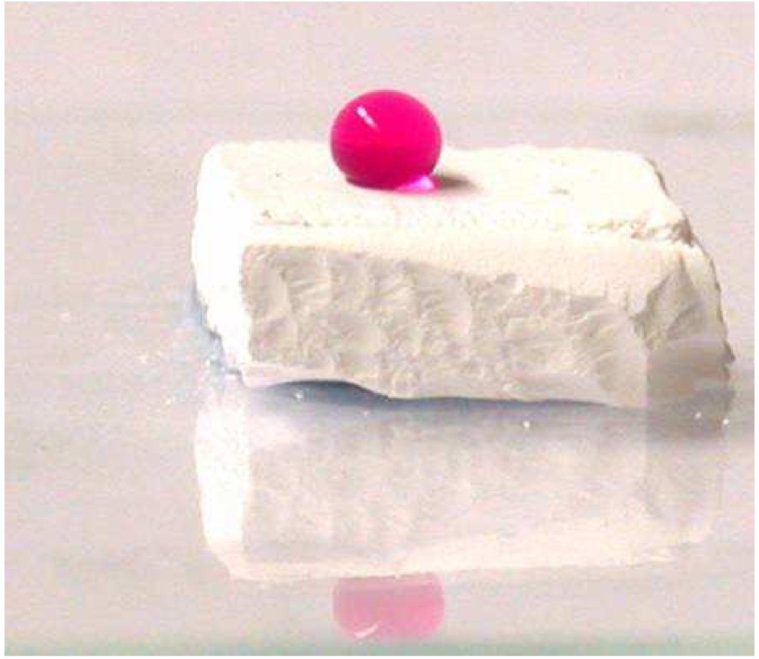


Flat & hydrophobic

Patterned & hydrophobic

References Shirtcliffe, N.J. *et al.*, Langmuir 21 (2005) 937-943; Adv. Maters. 16 (2004) 1929-1932; J. Micromech. Microeng. 14 (2004) 1384-1389. Roach, P., *et al.*, Soft Matter 4 (2008) 224-280.

Sol-Gel: Switching off Superhydrophobicity



Foam heated (and cooled) prior to droplet deposition

Mechanisms for Switching

- Temperature history of substrate
- Surface tension changes in liquid (alcohol content, surfactant, …)
- Electrowetting

Switch could trigger a large change in QCM signal ⇒ Sensor based on hydrophobicity

Reference Shirtcliffe, N.J. *et al.*, Chem. Comm. (25) (2005) 3135-3137 (Nature News "*Quick change for super sponge*" On-line 20/7/05). Shirtcliffe, N.J., *et al.*, Maters. Chem. & Phys. 103 (2007) 112–117.

Fundamentals of QCMs

Sensing Principles

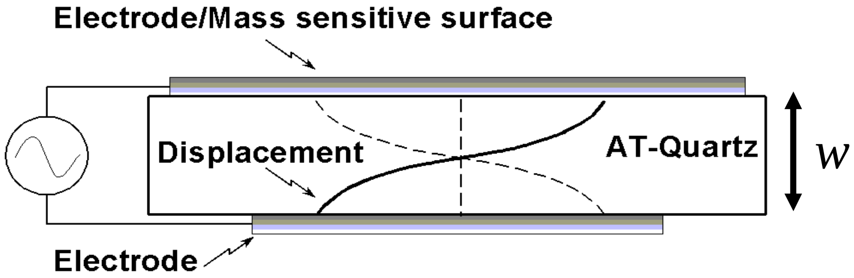
QCM/QCR Sensing Principles

Thickness Shear Mode Vibration

QCM has a sharp resonance

Frequency given by quartz thickness, w

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



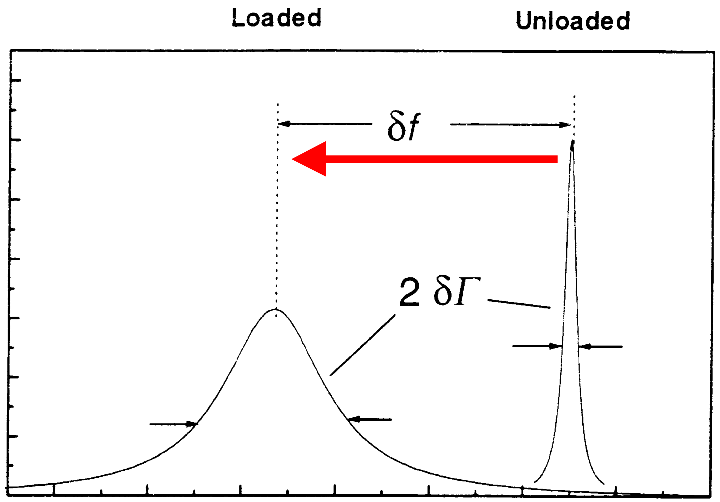
Mass Loading or Immersion

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

References 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

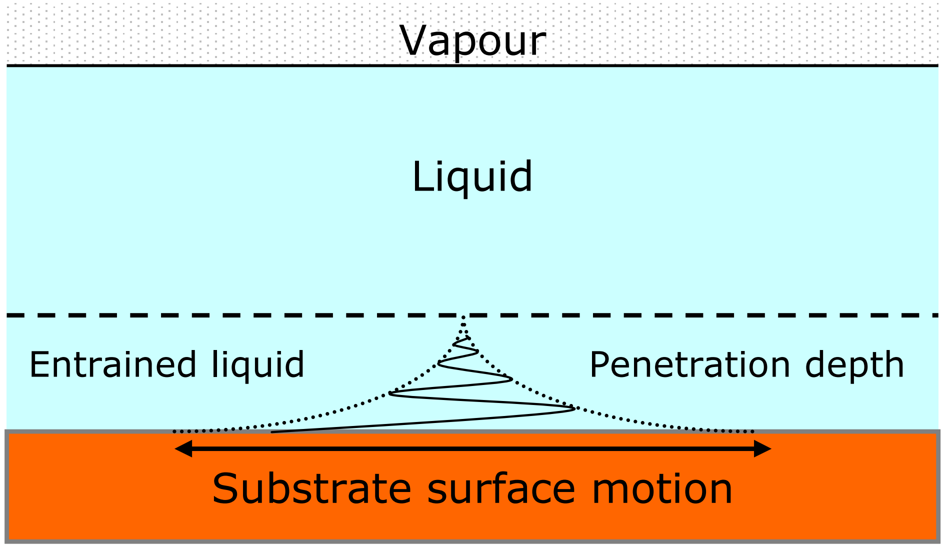
Shear Mode Vibration

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*

Hydrodynamic View

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)

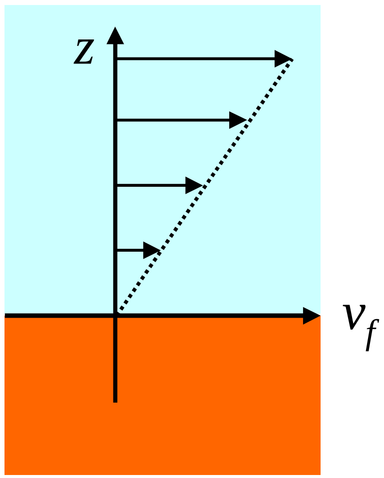
Provides dispersion equation and solution gives resonances

No-Slip Boundary Condition

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

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

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



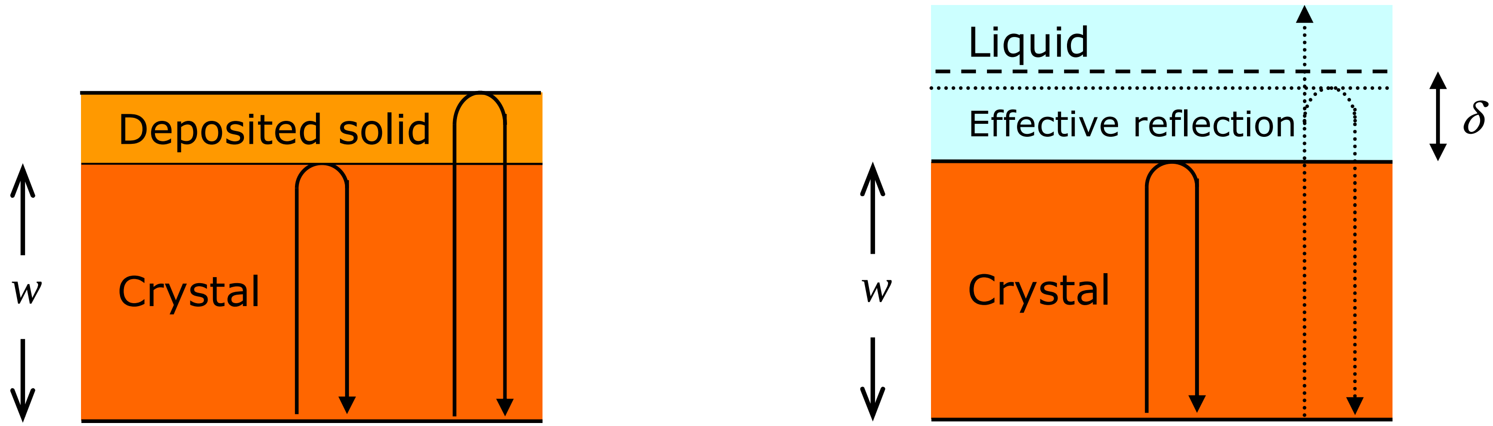
References McHale, G., Meas. Sci. Technol. 14 (2003) 1847-1853. McHale, G., *et al.*, J. Appl. Phys. 93 (2003) 675-690.

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: $B_{\uparrow}$

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

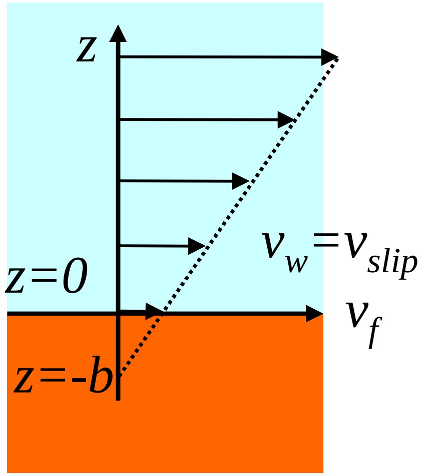
Superhydrophobic QCMs

Theoretical Concepts

Mathematical Formulation of Wall Slip

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

References McHale, G., Lücklum, R., J. Appl. Phys. 88 (2000) 7304-7312. McHale, G.; Newton, M.I., J. Appl. Phys. 95 (2004) 373-380. Ellis, J. G., *et al*., J. Appl. Phys. 94 (2003) 6201-6207.

Effective Sauerbrey "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 $\Delta m_f = b\rho_f$

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

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

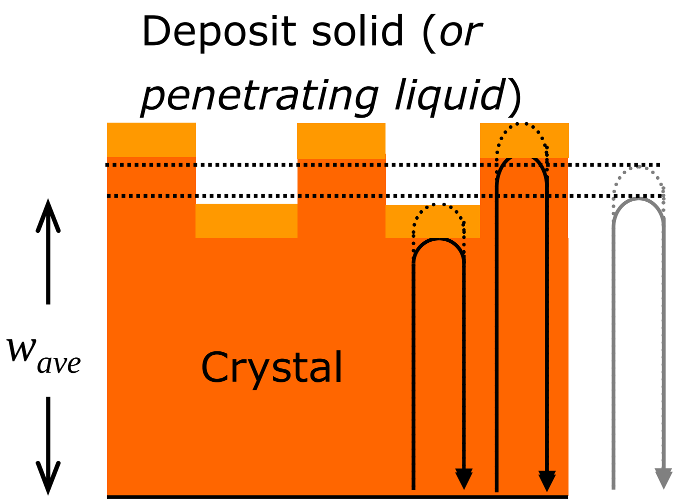
References G. McHale, R. Lücklum, M.I. Newton, *et al.*, J. Appl. Phys. 88 (2000) 7304-7312. McHale, G.; Newton, M.I., J. Appl. Phys. 95 (2004) 373-380.

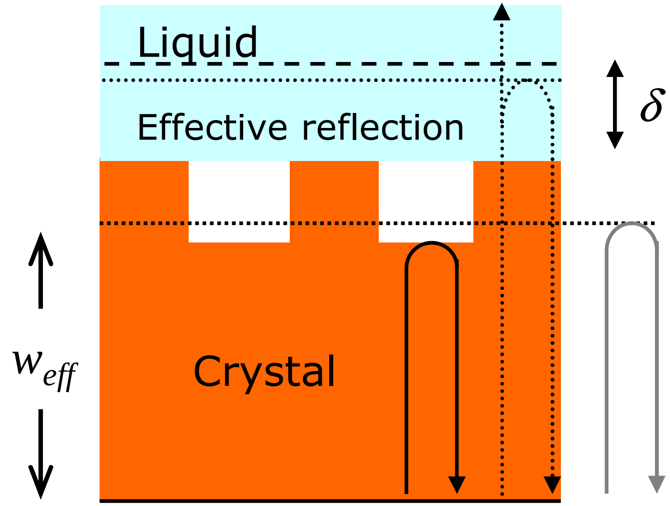
Acoustic Reflection View

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 so,

effective cavity length decreased: $f_{\uparrow}$

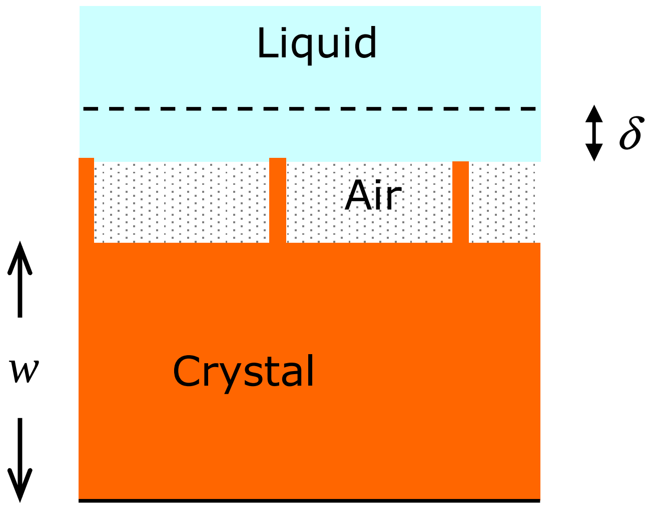
Skating form of superhydrophobicity offers possibility of new liquid phase responses

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

Extreme Superhydrophobic Case

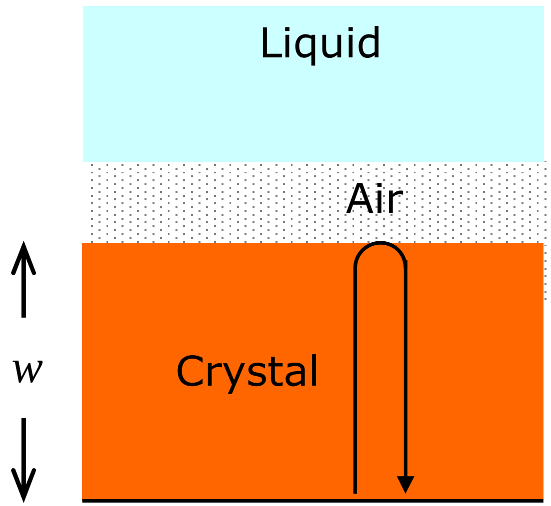
Water immersion $\Rightarrow$ Water skates across surface features and pressure (or other force) is needed to force capillary penetration

Superhydrophobic



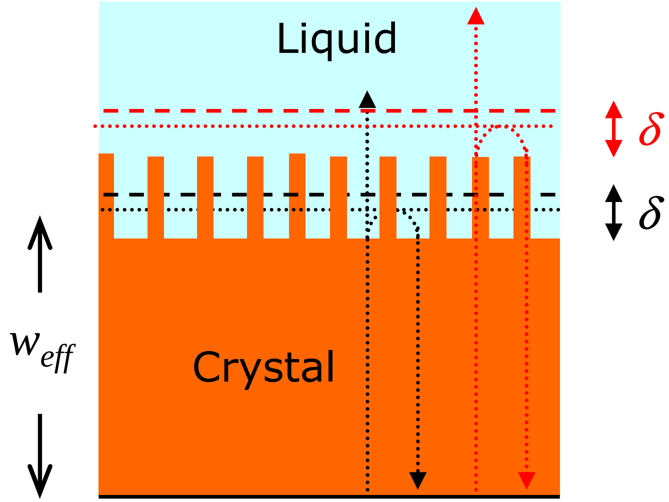
Coupling to liquid is at vanishingly small number of points

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

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

Experiments with QCMs

Superhydrophobic Surfaces

References Roach, P.; McHale, G.; *et al*., Langmuir 23 (2007) 9823-9830. Evans, C.R.; McHale, G., *et al*., Sens. Act. A 123-24 (2005) 73-76.

Superhydrophobic Surfaces on QCM's

Previous Literature Data on QCMs

1. Polyethylene glycol-water on a hydrophobic SU-8 micro-post QCM[1], Polystyrene with embedded PTFE based superhydrophobic surface[2], 0.6 μm silica nanoparticle layer superhydrophobic multiresonance device[3]
2. Water-glycerol on hydrophobic model system of SU-8 micro-posts (5μm diameter, 10μm centre-centre, 5-18μm tall) QCM's[4]

Experimental Data in this Talk

1. Review SU-8 micro-post data (5 μm, 138°; 10 μm, 143°; 15 μm, 151°; 18 μm, 155°)
2. New data using water-glycerol mixtures (0-80%), contact angles, BVD impedance fitting, bare (non-hydrophobised) & hydrophobised (Granger's)
3. Surfaces based on nano-particles

Titanium dioxide sol-gel (porous 1 μm) + Granger's

Before QCM experiment: 154°

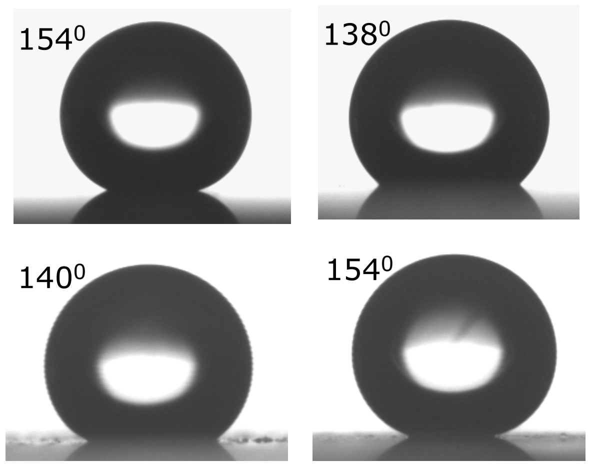
After QCM experiment: 138° (immobile)

Organo-silane treated silicon dioxide particles dusted onto 1.7 μm S1813 photoresist

Two samples of different particle sizes:

a1=5 nm. After experiment: 140° (immobile)

b1=3 nm. After experiment: >154° (mobile)



References [1]Evans, C., *et al*., Sens. Act. A 123-24 (2005) 73-76; [2]Fujita, M., *et al*., Jap. J. Appl. Phys., 44 (2005) 6726-6730; [3]Kwoun, S.J., *et al*., IEEE Trans. Ultrason. Ferroel. Freq. Ctrl 53 (2006) 1400-1403. [4]Roach, P., *et al*. Langmuir 23 (2007) 9823-9830.

Experiments with QCMs

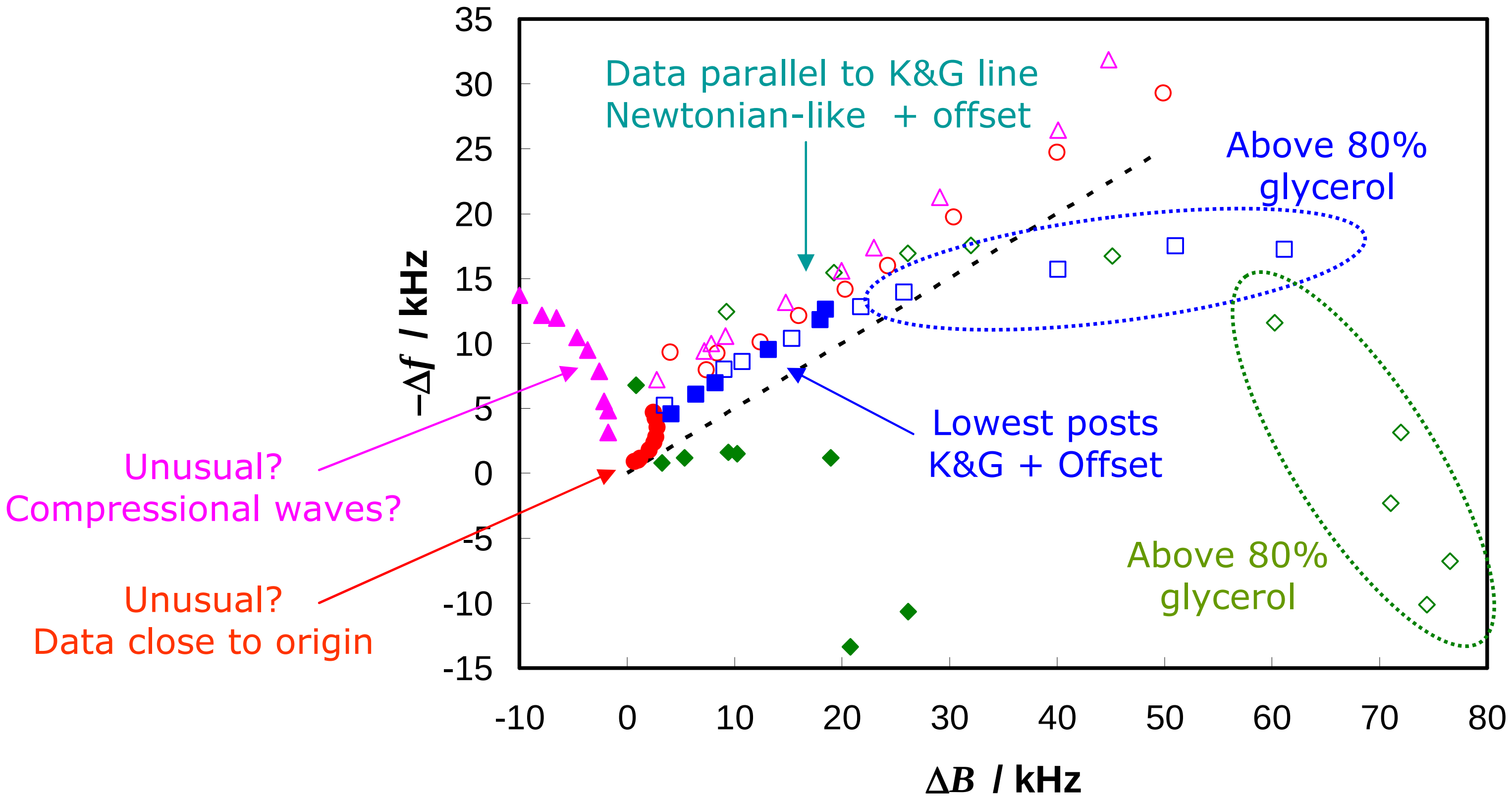
Superhydrophobic Micro-post Data

 References Roach, P.; McHale, G.; *et al*., Langmuir 23 (2007) 9823-9830.

NTU

Micro-Post Surfaces – Newtonian or Not?

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



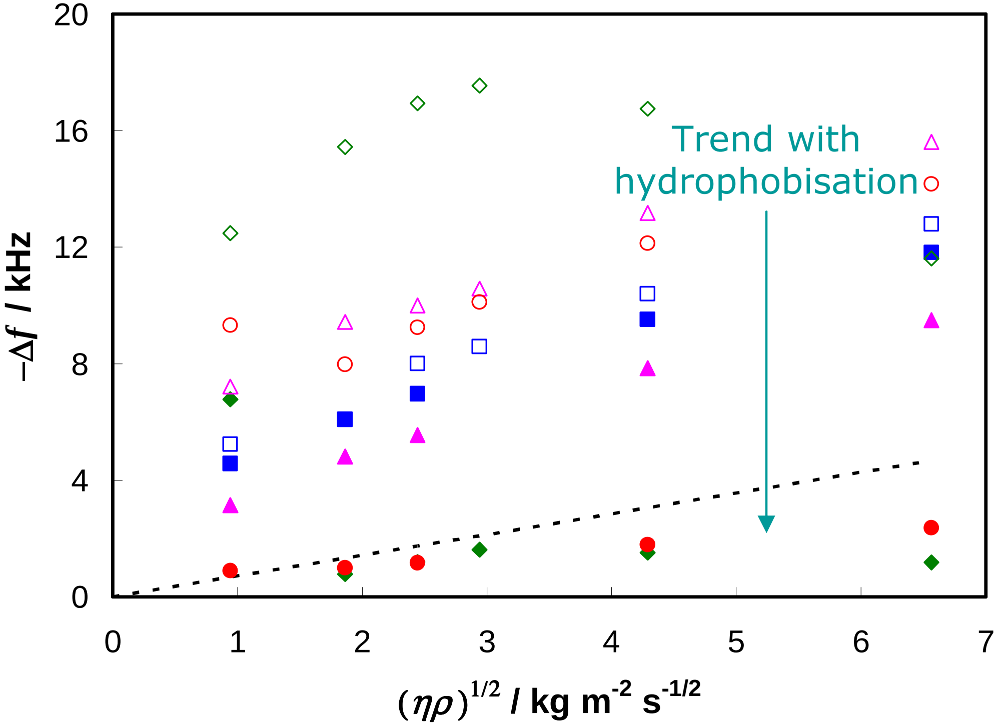
5μm =□□□ 10μm = ◇◇◇ 15μm = ΔΔΔ 18μm = ○○○

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

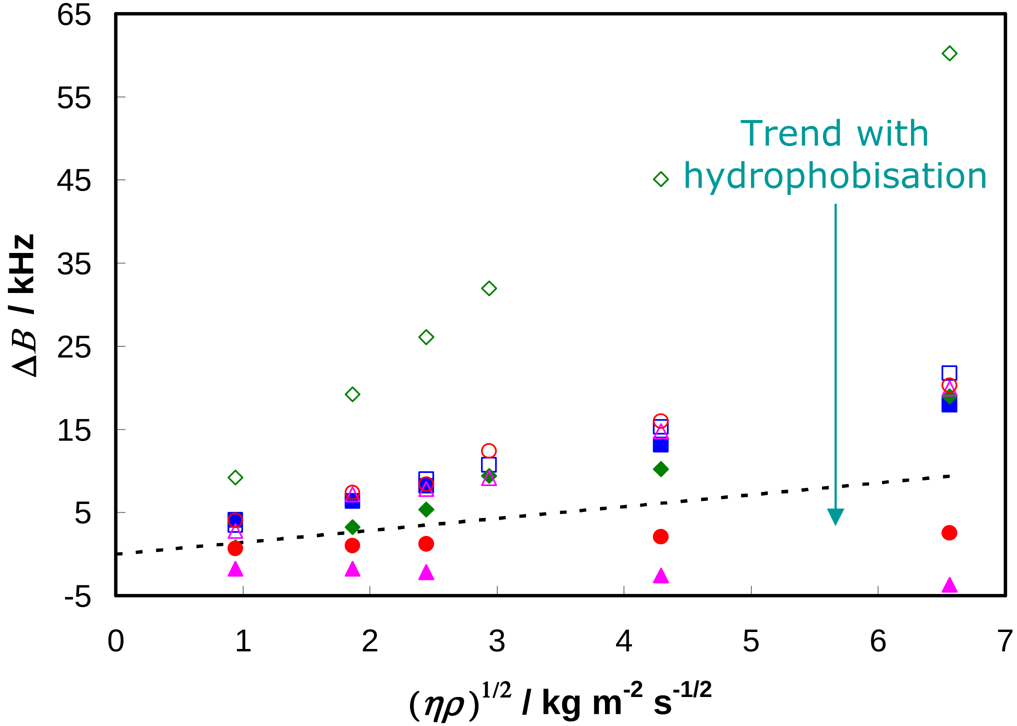
Hydrophobisation of posts changes type of response – all data generally closer to origin

Micro-Post Surfaces: Viscosity-Density

Frequency



Bandwidth



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

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

Tallest (18 µm) hydrophobic posts have coupling to liquid reduced below K&G levels

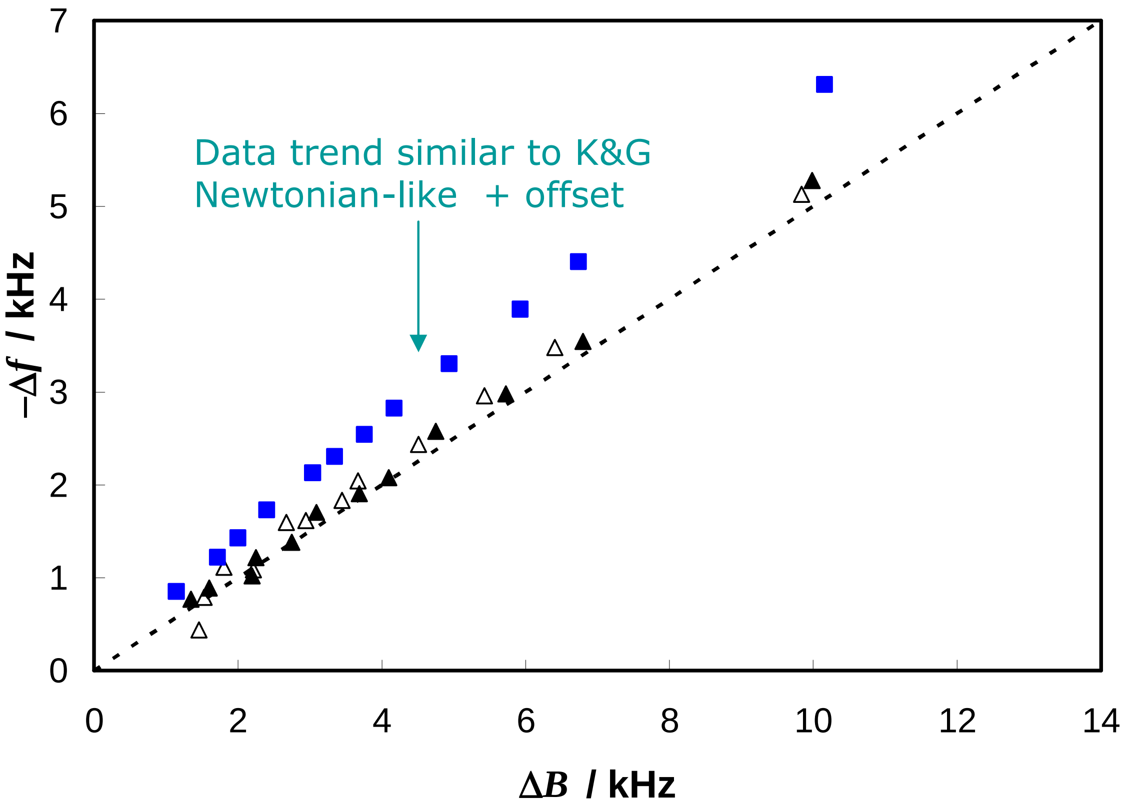
15 µm tall posts have unusual dB response (compressional wave generation?)

Experiments with QCMs

Hydrophobic Titanium Dioxide Data

Hydrophobic TiO_2 Surfaces – Newtonian or Not?

Water-glycerol solutions: 0-80%



Blank at 25 °C = ΔΔΔ

Hydrophobic crystal at 20 °C = ▲ ▲ ▲

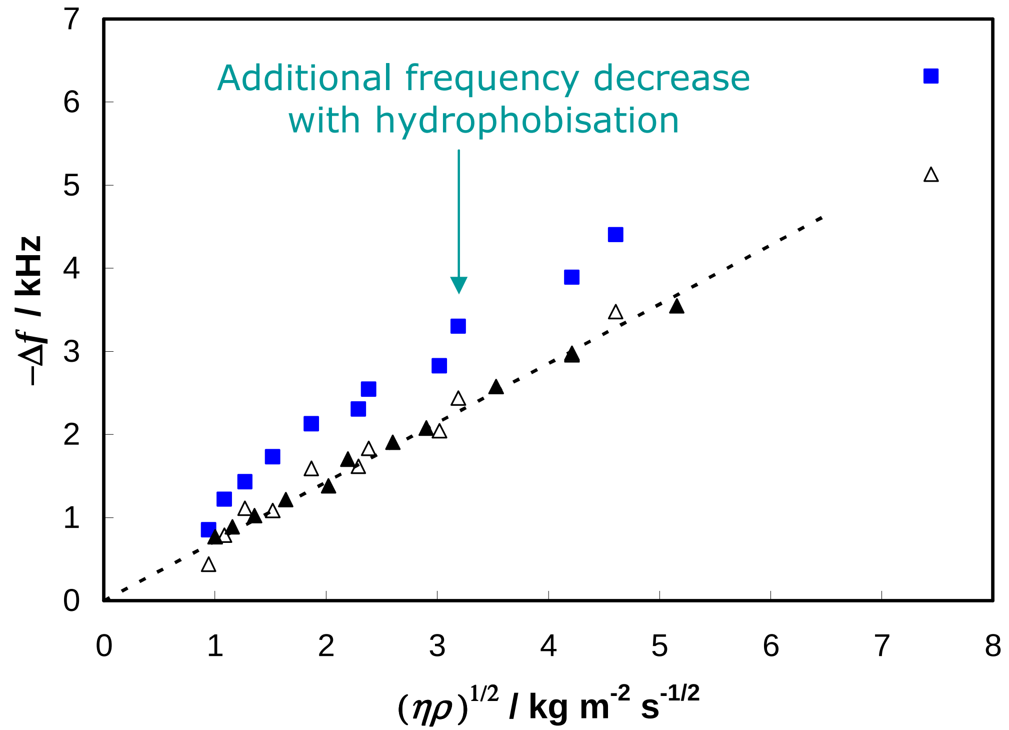
Hydrophobic TiO_2 = ■■■ at 25 °C

Kanazawa & Gordon Theory = - - - -

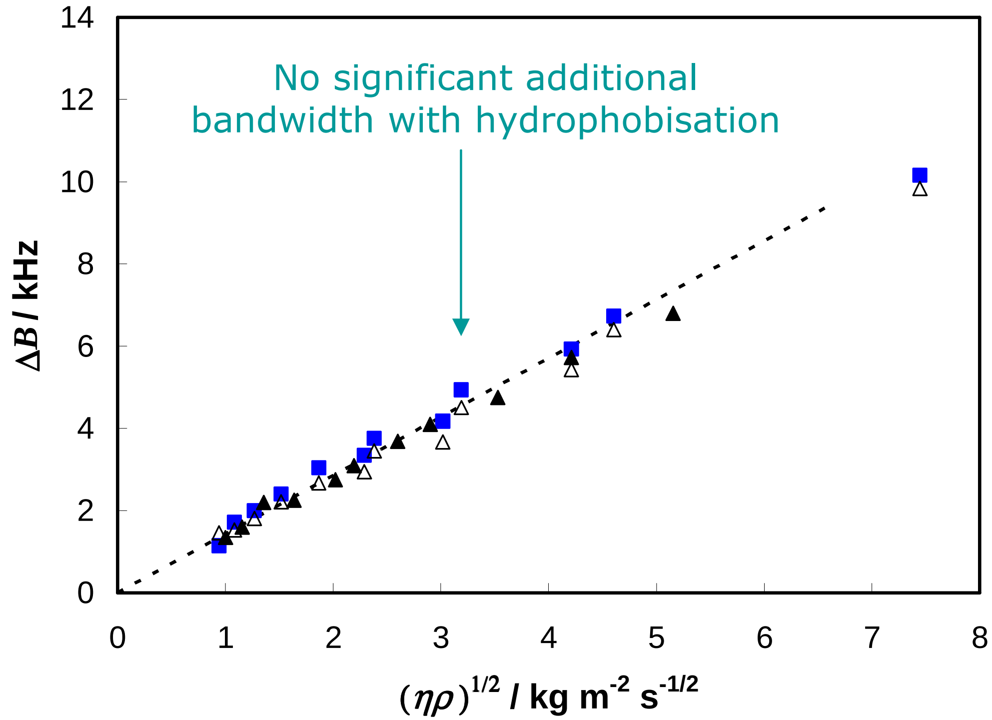
Newtonian-like + offset type of response

TiO_2 Surfaces: Viscosity-Density

Frequency



Bandwidth



Blank at 25 °C = ΔΔΔ

Hydrophobic crystal at 20 °C = ▲▲▲

Hydrophobic TiO_2 = ■■■ at 25 °C

Kanazawa & Gordon Theory = - - - -

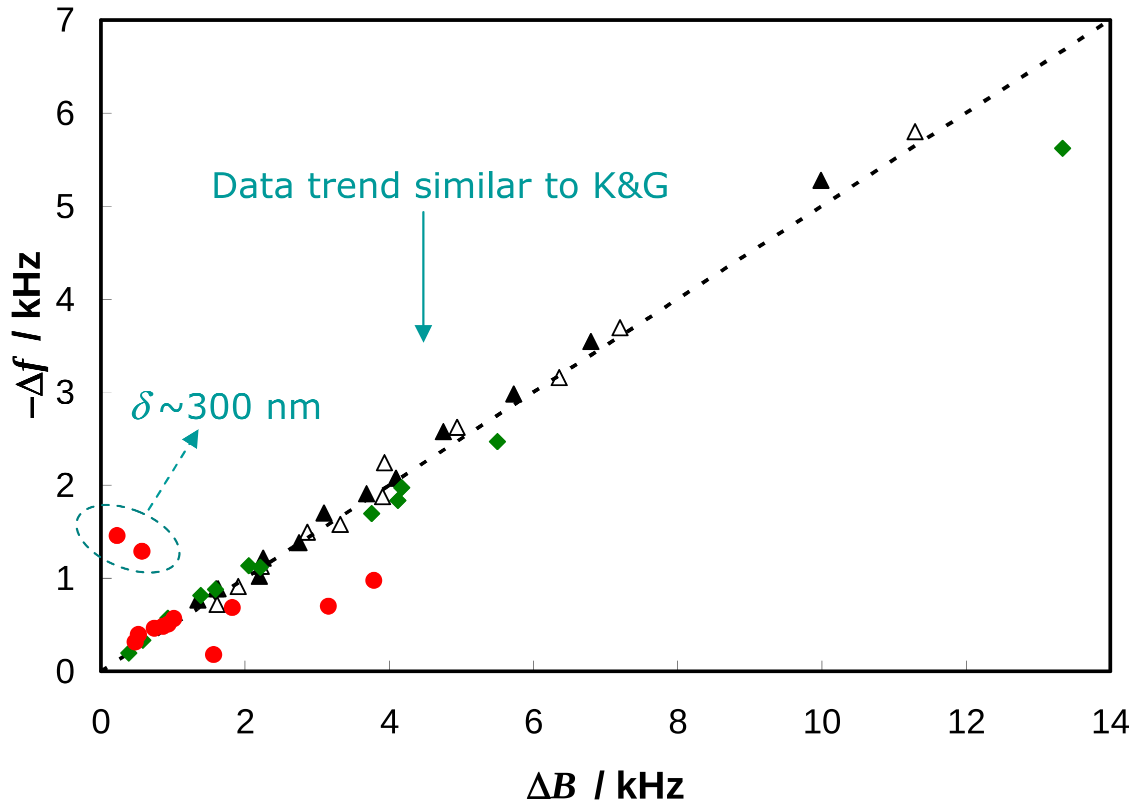
Shift is an additional frequency decrease beyond K & G rather than in dB. Consistent with "rigid liquid mass" from penetrating/Wenzel liquid (contact angle data/immobile drop)

Experiments with QCMs

Superhydrophobic Silicon Dioxide Data

Hydrophobic SiO_2 Surfaces – Newtonian or Not?

Water-glycerol solutions: 0-80%



Blank at 25 °C = ΔΔΔ

Hydrophobic crystal at 20°C = ▲▲▲

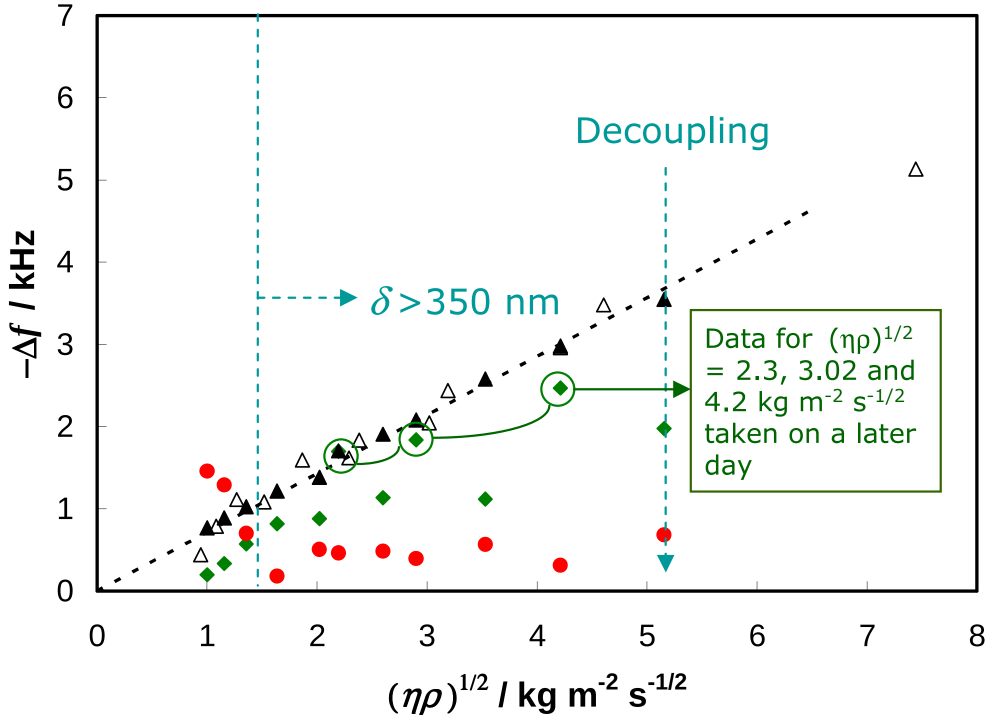
a1 (Super?)hydrophobic SiO_2 = ◆◆◆ at 20 °C

b1 Superhydrophobic SiO_2 = ●●● at 20 °C

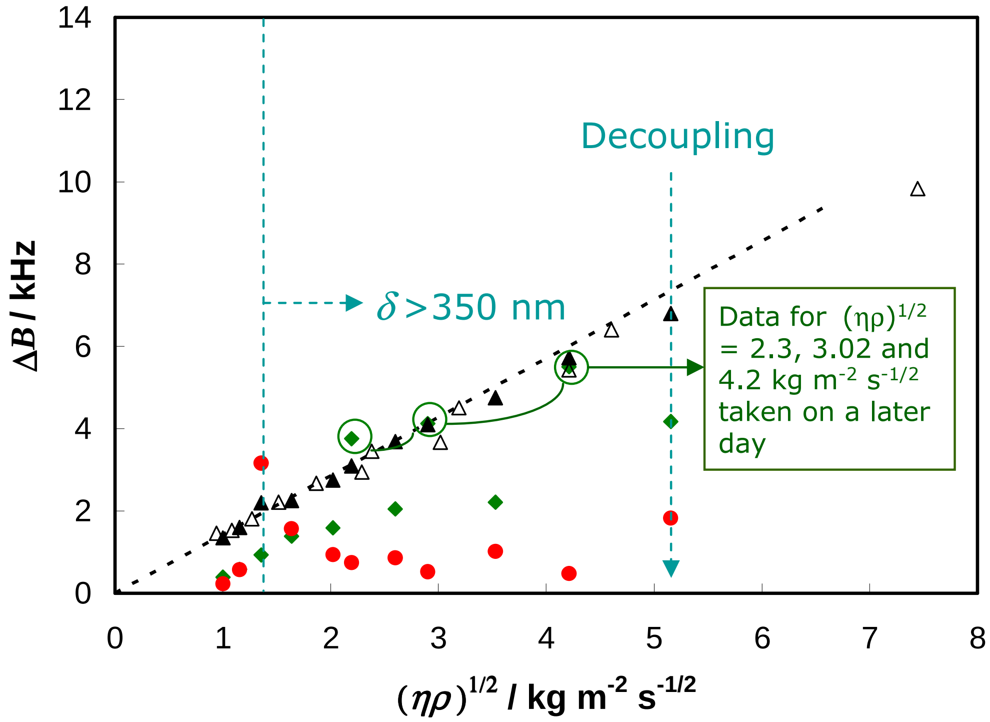
Data for a1 surface is Newtonian-like. Data for b1 is closer to origin, but more scattered

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

Conclusions

1. Surface Chemistry Changes QCM Sensor Response
   - Type of effect on rough/structured surface depends on aspect ratio
   - Type of effect depends on whether gas-liquid-vapor interfaces exist
2. Penetrating/Wenzel Form of Wetting Occurs for
   - Hydrophobic 5 μm tall posts and hydrophobic TiO_2
   - Hydrophobic TiO_2 follows expected trends of "trapped liquid mass"
     - $|\Delta f|$ larger than predicted by Kanazawa & Gordon and $|\Delta B|\sim$ K&G prediction
   - Hydrophobic 5 μm tall posts roughly follows trends of "trapped liquid mass"
     - $|\Delta f|$ larger than predicted by Kanazawa & Gordon and $|\Delta B|$ "slightly" > K&G prediction
3. Skating/Cassie-Baxter Form of Wetting Occurs for
   - Hydrophobic 18 μm tall posts and b1 superhydrophobic SiO_2
   - Both follow expected trends from acoustic reflection view
     - Both $|\Delta f|$ and $|\Delta B|$ much smaller than K&G prediction
4. Other Comments
   - a1 (super?)hydrophobic SiO_2 surface was unstable becoming a Wenzel surface
   - Penetration depth ~ surface feature size may create resonances

Acknowledgements

1. IEEE FCS Technical Programme Committee

    Invitation to talk

2. Internal Collaborators

    Dr Mike Newton (Concepts and QCM experimental development)
    Dr Neil Shirtcliffe (Materials methods)
    Dr Paul Roach (Materials methods and QCM experiments)
    Dr Carl Evans, Mr Steve Elliott (QCM experiments)

3. External Colleagues who’ve motivated and discussed work

    Dr Ralf Lücklum
    Professor Mike Thompson, Dr Gordon Hayward, Mr Jon Ellis

4. Funding Agencies

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    Dstl/Dr Stuart Brewer

The End

Key Parameters and Length Scales?

Superhydrophobicity

Gaps less than capillary length of liquid ~ 2.73 mm for water

Aspect ratio = height-to-lateral separation of features > 1

Cassie-Baxter contact angle > 150°

Typically, solid surface fraction, f_s <20% and hydrophobicity of surface, θ_e ~110°

Low contact angle hysteresis (< 5°) so droplet rolls easily

Decoupling QCM

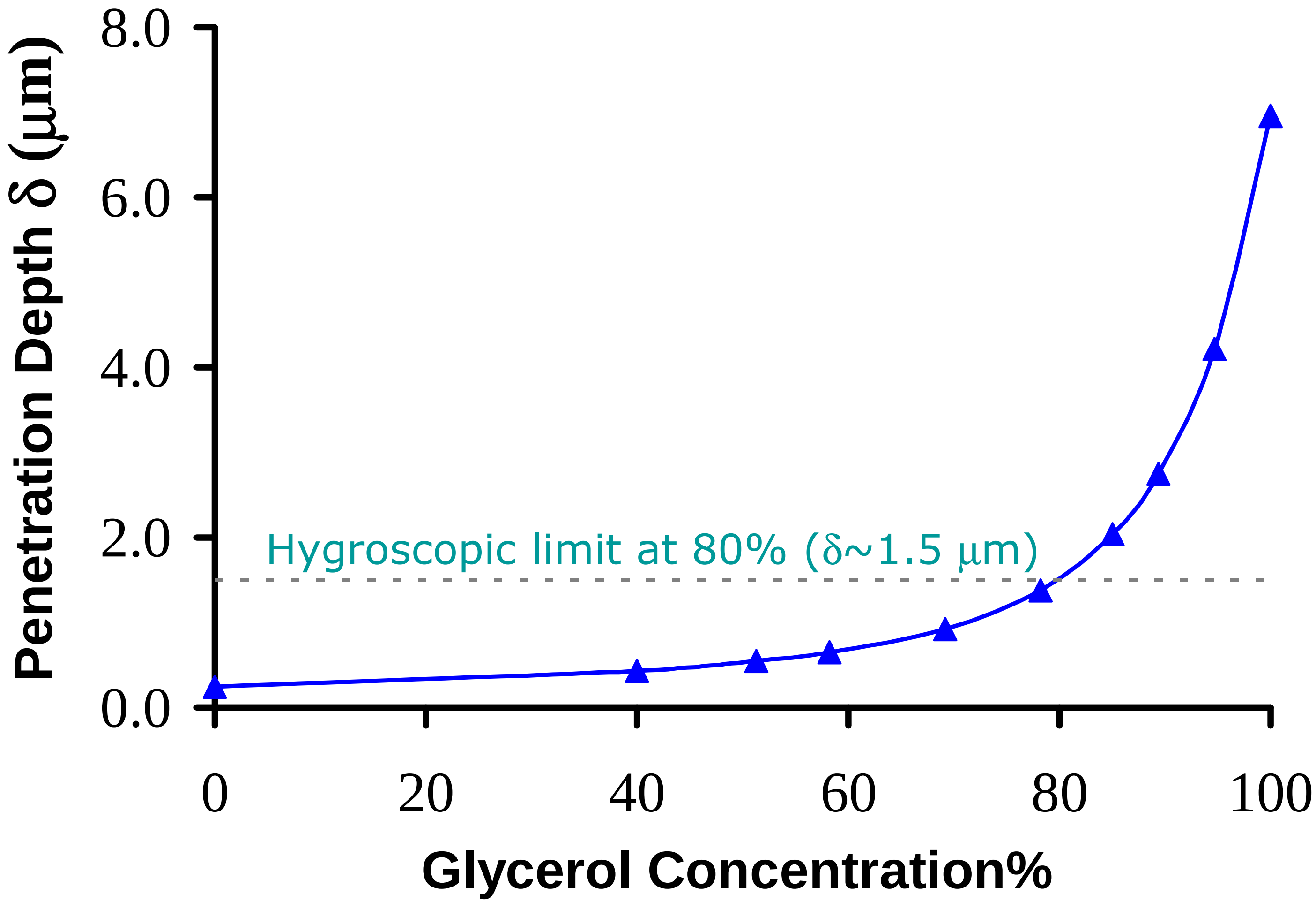
Low solid surface fraction (so reflection from troughs dominates)

Lateral separation of features > penetration depth

Height of features compared to penetration depth?

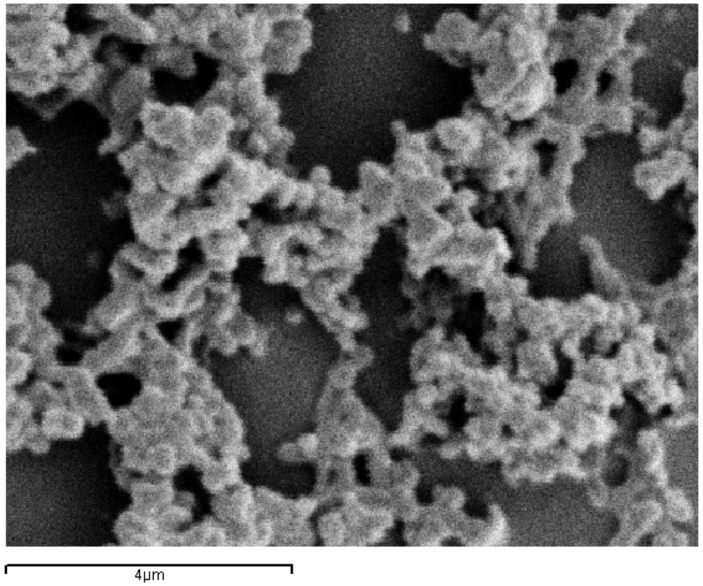
Acoustic reflection coefficient for substrate-liquid interface?

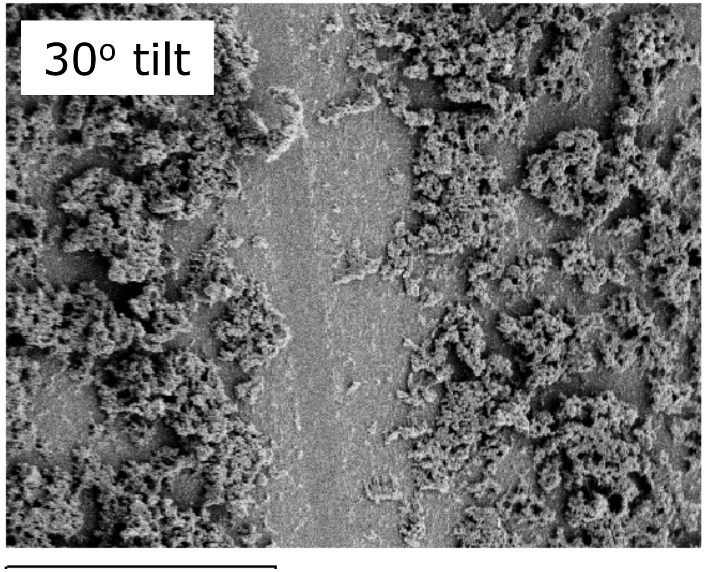
Water-Glycerol Mixtures - Penetration Depth

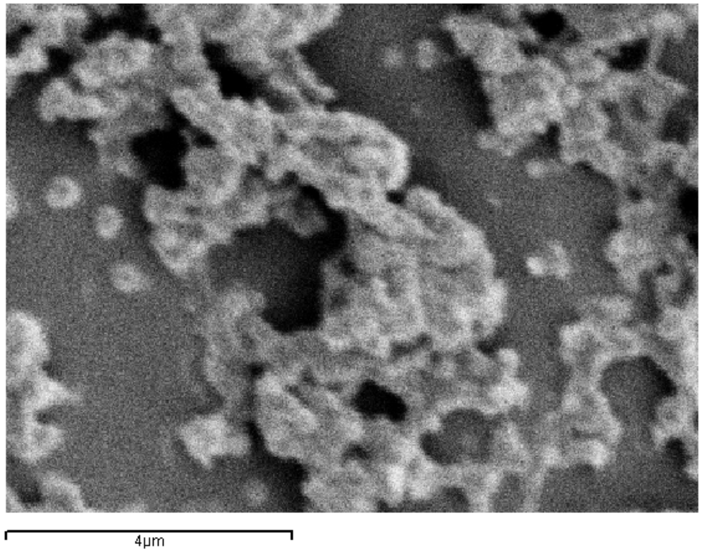


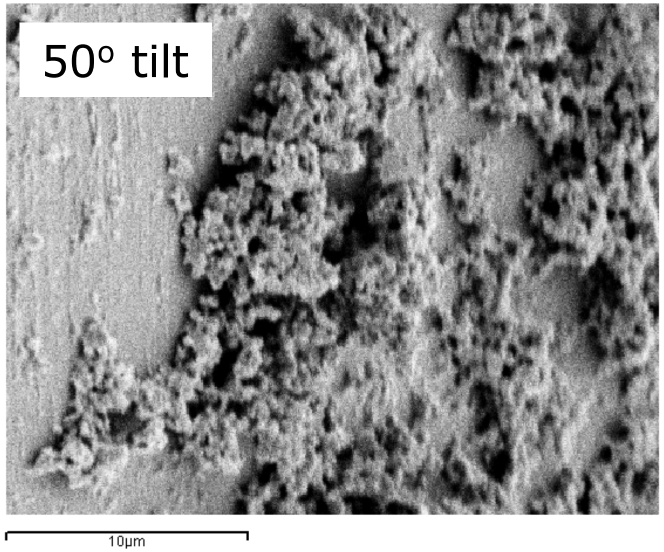
QCM behaves as if decoupled from the liquid, unless liquid penetrates into structure

TiO_2 sol-gel + Granger's coating

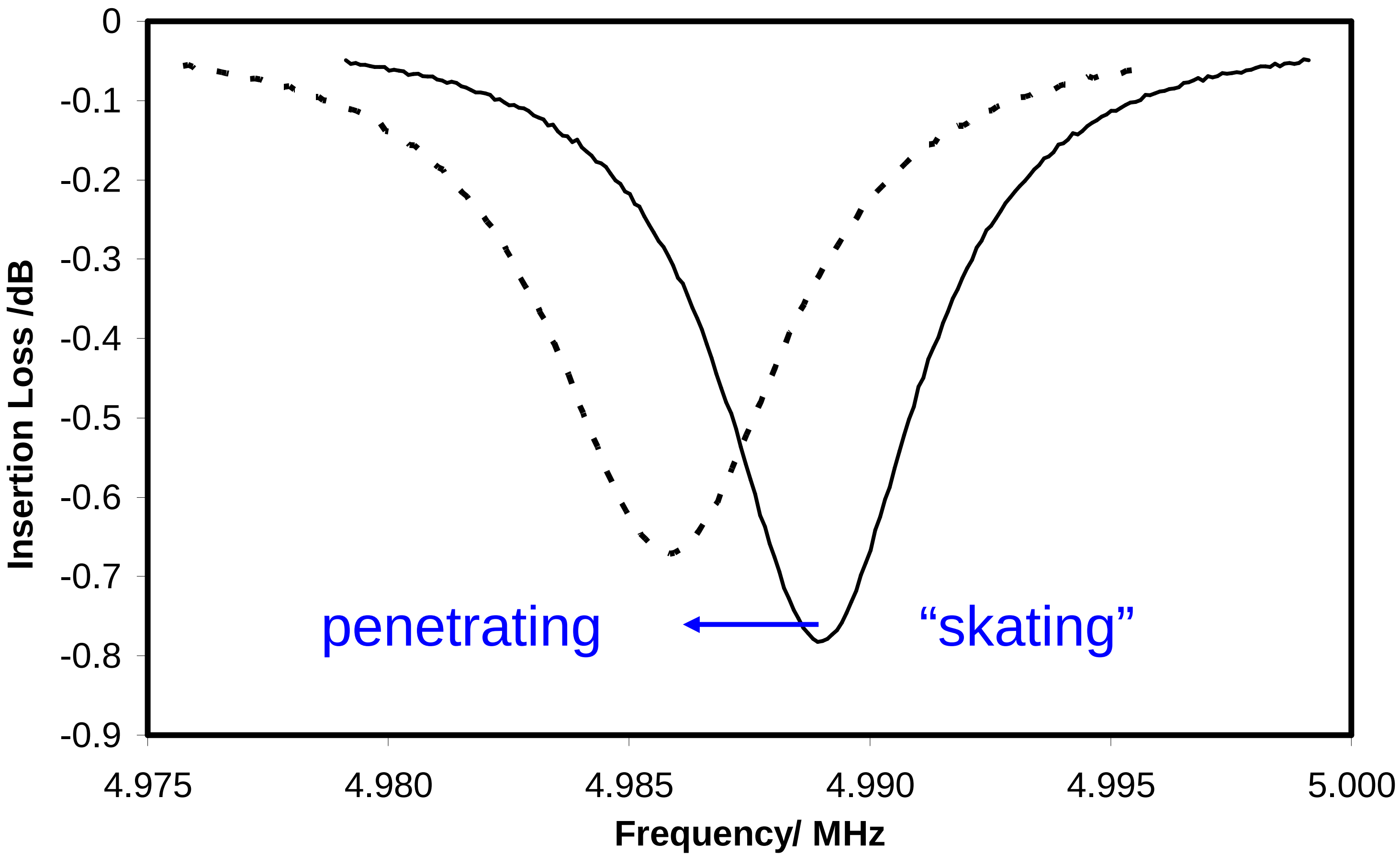








QCM Confirmation of “Skating”



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