Quartz Crystal Resonator with a Superhydrophobic Surface

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Overview

1. Superhydrophobicity & Slip

2. QCM Surfaces

3. Data for Superhydrophobic QCM

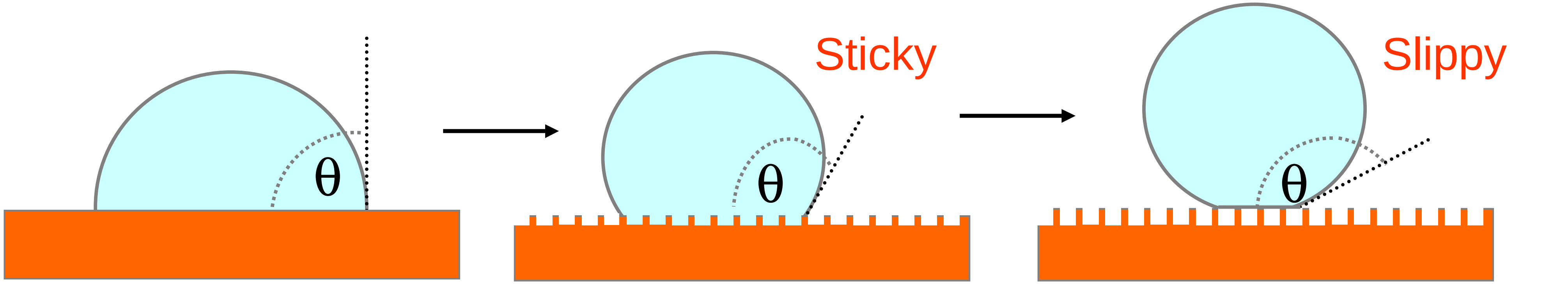
4. Conclusions

Superhydrophobicity and Slip

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 Eq.

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

Cassie-Baxter Eq

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

Chemistry

Young’s Law θ_e

Roughness

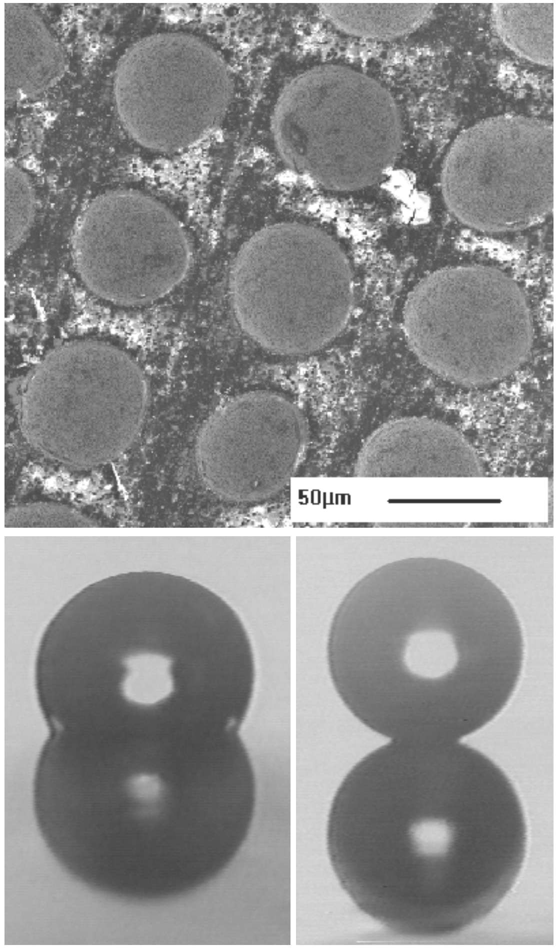
r = true area/planar projection

Topography

f_s = solid surface fraction

Topographic Enhancement of Water Repellence

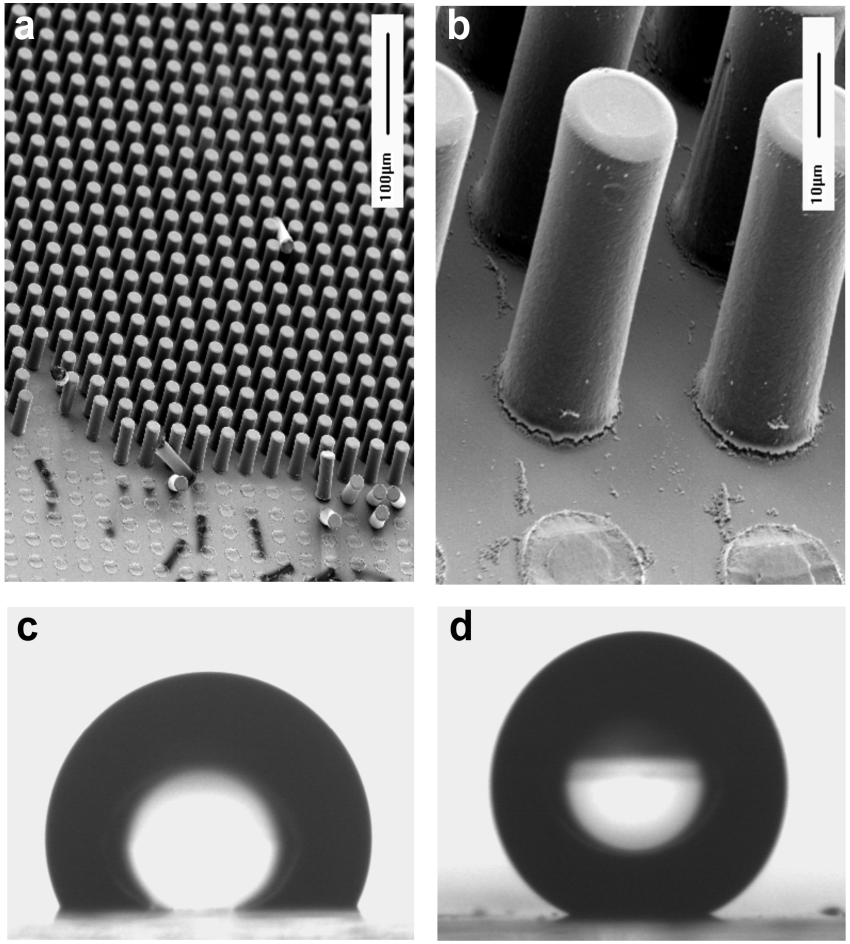
Etched Metal



Flat & hydrophobic

Patterned & hydrophobic

Polymer Microposts



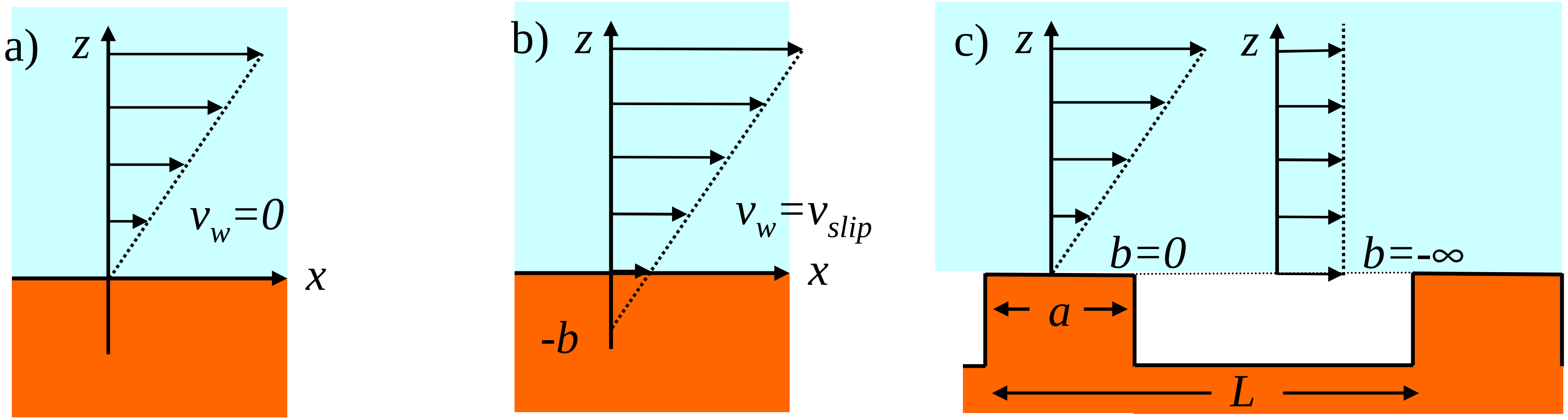
Flat & hydrophobic

Patterned & hydrophobic

References Shirtcliffe,*et al.*, *Langmuir* **21**, 2005, 937; *Adv. Maters.* **16**, 2004, 1929; *J. Micromech. Microeng.* **14**, 2004, 1384.

Slip by Simple Newtonian Liquids

No Slip | Slip | Mixed



Experimental Evidence – Steady Flow

1. Theory[1,2] supported by simulations suggests $b=L\, f(\varphi_s)/2\pi$
2. Micro-PIV experiments detailing flow profiles[3] (h=1-7 μm ⇒ $b=0.28L$)
3. Cone-and-plate rheometer experiments[4] – drag reduction > 10%
4. Hydrofoil in a water tunnel experiments[5] – drag reduction of 10%

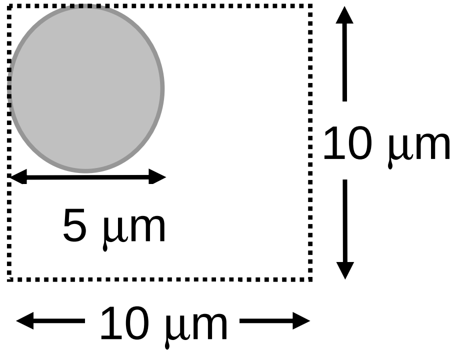
References [1]Philip, *Z. Angew. Math. Phys.* **23**, 1972; [2]Lauga & Stone, *J. Fluid Mech.* **489**, 2004; [3]Joseph *et al*., *Phys. Rev. Lett.* **97,** 2006;[4]Choi & Kim, *Phys. Rev. Lett.* **96**, 2006; [5]Gogte, *et al. Phys. Fluids* **17**, 2005.

QCM Surfaces

QCM with Micro-Post Textures

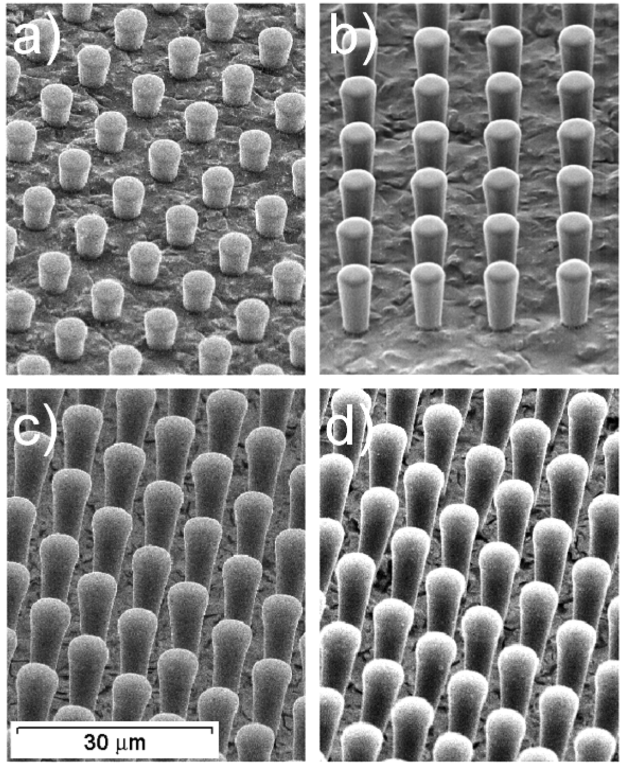
Previous Data on QCMs

1. Polyethylene glycol-water on a hydrophobic micro-post QCM[1]
2. Polystyrene with embedded PTFE based superhydrophobic surface[2]
3. 0.6 μm silica nanoparticle layer superhydrophobic multirersonance device[3]



New Experiments in this Talk

1. SU-8 micro-posts 5, 10, 15, 18 μm tall
2. Water-glycerol mixtures (0-100%)
3. Bare (non-hydrophobised) & hydrophobised
4. Contact angles
5. Impedance spectra fitted to BVD model



References [1]Evans et al.,. Sens. Act. A 2005, **123-24**, 73; [2]Fujita, et al., Jap. J. Appl. Phys. 2005, **44**, 6726; [3]Kwoun, et al., IEEE Trans. Ultrason. Ferroel. Freq. Control. 2006, **53**, 1400.

Contact Angle Data

Concentrations:	0%	40%	51.3%	58.2%	69.2%	78.2%
Bare flat SU-8, θ_s	75°	69°	73°	66°	68°	65°
Hydrophobic flat, θ_s^H	115°	113°	105°	109°	100°	111°
Bare 5 μm post, θ	106°	101°	95°	96°	88°	86°
Hydrophobic 5 μm post, θ^H	155°	150°	152°	149°	152°	151°
Bare 10 μm post, θ	118°	121°	109°	111°	103°	99°
Hydrophobic 10 μm post, θ^H	151°	148°	147°	148°	151°	149°
Bare 15 μm post, θ	119°	127°	117°	95°	115°	118°
Hydrophobic 15 μm post, θ^H	143°	149°	143°	147°	144°	148°
Bare 18 μm post, θ	123°	117°	113°	120°	106°	116°
Hydrophobic 18 μm post, θ^H	138°	149°	138°	148°	137°	150°

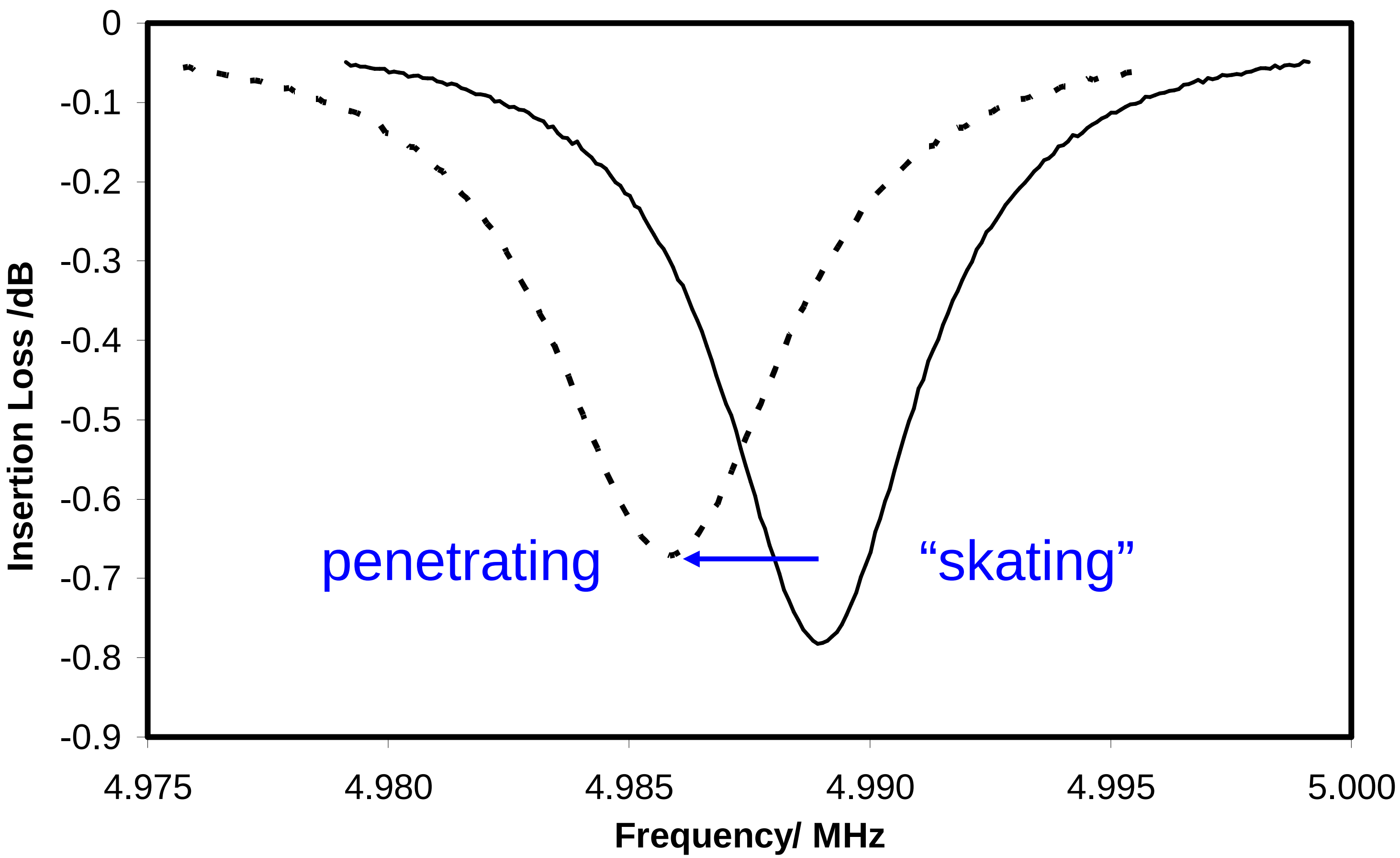
Cassie-Baxter Theory

Bare posts should give (138±2)°

Hydrophobic posts should be (150±3)°

1. ***Partial penetration of bare posts***
2. ***"Skating" on hydrophobised posts***

QCM Confirmation of “Skating”



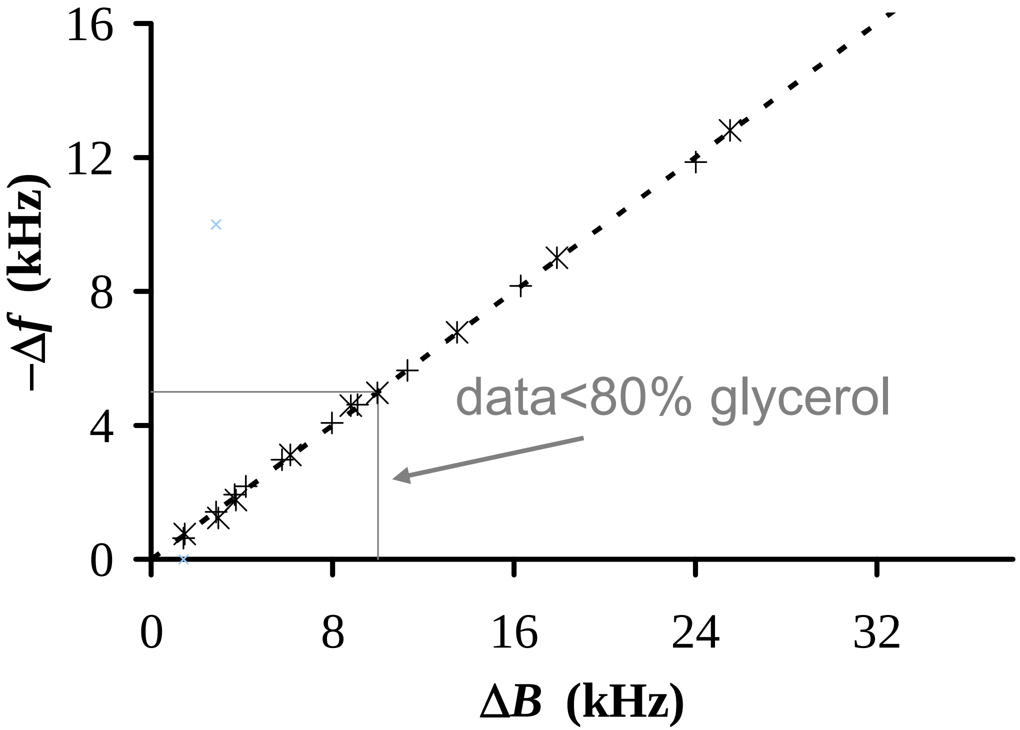
Hydrophobised 18 μm micro-posts
Solid-line is before pressure applied
Dotted curves is after pressure is applied

Visually confirmed water ingress after pressure applied

Data for Superhydrophobic QCM’s

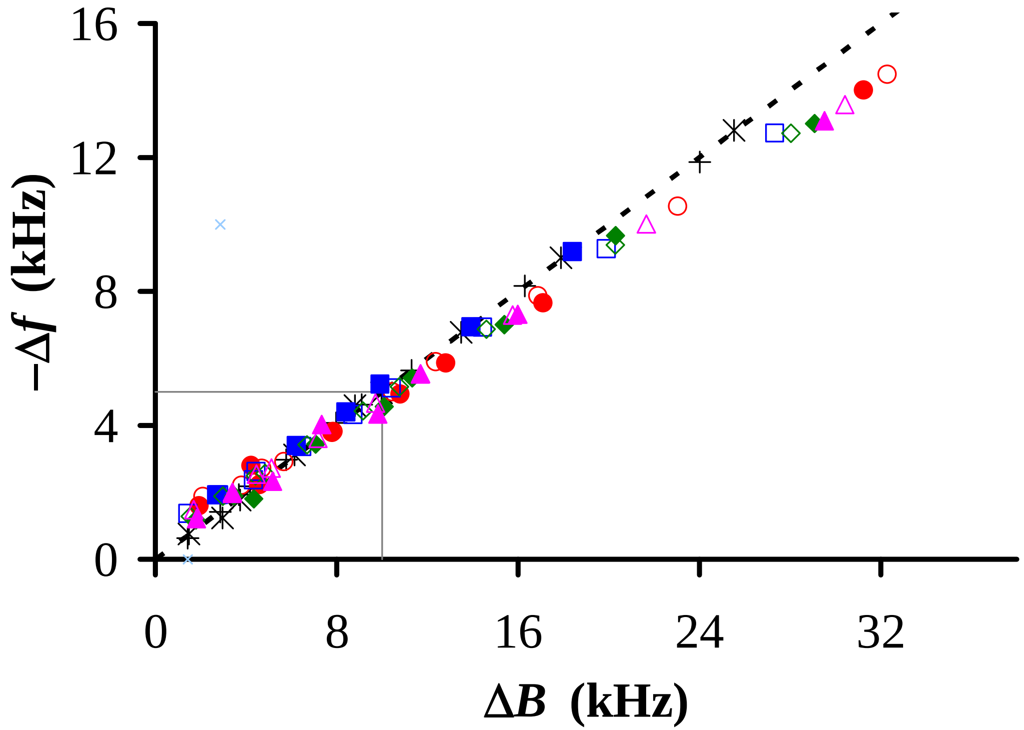
Flat Surfaces – Newtonian Liquid

Polished Crystal



Bare (non-hydrophobised) = +++
Hydrophobised = ✳✳✳
Kanazawa & Gordon Theory = - - - -

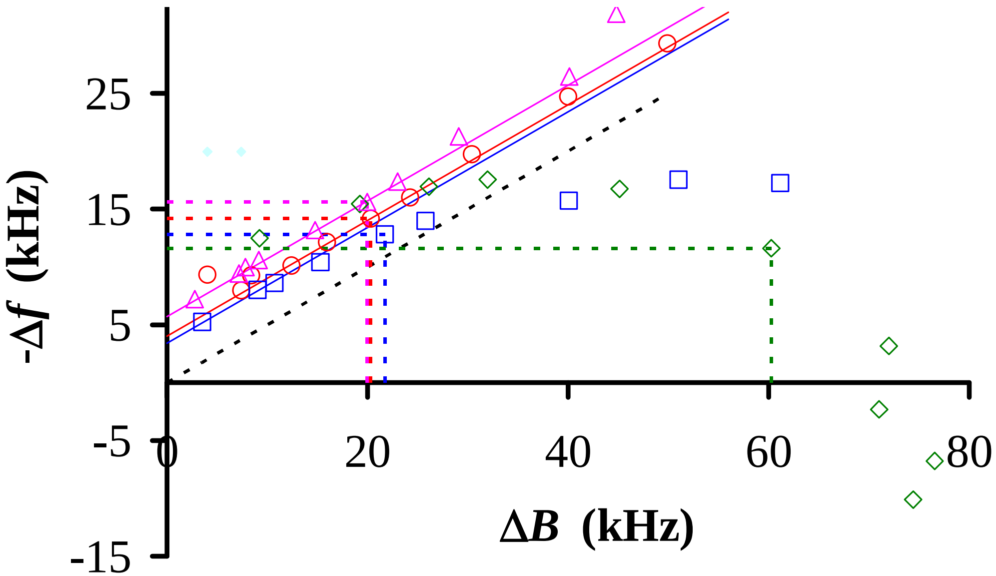
Spin Coated SU-8



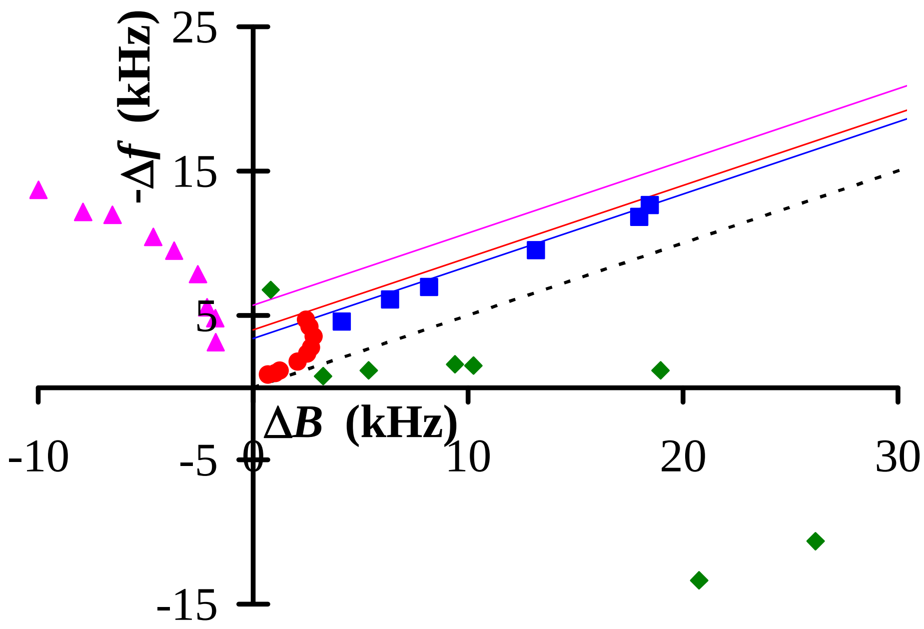
5μm = □□□ 10μm = ◇◇◇
15μm = ΔΔΔ 18μm = ○○○
Filled symbols = hydrophobised

Micro-Post Surfaces – Newtonian or Not?

Bare (non-hydrophobised)



Hydrophobised



5μm = □□□ 10μm = ◇◇◇

15μm = ΔΔΔ 18μm = ○○○

Filled symbols = hydrophobised

Data<80% glycerol = dotted rectangles

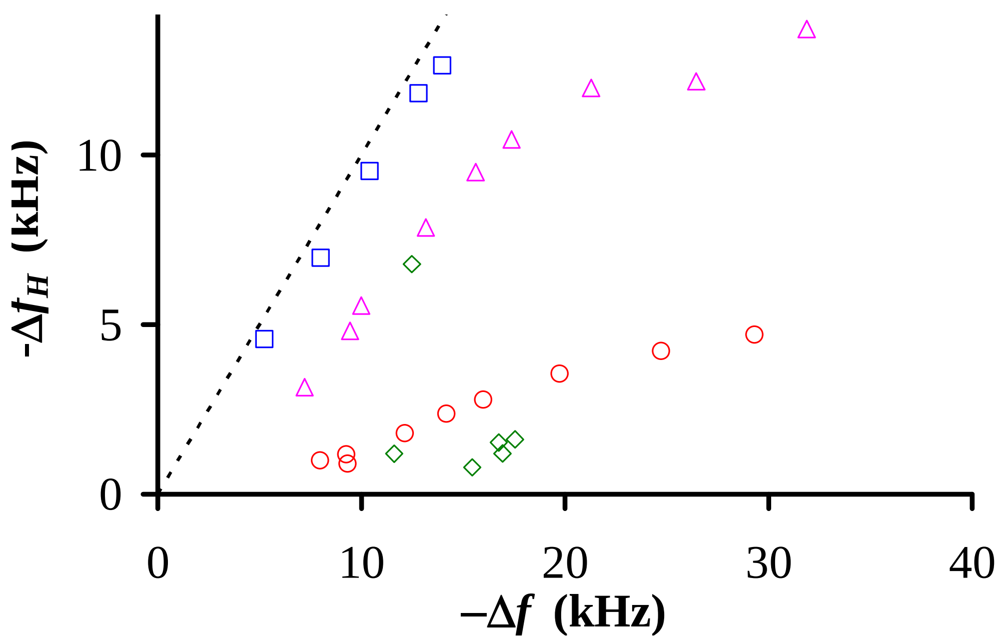
Kanazawa & Gordon Theory = - - - -

Solid lines = Guide to eye for 0.5 slope

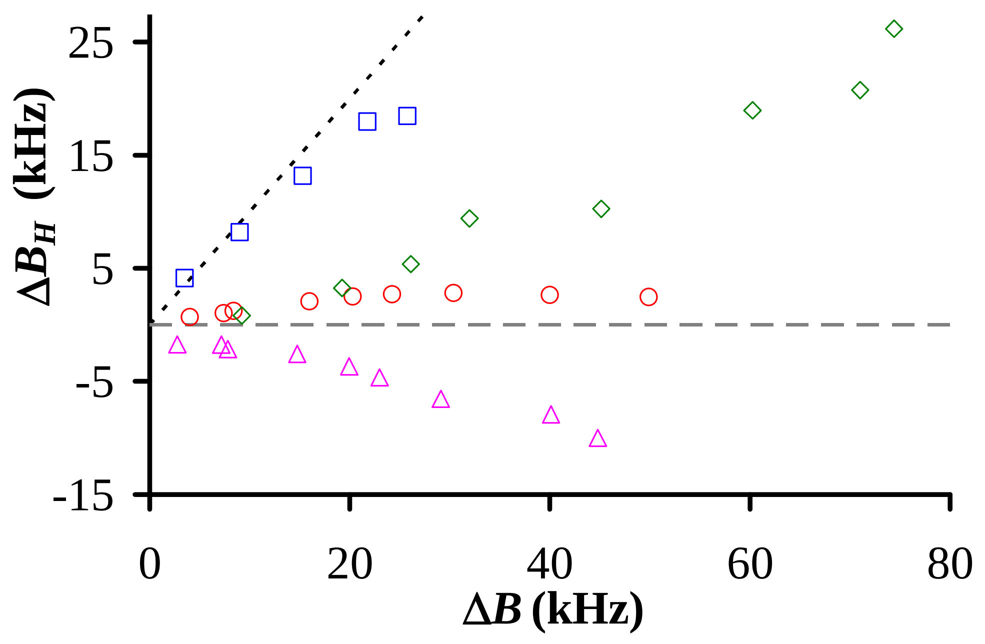
Hydrophobisation of taller posts changes type of response

Micro-Post Surfaces: Hydrophobised v Bare

Frequency



Bandwidth

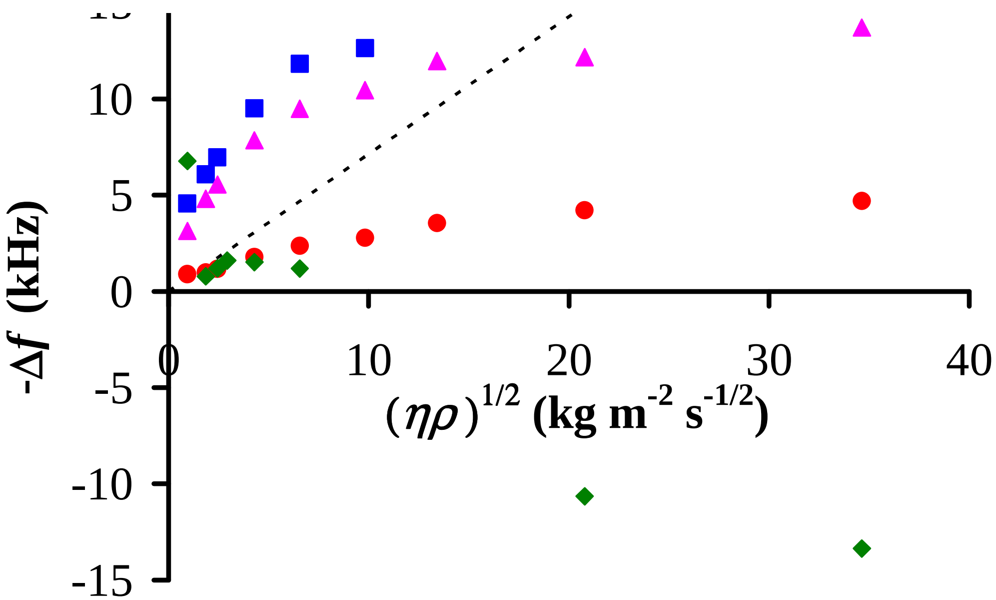


5μm =□□□ 10μm = ◇◇◇
15μm = ΔΔΔ 18μm = ○○○

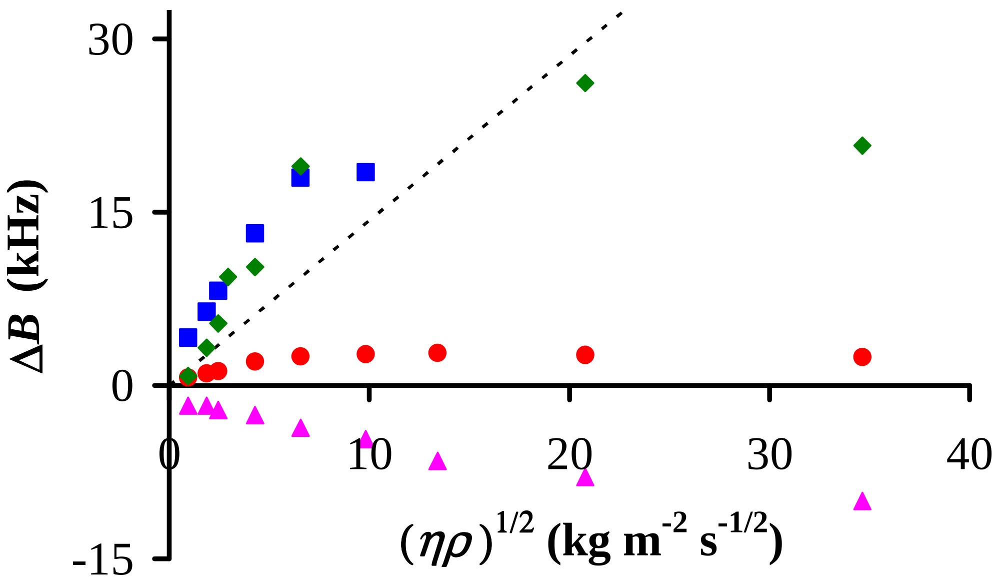
Taller hydrophobic posts decouple response from liquid

Micro-Post Surfaces: Viscosity-Density

Frequency



Bandwidth



5μm = □□□ 10μm = ◇◇◇ Filled symbols = hydrophobised

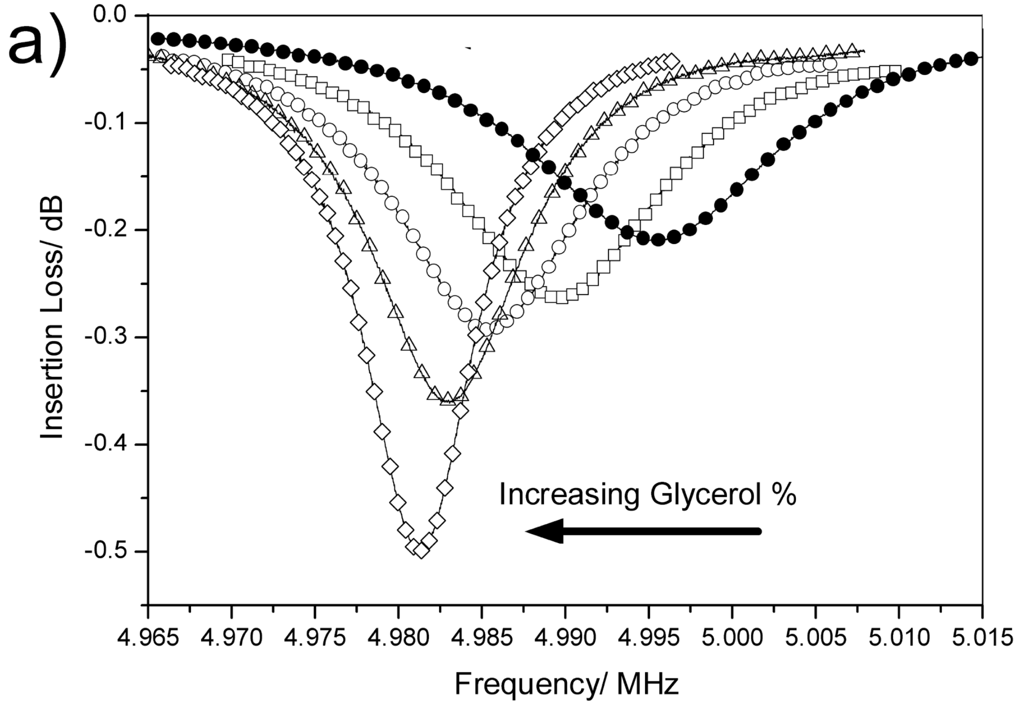
15μm = ΔΔΔ 18μm = ○○○ Kanazawa & Gordon Theory = - - - -

Tallest (18 μm) hydrophobic posts have reduced coupling to liquid

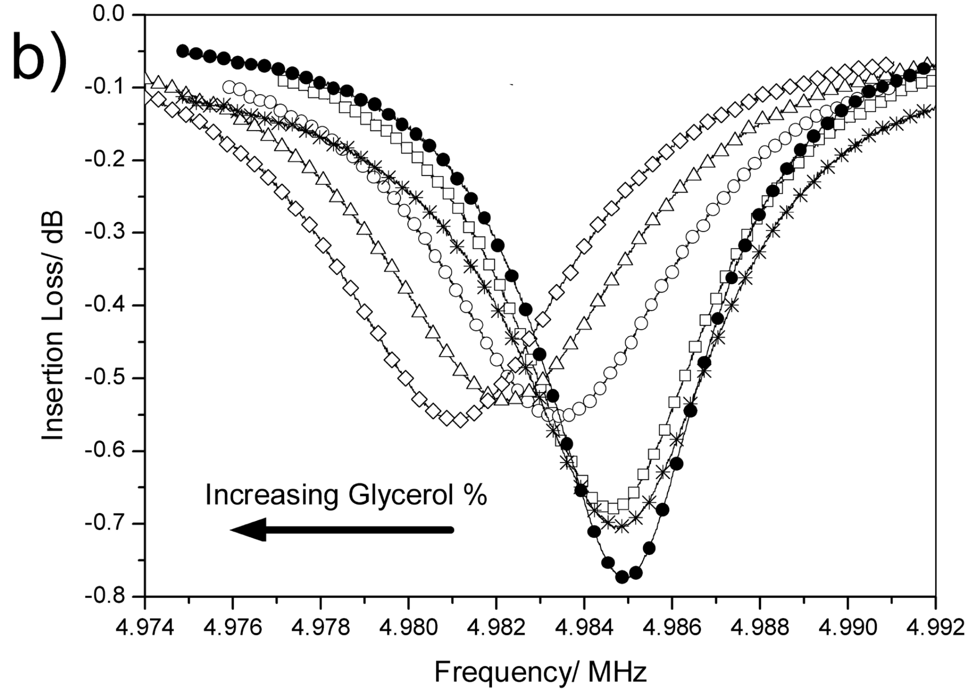
10 μm and 15 μm tall posts have unusual response

QCM Spectra

Hydrophobised 15 μm



Hydrophobised 18 μm



Resonance sharpens with increasing viscosity-density

Frequency and bandwidth shifts are far less than K&G prediction

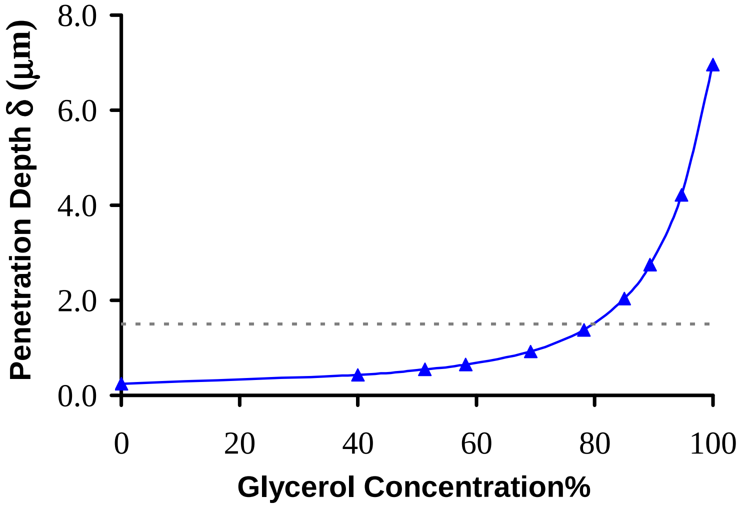
Discussion Points?

1. Resonances

   Length scales of features?

   Compressional waves?

   Penetration depth issues?



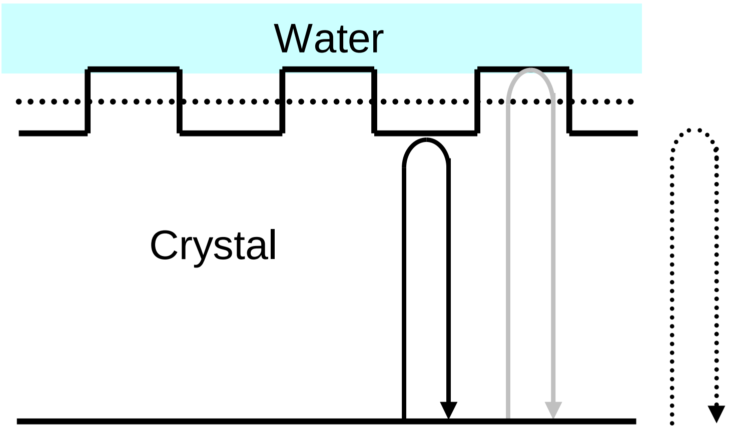
2. Types of Response

   Viscoelasticity in air and/or in liquid?

   Trapped “mass”, decoupling and slip?

   Sharpening resonances?

   Positive frequency shifts?



3. Sensor Problems and Potential

   Real surfaces are not polished crystals with fixed hydrophobicity

   Design recognition layer that switches to hydrophilic on binding?

Conclusions

1. Water/Glycerol on Micro-Posts

   Bare/non-hydrophobised ⇒ Partial penetration of liquids

   Hydrophobised ⇒ Superhydrophobic surfaces

2. Water/Glycerol Response of Micro-Post QCM's

   Bare/non-hydrophobised ⇒ Newtonian-like response (conc<80%)

   Hydrophobised ⇒ Change of type of response for height>5 μm

3. Unusual Responses for Hydrophobised Micro-Posts

   All curves shower a lower magnitude of response (decoupling)

   Resonances can sharpen with increasing viscosity-density product

   Tallest case (18 μm) shows most decoupling

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NOTTINGHAM TRENT UNIVERSITY

QCM: Slip Boundary Condition v Trapped Mass

- Acoustic Impedance[1]
  - Use slip length, b, and look at first order calculation

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

- Newtonian Liquid[2]
  - Kanazawa result for no-slip
  - Small "slip" correction uses b/δ

$$Z_L^{no\,slip} \approx \sqrt{i\omega\rho_f\eta_f}$$

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

"slip" correction

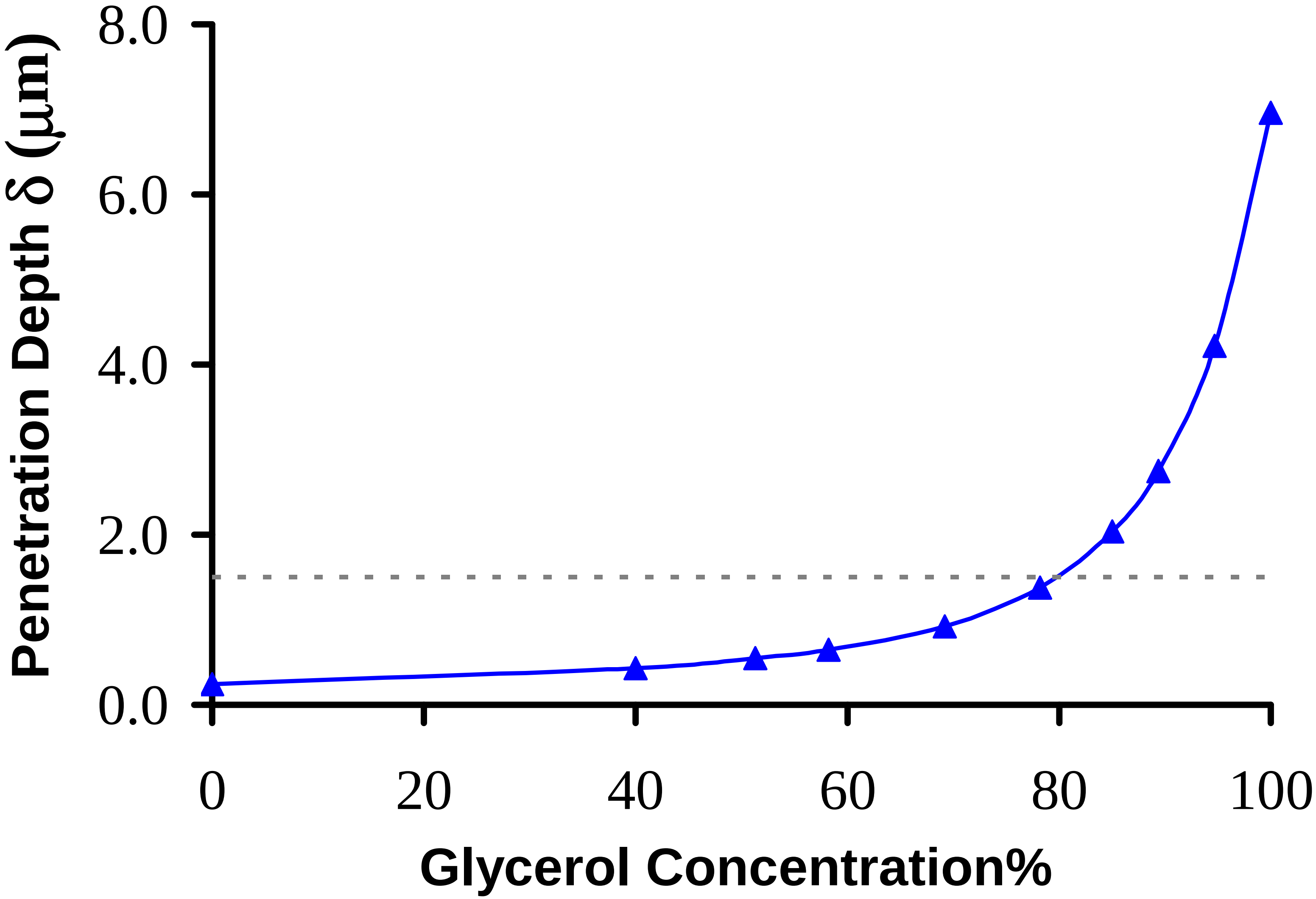
- Negative b and Trapped Mass[2,3]
  - Define a mass as $\Delta m_f = b\rho_f$

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

Sauerbrey result for "rigid" liquid mass

References [1]McHale *et al.*, *J. Appl. Phys.*, **88**, 2000, 7304-7312; [2]McHale & Newton, *J. Appl. Phys.* **95**, 2004, 373-380; [3]S. J. Martin, *et al.*, *Anal. Chem.*, **65**, 1993, 2910-2922; see also Ellis *et al.*, *J. Appl. Phys.* 94, 2003, 6201-6207.

Resonances with Penetration Depth

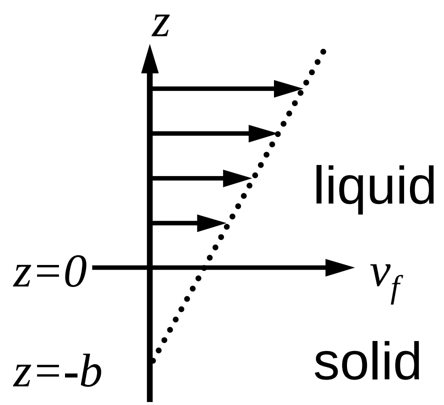


“Slip” Boundary Condition v Trapped Mass

Average Position of Solid-Liquid Interface

Slip length, b, to model average position of an interface

Negative b ⇒ Effective interface moves to liquid side of boundary



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

Negative Slip Length

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

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

Sauerbrey result for trapped “rigid” liquid mass

References [1]McHale & Newton, *J. Appl. Phys.* 2004, **95**, 373..

Acoustic Reflection View

Substrate Supports Standing Waves

Cavity length increases ⇒ additional frequency decrease

Limitations on "Slip" B.C./Trapped Mass View

Effectively assuming equal reflectivity at peaks and troughs of topography

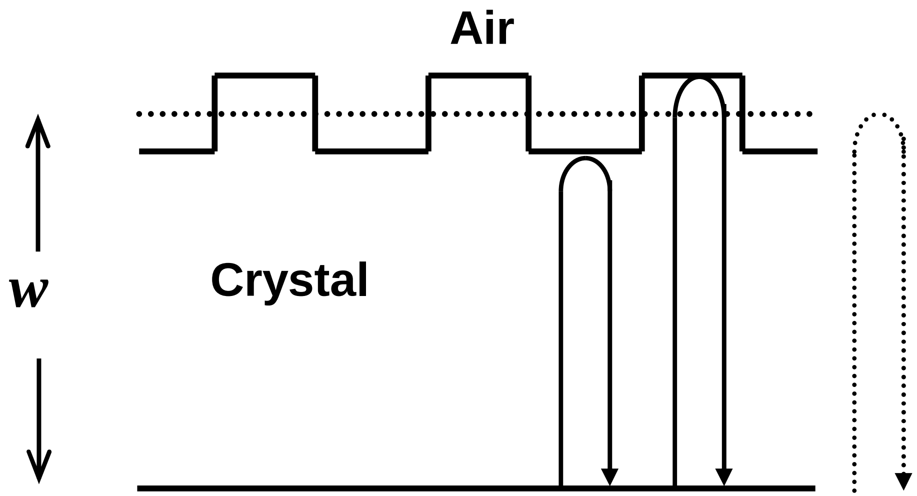
Cannot necessarily use additivity of liquid entrainment + trapped mass when incomplete liquid penetration occurs

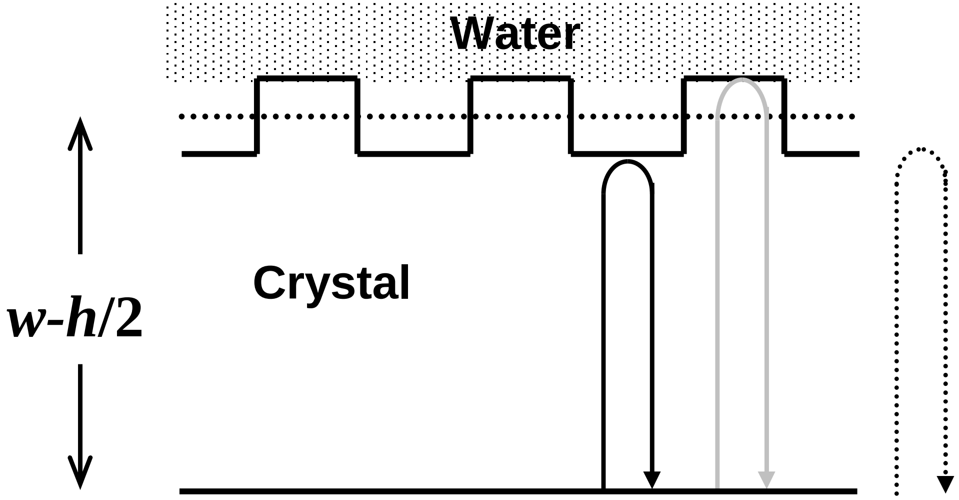
A Mechanism for Positive Frequency Shifts?

- Effective Acoustic Cavity Length

Air ⇒ top surface of crystal has uniform reflectivity

Water ⇒ if air "trapping" occurs, reflectivity of peaks and troughs differs





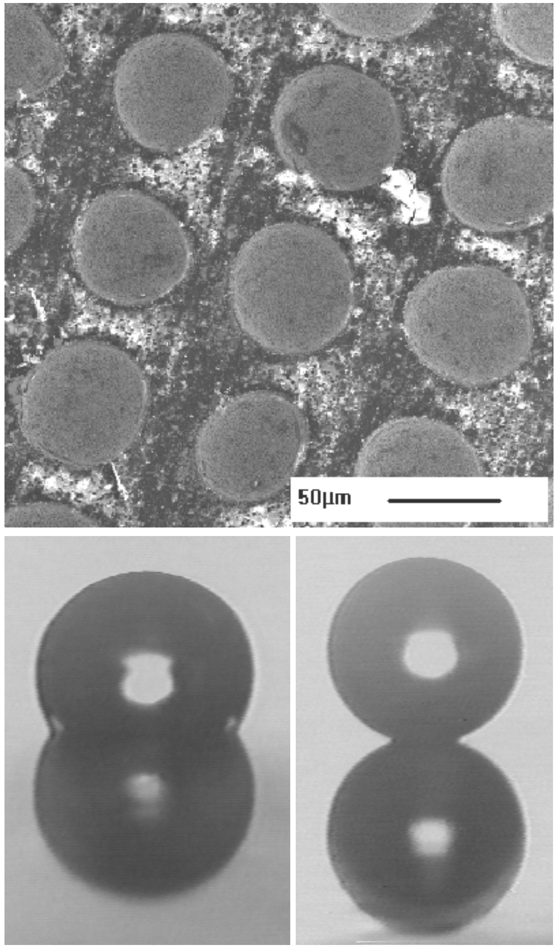
Average cavity length exists

Average cavity length decreases

$v = f\lambda \Rightarrow f$ increases

Topographic Enhancement of Water Repellence

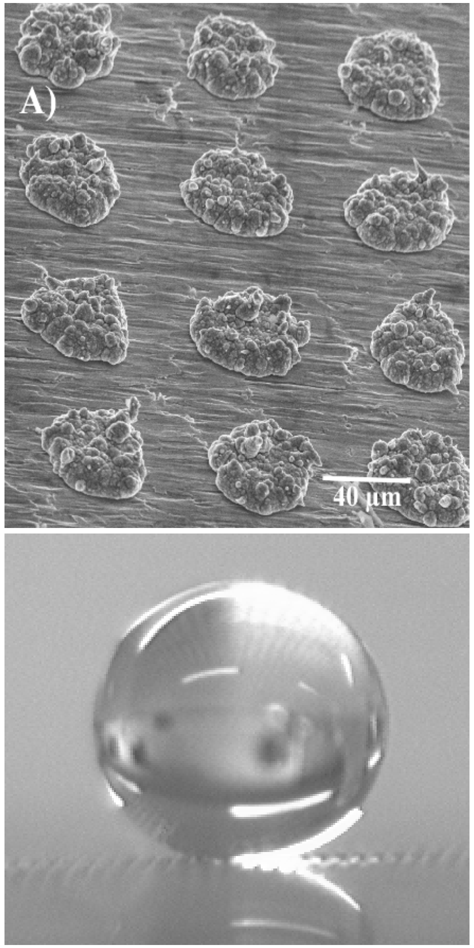
Etched Metal



Flat & hydrophobic

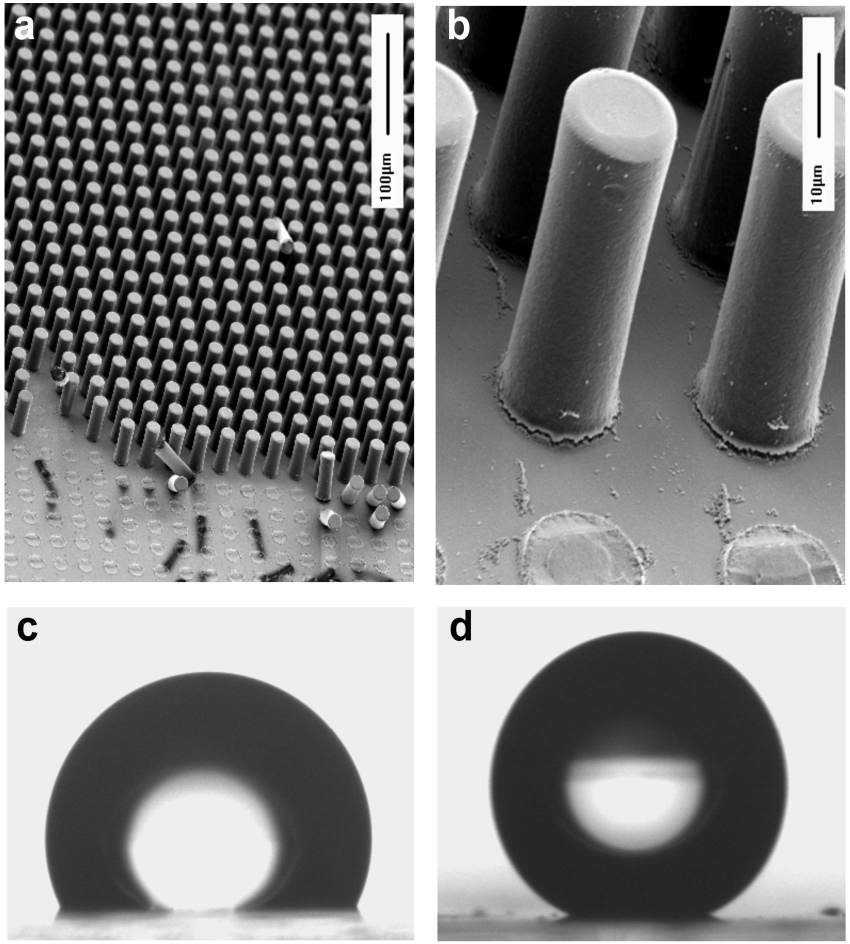
Patterned & hydrophobic

Deposited Metal



Patterned & hydrophobic

Polymer Microposts



Flat & hydrophobic

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