Super-hydrophobicity:
Implications for Quartz Crystal Resonators

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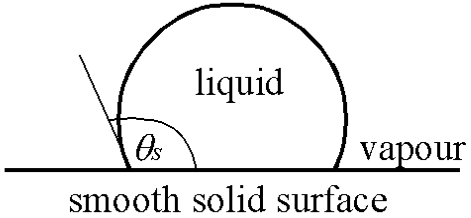
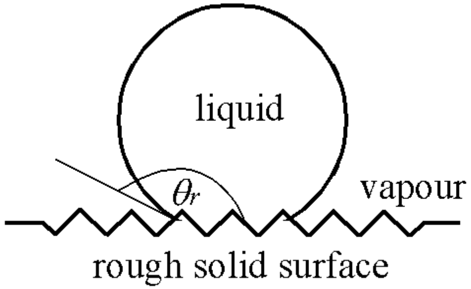
Overview

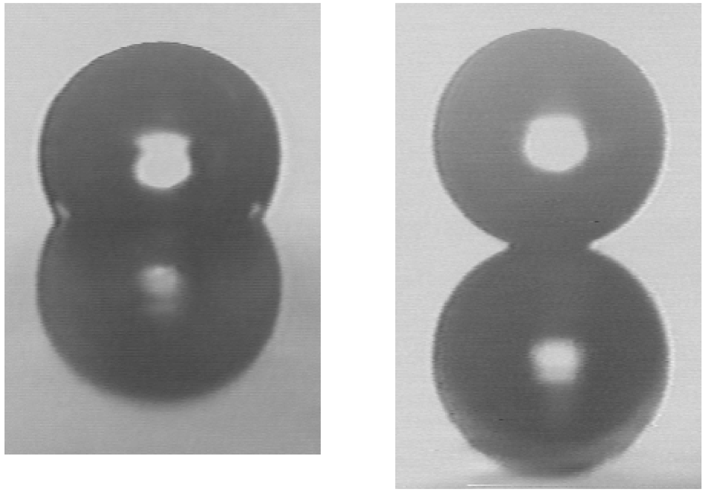
1. Wetting and Topography
    - Super-hydrophobicity
    - Roughness and Air Trapping/Liquid Penetration
    - Surface Structures - Lithographic Fabrication
2. Theoretical Ideas for Acoustic Waves
    - Acoustic Reflections - Positive Δf ?
    - “Slip” Boundary Conditions and Trapped Mass
3. Experimental Data
    - Acoustic Reflections - Positive Δf ?

Super-hydrophobic Surfaces

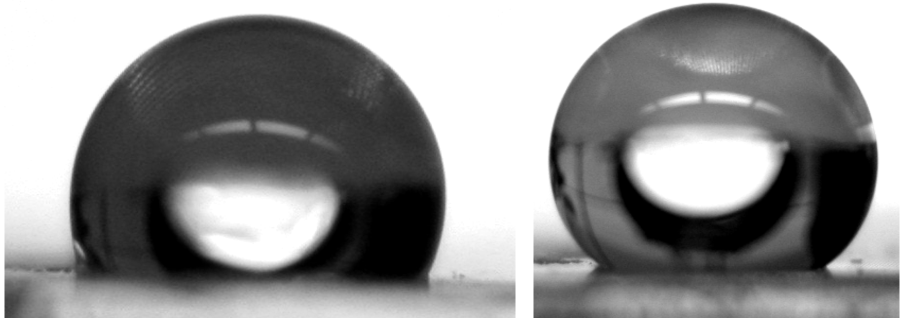




Water Drop (~ 2 mm)

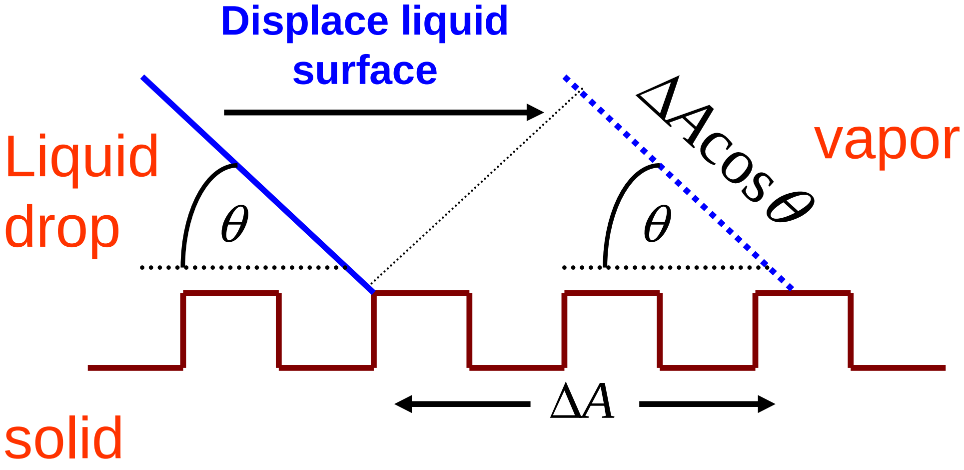


- Hydrophobised SU-8 - Flat versus Circular Pillars
  - Height is 30 µm, diameter is 15 µm and separation is 15 µm



Wetting and Topography

Complete Penetration

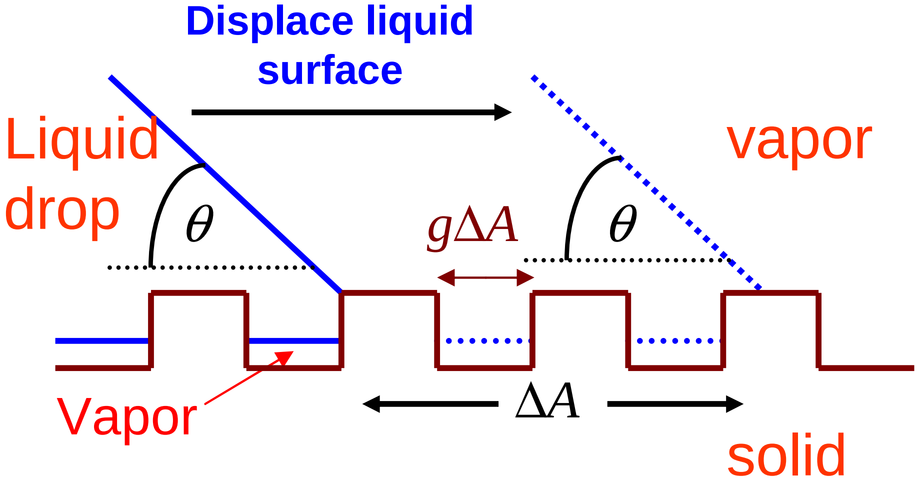

Displace liquid surface

Liquid drop

vapor

solid

Air “Trapping”


Displace liquid surface

Liquid drop

vapor

Vapor

solid

Surface Free Energy Changes

$$\Delta F = (\gamma_{SL} - \gamma_{SV})\, r\Delta A + \gamma_{LV} \cos\theta\Delta A$$

$$\Delta F = (\gamma_{SL} - \gamma_{SV})\, fr\Delta A + \gamma_{LV}\, g\Delta A + \gamma_{LV} \cos\theta\Delta A$$

Wenzel’s Eqn

$$\cos\theta_e^R = r(\gamma_{SV} - \gamma_{SL}) / \gamma_{LV} = r\cos\theta_e^s$$

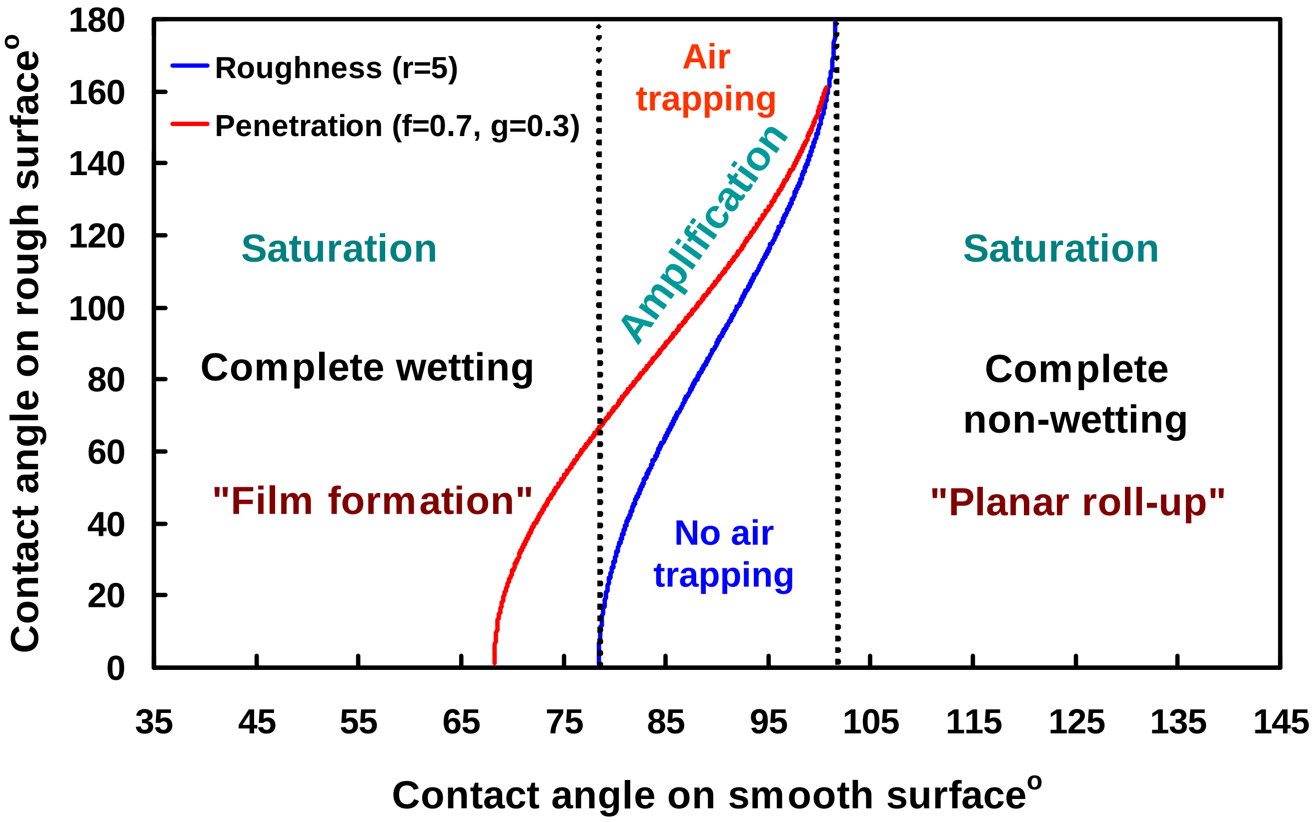
$r = \Delta A_{true} / \Delta A$ = roughness factor

Modified (Cassie Style) Eqn

$$\cos\theta_e^R = rf\cos\theta_e^s - g$$

f = fraction of rough surface wet

Effect of Topography - Equilibrium



Roughness/Topography

θ_e^s > threshold

⇒ enhances hydrophobicity

θ_e^s < threshold

⇒ enhances film formation

Super-hydrophobic

Air “trapping” (“Skating case”)

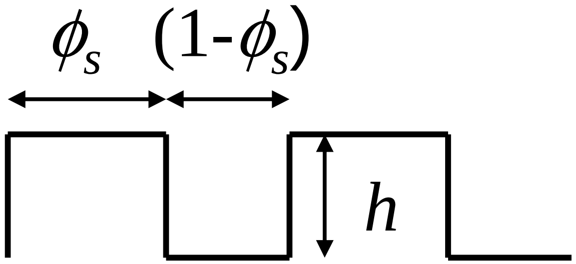
⇒ most existing examples

Pressure

⇒ air trapping disappears

Effect of Topography - Air “Trapping”

- Liquid Penetration into Texture



ϕ_s=solid fraction, (1- ϕ_s)=liquid fraction

r = roughness

Liquid <u>film</u> penetrates when:

Critical angle θ_c is in 0 to 90° range

$$\cos\theta_e^S > \frac{1-\phi_S}{r-\phi_S} = \cos\theta_c$$

- “Skating” Drop

Liquid bridges from one peak to next

$$\cos\theta_e^R = -1+\phi_S\left(\cos\theta_e^S+1\right)$$

- Air “Trapping” and Roughness

Sinusoidal model gives critical roughness for installation of horizontal contact line

(e.g. for 120°, r_c=1.75 ⇒ jump in θ_e^R to > 150°)

$$r_c = 1+\frac{\tan^2\theta_e^S}{4}$$

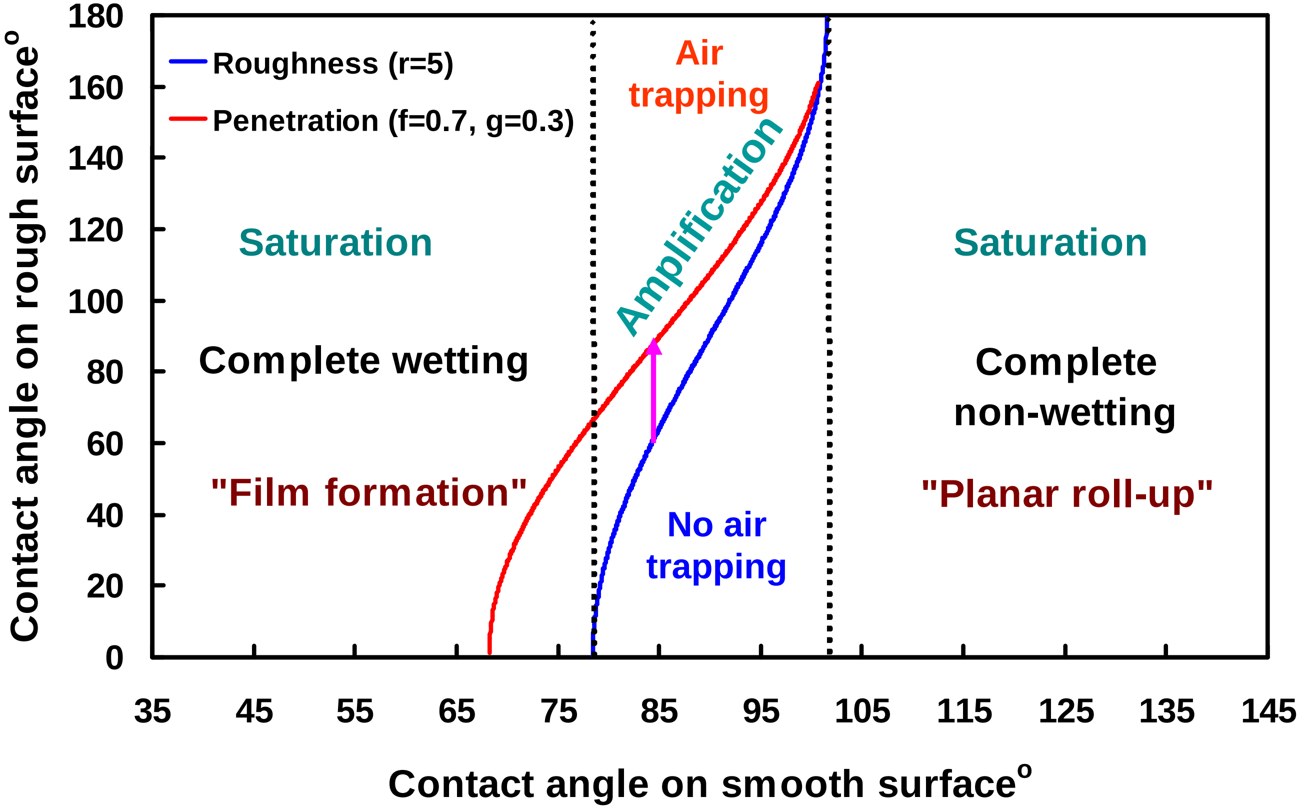
Also, sharp features promote “skating”

Effect of Topography - Aspect Ratio

- Air Trapping and Aspect Ratio

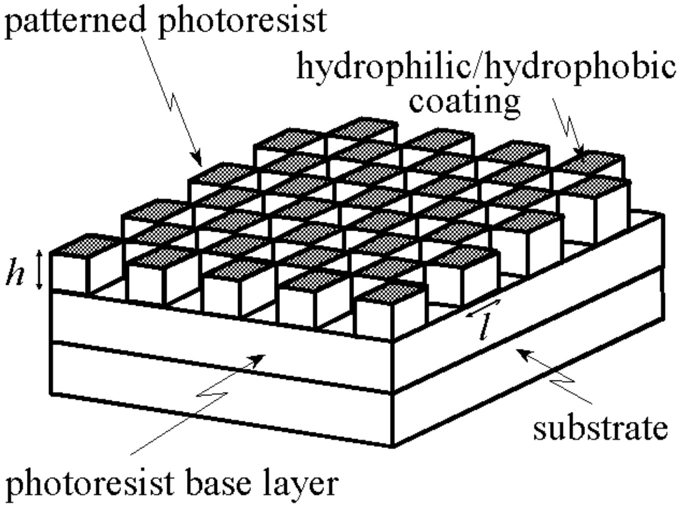
  As roughness increases system jumps from blue to red curve

  Alternatively, for given roughness, jump occurs as smooth surface angle increases



Experimental Approach

Lithographic Principle



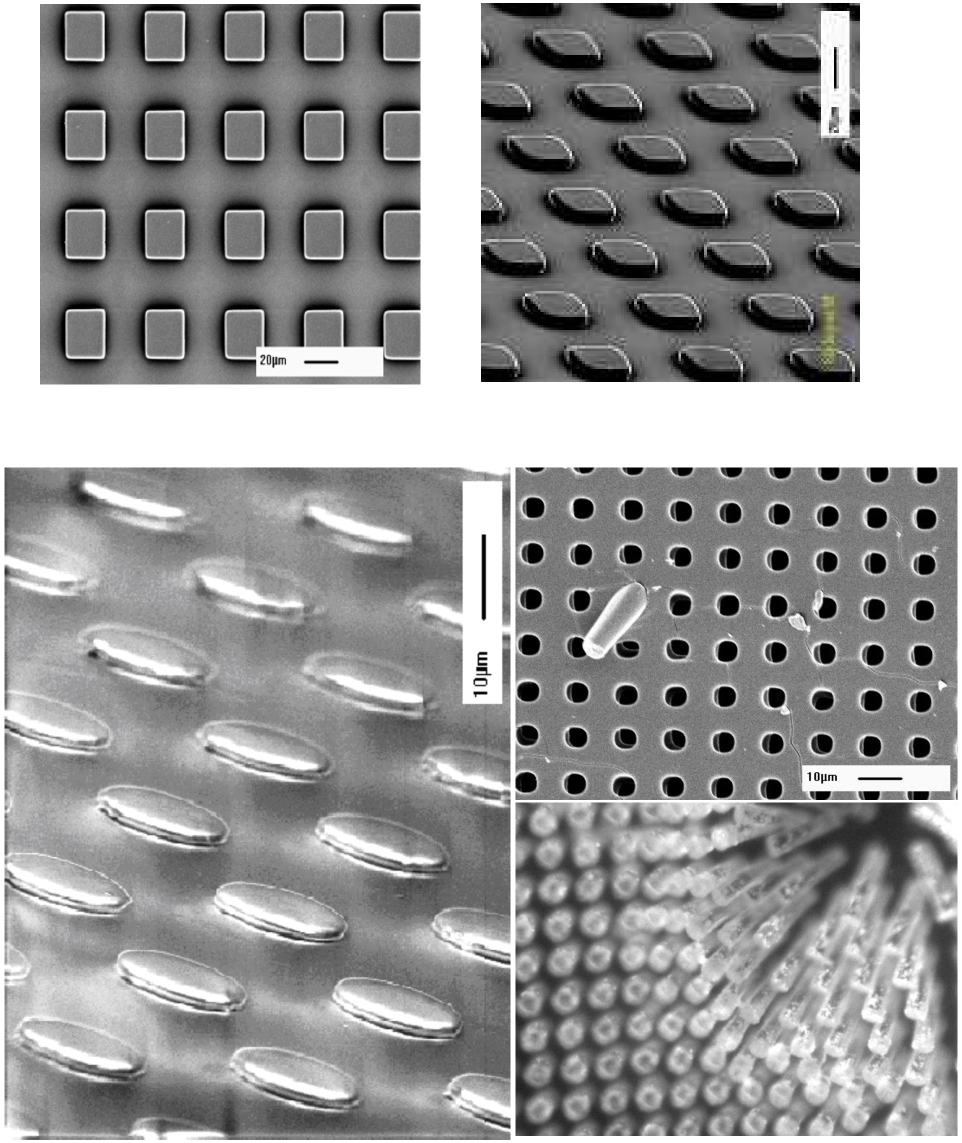
SU-8 Photoresist

Pillars or Holes

- 2-30 μm diameters
- Square lattices
- Different shapes
- Height varied 0 to 30 μm
- *(bottom image is 4 μm pattern)*

Maxtek and Network Analyser

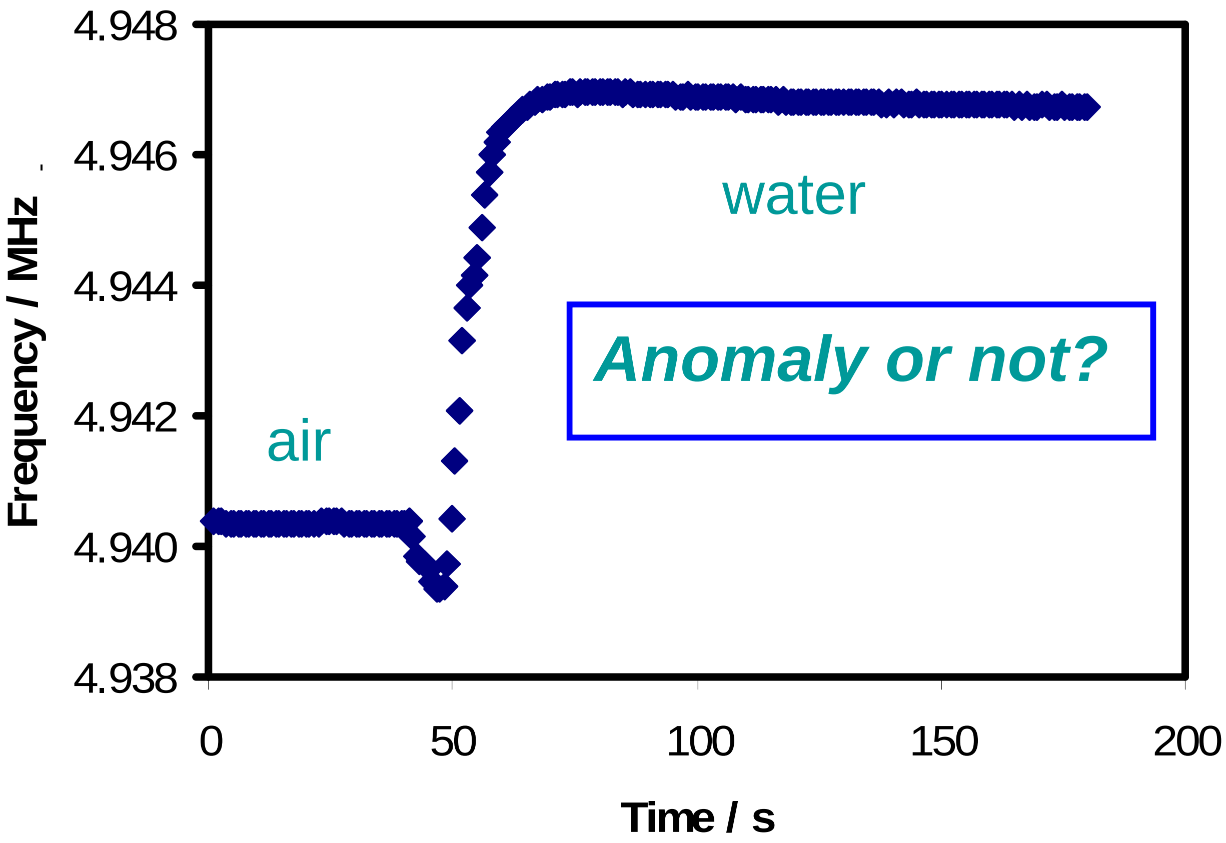
SEM Images



Super-hydrophobic QCR - First View

- Effect on QCR?

Response in air versus response in water (Maxtek system)



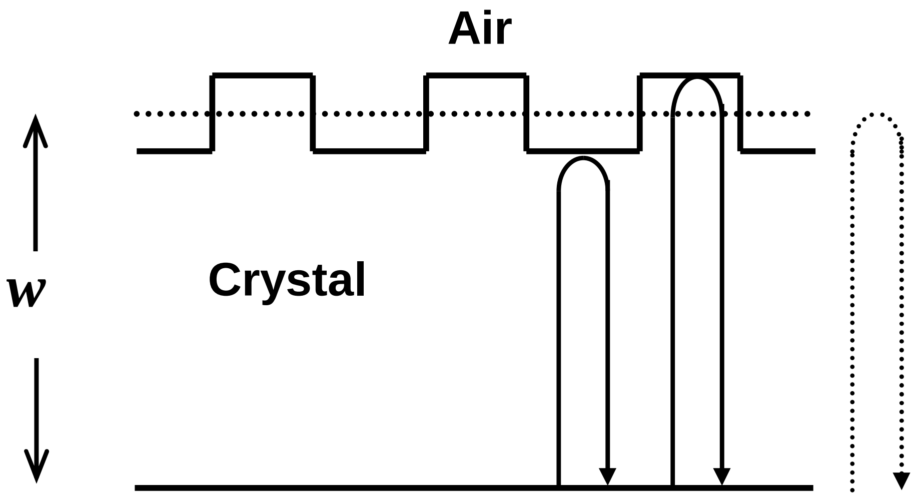
- Is it possible to have a positive frequency shift?

A Mechanism for Positive Frequency Shifts?

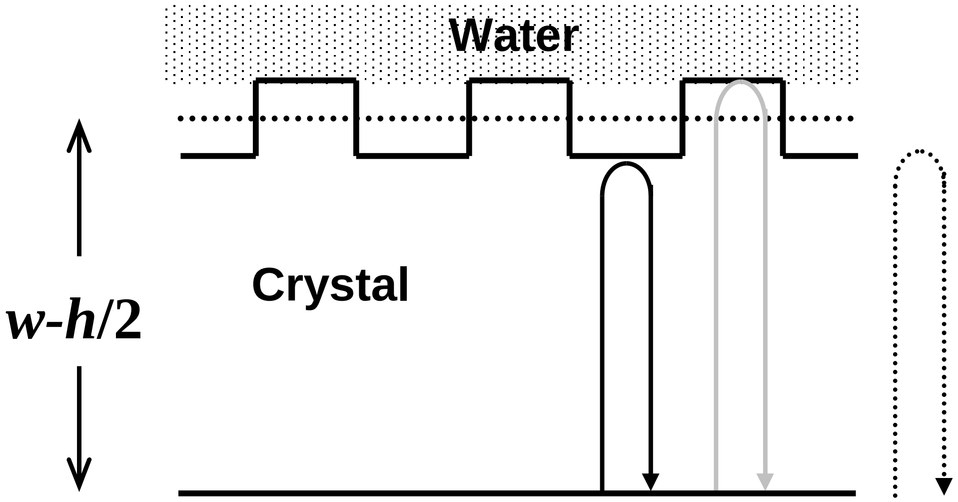
- Effective Acoustic Cavity Length

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

$v=f\lambda$ ⇒ f increases

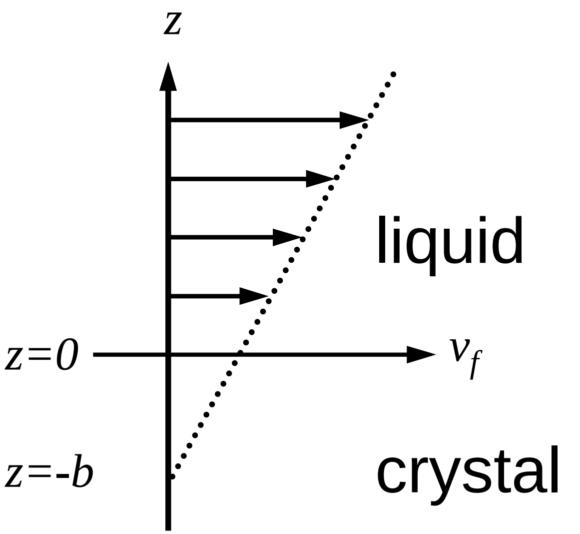
“Slip” Boundary Condition

- Average Position of Reflecting Interface
  - Slip length, b, to model average position of a rough/diffuse or patterned solid-liquid interface (i.e. not molecular slip)
- Boundary Condition
  - Extrapolate fluid speed gradient from bulk liquid

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

to first order equivalent to condition on stress at interface

$$v_s(z=0) - v_f(z=0) = -b\left(\frac{dv_f}{dz}\right)_{z=0}$$



Negative b

effective interface moves to liquid side of boundary

“Slip” Boundary Condition v Trapped Mass

- Acoustic Impedance
  - 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
  - Kanazawa result for no-slip
  - “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

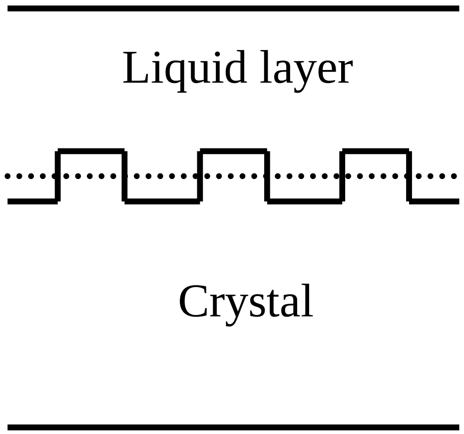
- Negative b and Trapped Mass
  - Define a mass as $\Delta m_f = b\rho_f$

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

Sauerbrey result for “rigid” liquid mass

Diagrammatic Interpretation

- Negative Slip Length



slip boundary condition

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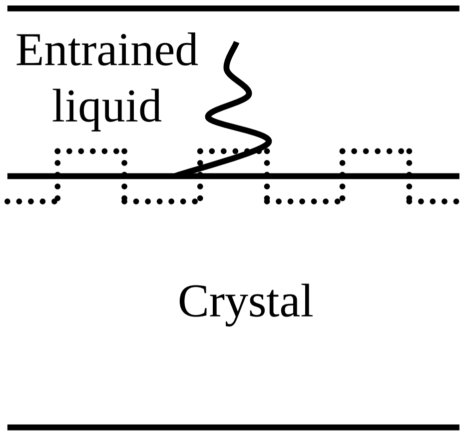
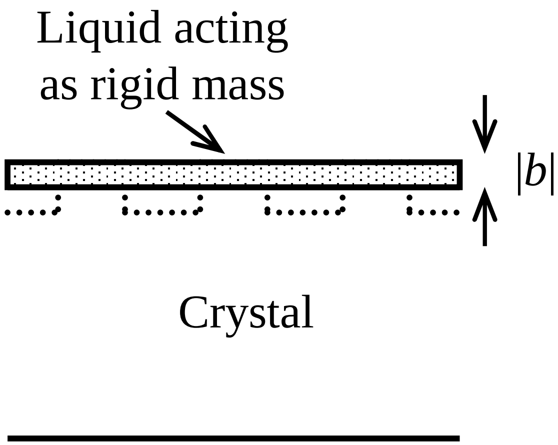
Kanazawa liquid response



no-slip boundary condition

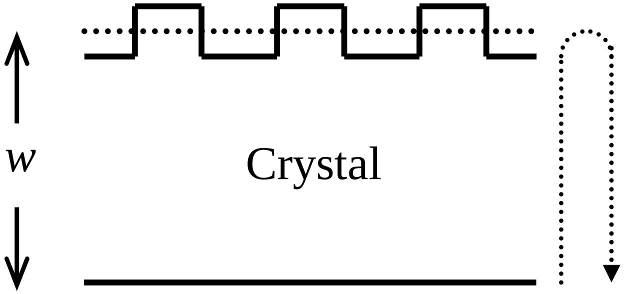
+

Sauerbrey "liquid" mass response



rigid "water" mass layer

- Acoustic Reflection View



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Viscous Entrainment

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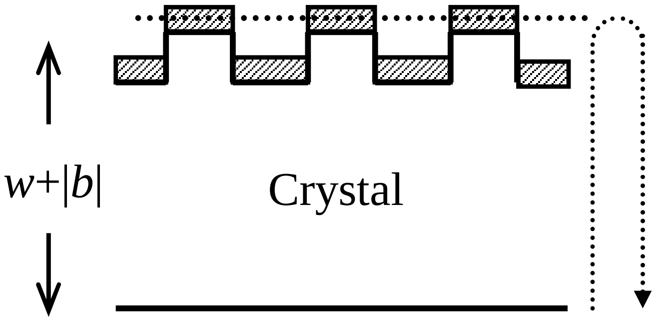


i.e. additional frequency decrease

Order of Magnitude Estimates

- Limitations on “Slip” B.C./Trapped Mass View?
  - Effectively assuming equal reflectivity at peaks and troughs of topography/roughness

  $\Rightarrow$ Cannot necessarily use additivity (liquid entrainment + trapped mass) when air trapping occurs

- Positive Δf?

  Air “trapping” increasing f versus entrainment decreasing f?

- Effective QCR Cavity Lengths, w

  $v=f\lambda \quad \Rightarrow \quad \Delta w/w = -\Delta f/f$ (*v* approx constant)

  f = 5 MHz w = 330 μm

Δw	$\lvert \Delta f \rvert$
100 Å	150 Hz
100 nm	1.5 kHz
1 μm	15 kHz
10 μm	150 kHz

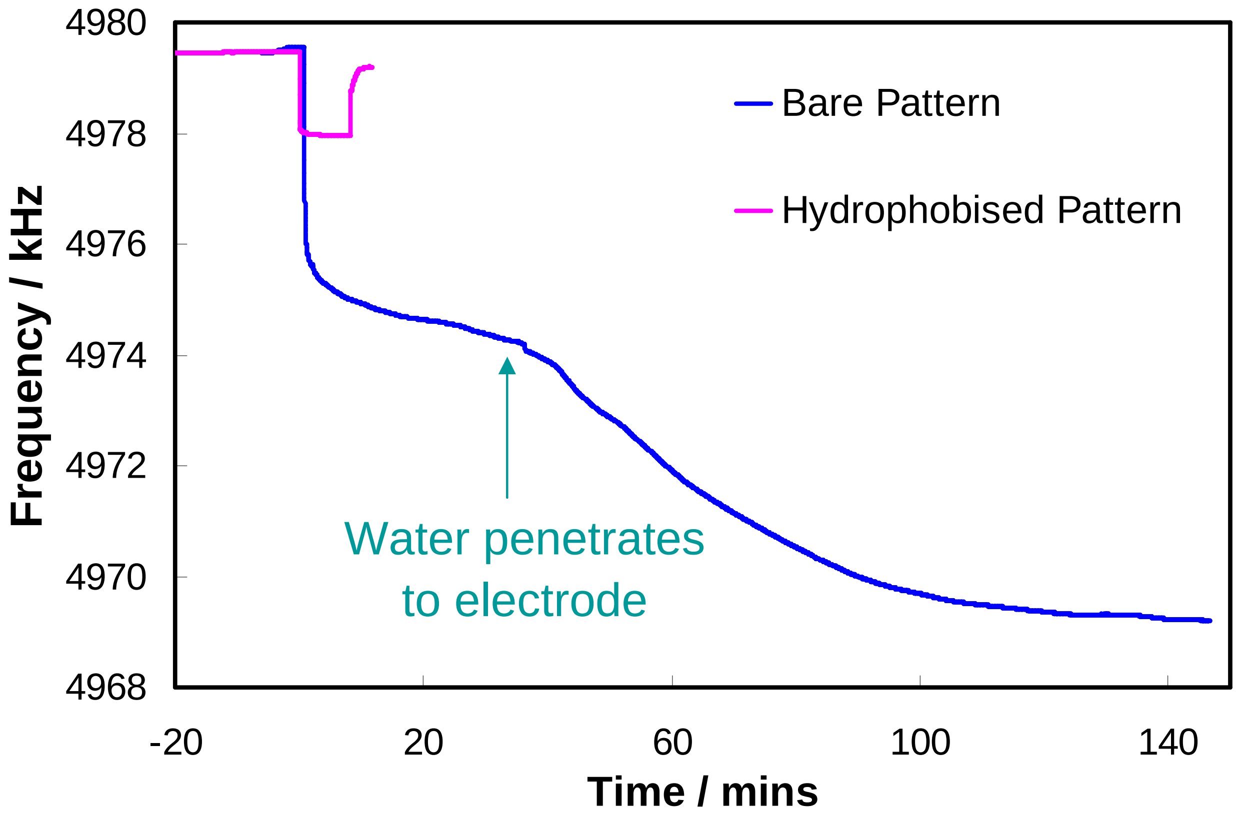
Liquid Penetration of Patterned QCR

- Non-hydrophobised Pillars on QCR

  5 µm diameter and 8 µm high

  Response to water (Maxtek)

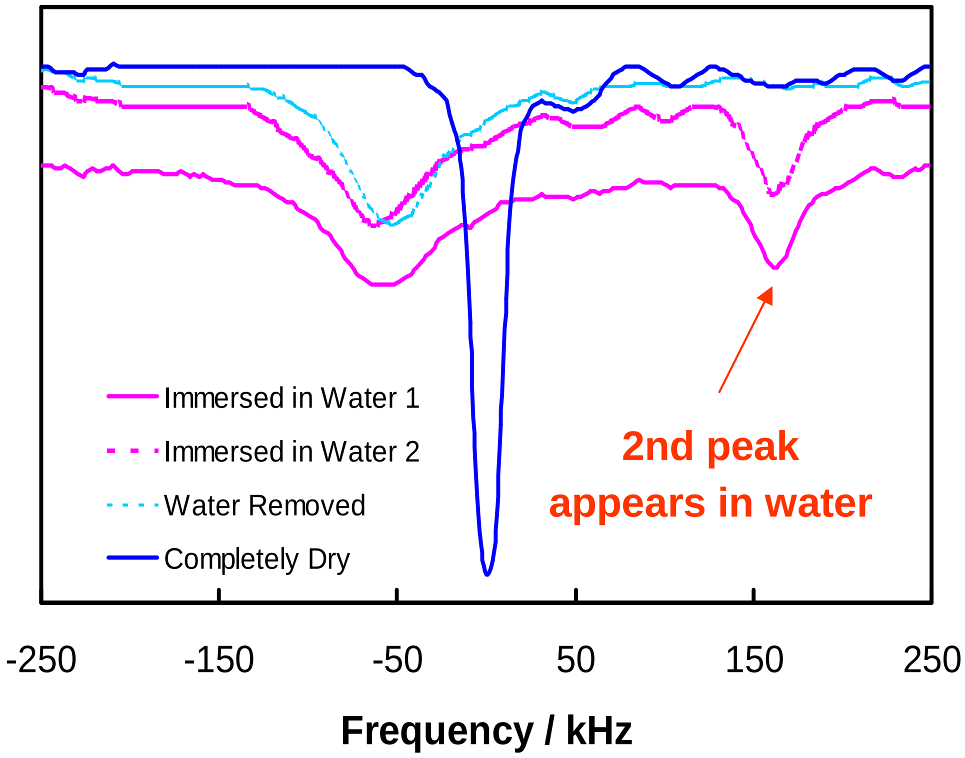
  Response changes as water penetrates into pattern from edge



Super-hydrophobic QCR

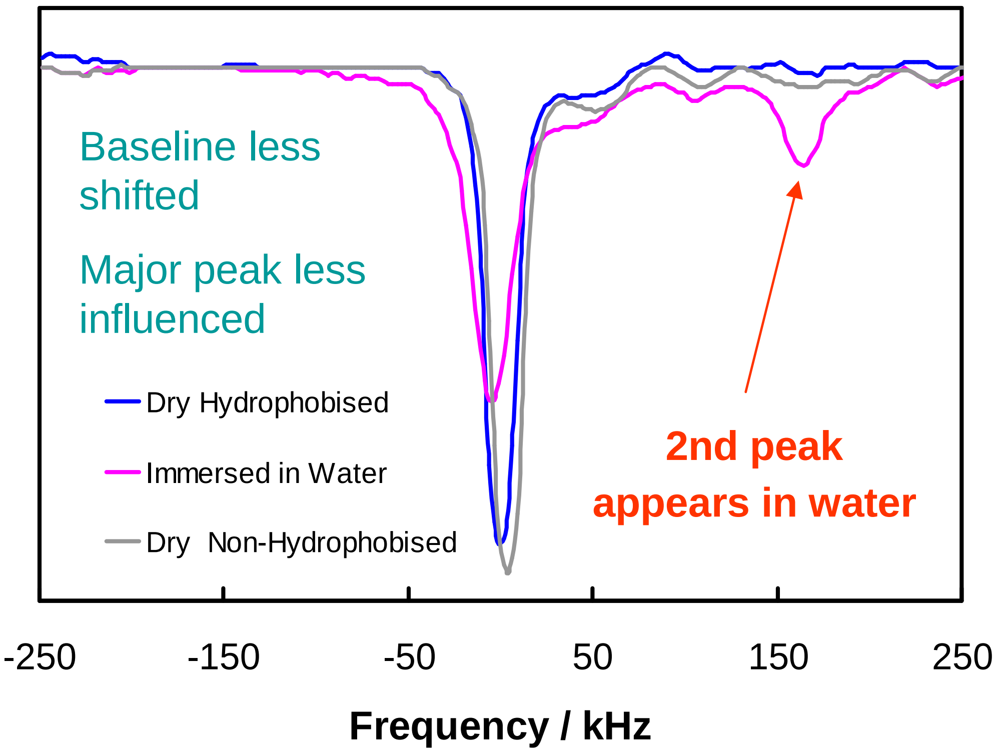
- Pattern Composed of Holes (& Network Analyser)

Non-hydrophobised



2nd peak appears in water

Hydrophobised



Baseline less shifted

Major peak less influenced

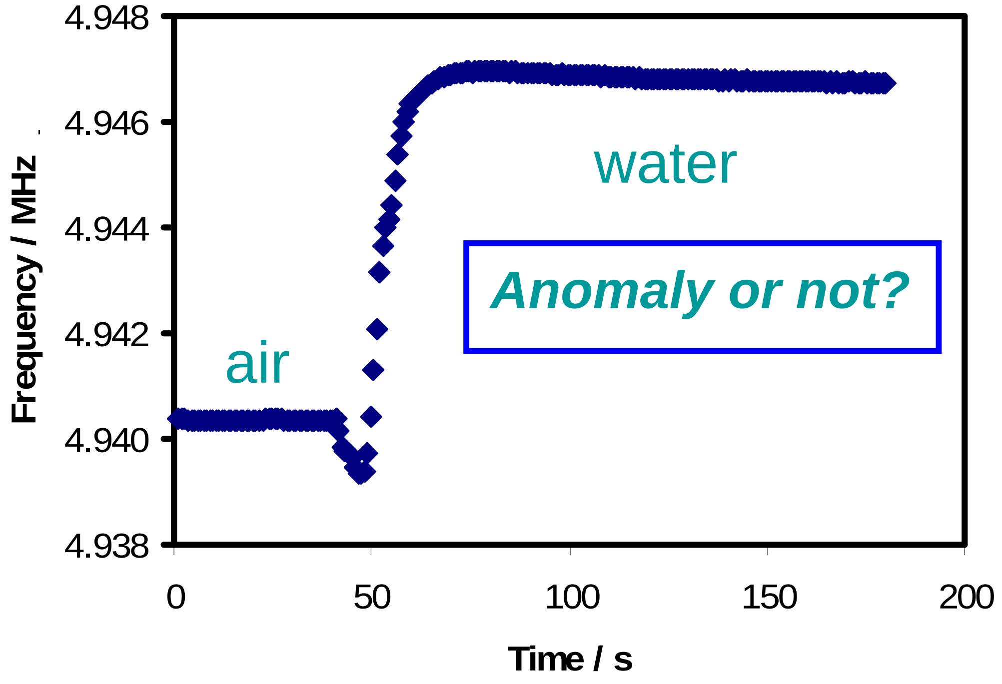
2nd peak appears in water

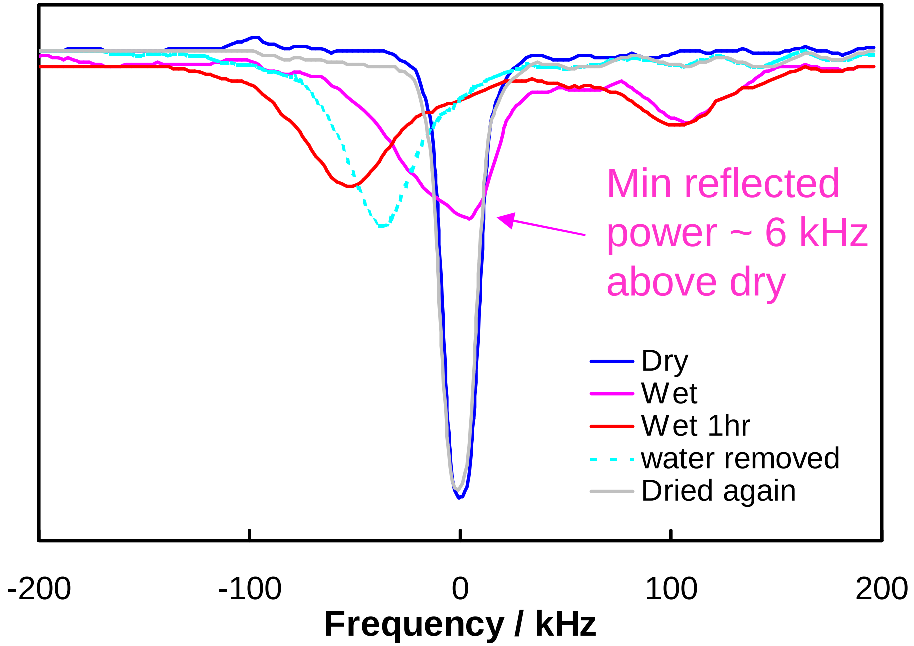
Single resonance in air, but double resonance in water

Positive Frequency Shift - Anomaly?

- Recall the Anomaly

Spectrum measured months later using same device





- Micro-roughness?

For small peak-trough separation, double resonance will merge and distort shape of peak in water. Double resonance only occurs in liquid. Peak in water may appear to have higher *f* than in air.

Conclusions

Achievements

- Controlled Surface Structure
  - Super-hydrophobic surfaces
- Concept of Acoustic Reflection
  - Applied to patterned surfaces
- “Slip” Boundary Condition
  - Negative length = trapped mass
- Preliminary QCR Measurements
  - Network analyser v Maxtek

Comments

- Micron Length/Height Scales
  - Applied to QCR
- Positive Frequency Shifts?
  - Entrainment versus cavity length
- “Trapped” Air?
  - Reflectivity of peaks v troughs
- Resonances
  - Double resonance in liquid

The End

Acknowledgements

- Gordon Hayward and Jon Ellis
  - Matching slip length to slip parameter in boundary condition
- Mike Thompson and Richard Cernosek
  - Wetting, slip and diffuse interface concepts
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  - Air trapping and wetting
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  - Maxtek QCM experiments