Hydrophobic Effects and Acoustic Wave Response

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Overview

1. Ideas

- Contact angles and cavity lengths
- Molecular slip
- Surface structure
- Diffuse boundaries

2. Models & Interpretations

- Effective acoustic interface
- Sauerbrey "liquid mass"
- Acoustic reflections

3. Experiments & Results

- QCR surfaces with pillars
- Pillars and hydrophobicity

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Hydrophobic Effects

Key Ideas

Liquids Response and Modelling

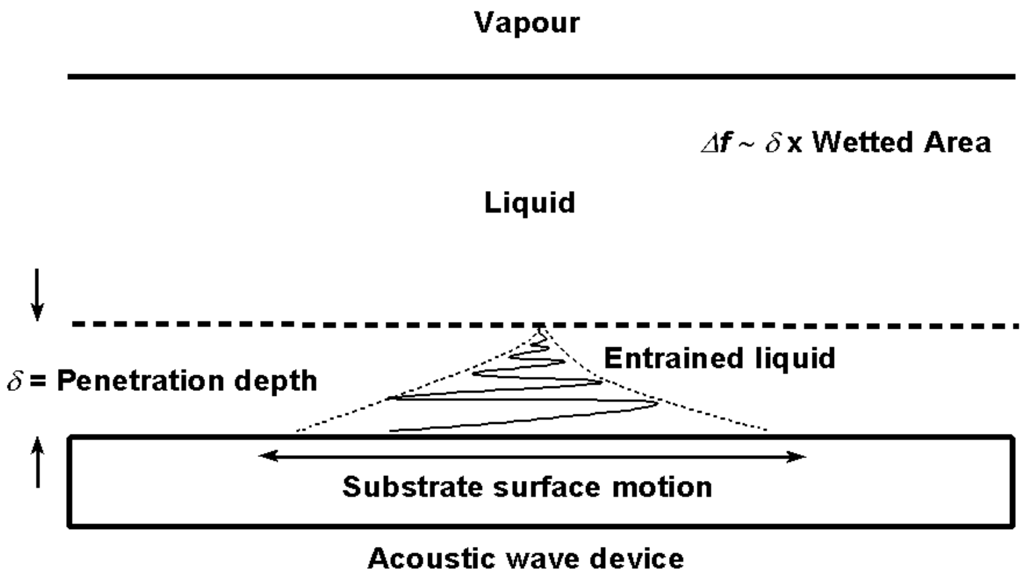
Shear Mode Vibration

Entrains liquid

Liquid oscillation decays

Penetration depth

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



Modelling

Navier-stokes equations in liquid (or equivalent ones if a polymer)

Wave equations in solid

Vanishing stress at liquid surface

Match speeds at solid-liquid boundary

→ Kanazawa-Gordon & Sauerbrey/Polymer Models

Assumes i) matching of speeds at physical location of boundary

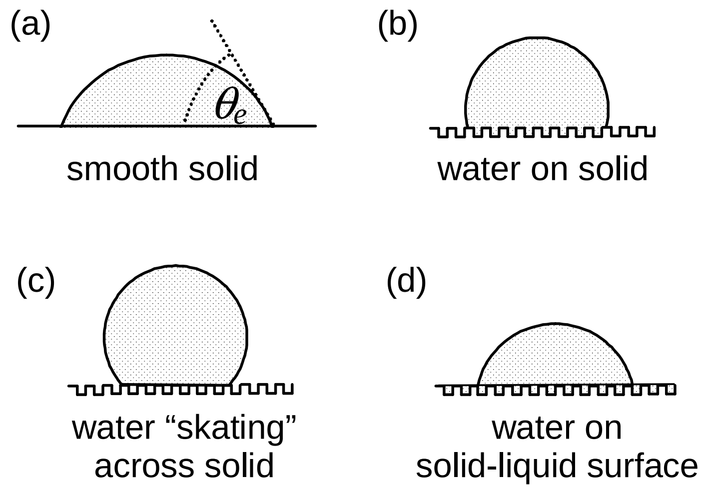
and ii) uniform solid-liquid boundary

Contact Angles and Cavity Lengths

Contact Angle

Indicates relative interfacial energies

Ability to penetrate surface features



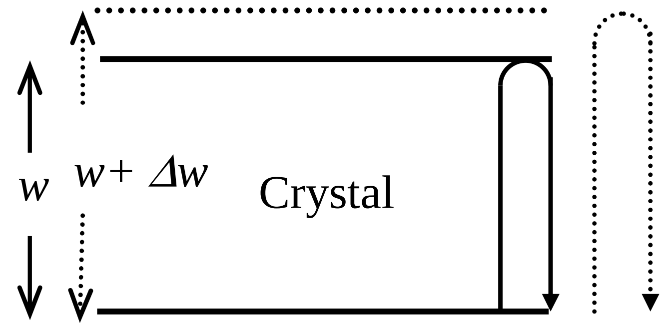
Resonant Cavity

QCM as standing wave cavity with □$w=\lambda/2$

Added mass moves effective boundary

Added liquid moves effective boundary by ~ penetration depth

Sauerbrey and Kanazawa-Gordon Eqns follow



Effective cavity smaller ⇒ higher frequency

Effective cavity larger ⇒ lower frequency

Potential Problems 1 – Molecular Slip

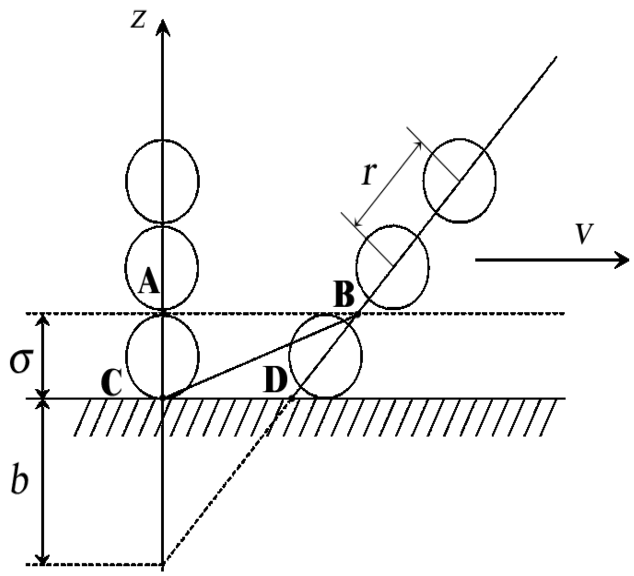
Molecular Slip

Surface mobility is different to bulk

Blake-Tolstoi theory

Surface-to-bulk mobility

$$\frac{u_s}{u} = \exp\left[\alpha A \gamma^{LV} (1 - \cos\theta)/kT\right]$$



Dependence on contact angle

Slip length b

$$b = r\left(\exp\left[\alpha A \gamma^{LV} (1 - \cos\theta)/kT\right] - 1\right)$$

Wetting Case $\theta = 0^o$

Bulk and surface mobility's identical

Slip length vanishes

Friction coefficient $k = \eta_f / b$ infinite

Non-Wetting Case $\theta = 180^o$

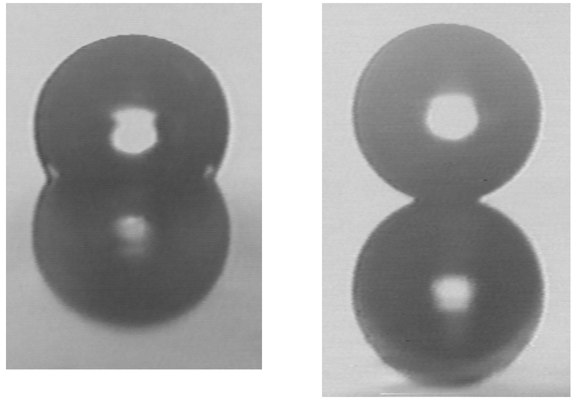
Surface mobility exponentially large

Slip length exists

Friction coefficient $k = \eta_f / b$ reduces

J.S. Ellis, G. McHale, G.L. Hayward & M. Thompson, J APPL PHYS 94 6201-6207 (2003)

Potential Problems 2 – Surface Structure



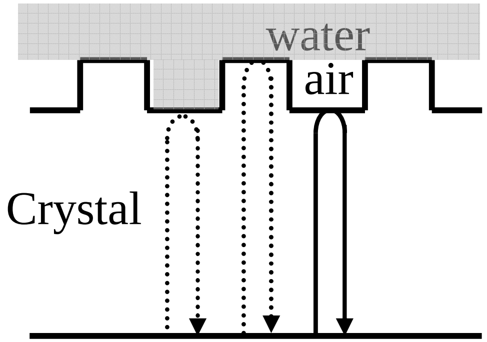
Capillary Penetration

Liquid skates across solid surface

Same hydrophobicity

Different surface structure

Super-hydrophobic effect



Laterally Dependent Acoustic Reflectivity

Multiple cavity lengths

Varying strength of reflection

Change in position of effective acoustic interface

Wetting Case θ=0^o

Reflectivity's at all places equivalent

Effective cavity length is an average

Defines slip length b=0

Non-Wetting Case θ=180^o

Incomplete liquid penetration

Reflectivity changes effective cavity

Slip length b exists

Potential Problems 3 – Diffuse Boundary

Hard Solid-Liquid Interface

Boundary is well-defined so no problems

Examples: QCM as film thickness monitor in vacuum chamber
QCM as viscosity-density sensor in Newtonian liquid
QCM for mass deposition in liquid

Soft Boundary

“Dressed surface”

Example: Surfaces with anchored chains
Vesicles - “Bags of water” in water

Porous-Hard Boundary

Example: Super-fluid resonator cavity with sintered boundary linings

Issue: Effective acoustic interface versus physical boundary

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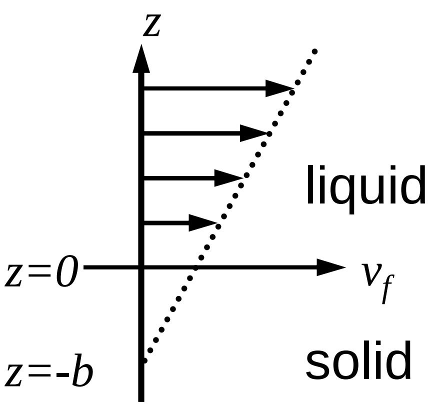
Hydrophobic Effects

Models & Interpretations

Mathematical Formulation of Wall Slip

Flow Profile

With Slip length



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

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

G. McHale, R. Lücklum, M.I. Newton, *et al.*, J APPL PHYS 88, 7304-7312 (2000)
G. McHale & M.I. Newton, J APPL PHYS 95 373-380 (2004)

Slip and Effective Sauerbrey "Liquid Mass"

Equations of Motion

Solve with slip boundary condition[1]

Consider in terms of slip length[2] and interpret solution for small *b*

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 $\Delta m_f = b\rho_f$

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

Sauerbrey result for additional trapped "rigid liquid mass"

[1]G. McHale, R. Lücklum, M.I. Newton, *et al.*, J APPL PHYS 88, 7304-7312 (2000)

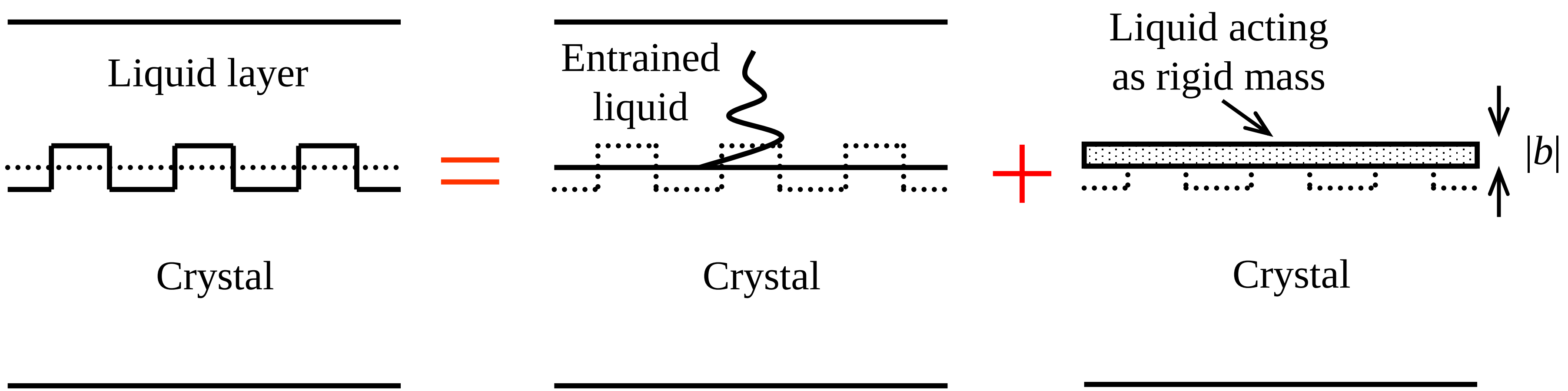
[2]G. McHale & M.I. Newton, J APPL PHYS 95 373-380 (2004)

Pictorial Interpretation

Negative Slip Length

slip boundary condition = no-slip boundary condition + rigid “water” mass layer

(Kanazawa liquid response) (Sauerbrey “liquid mass” response)



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

Hydrophobic Effects

Experiments & Results

Super-Hydrophobic Crystals

Patterned Crystals

SU-8 patterns on 5 MHz quartz crystals

Pillars of 5 μm diameter, 10 μm cnt-cnt

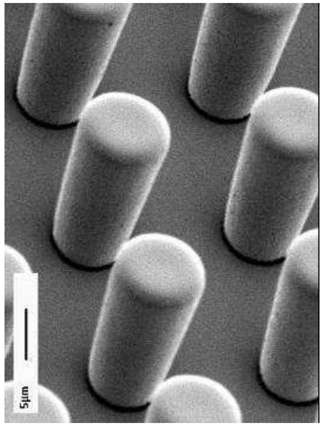
Heights of 3 μm to 10 μm

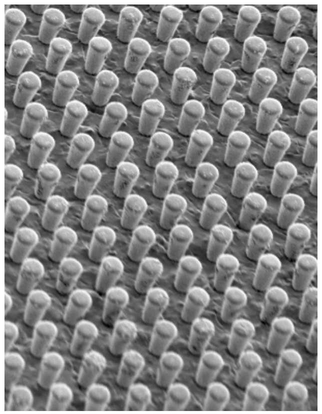
Preliminary Experiments

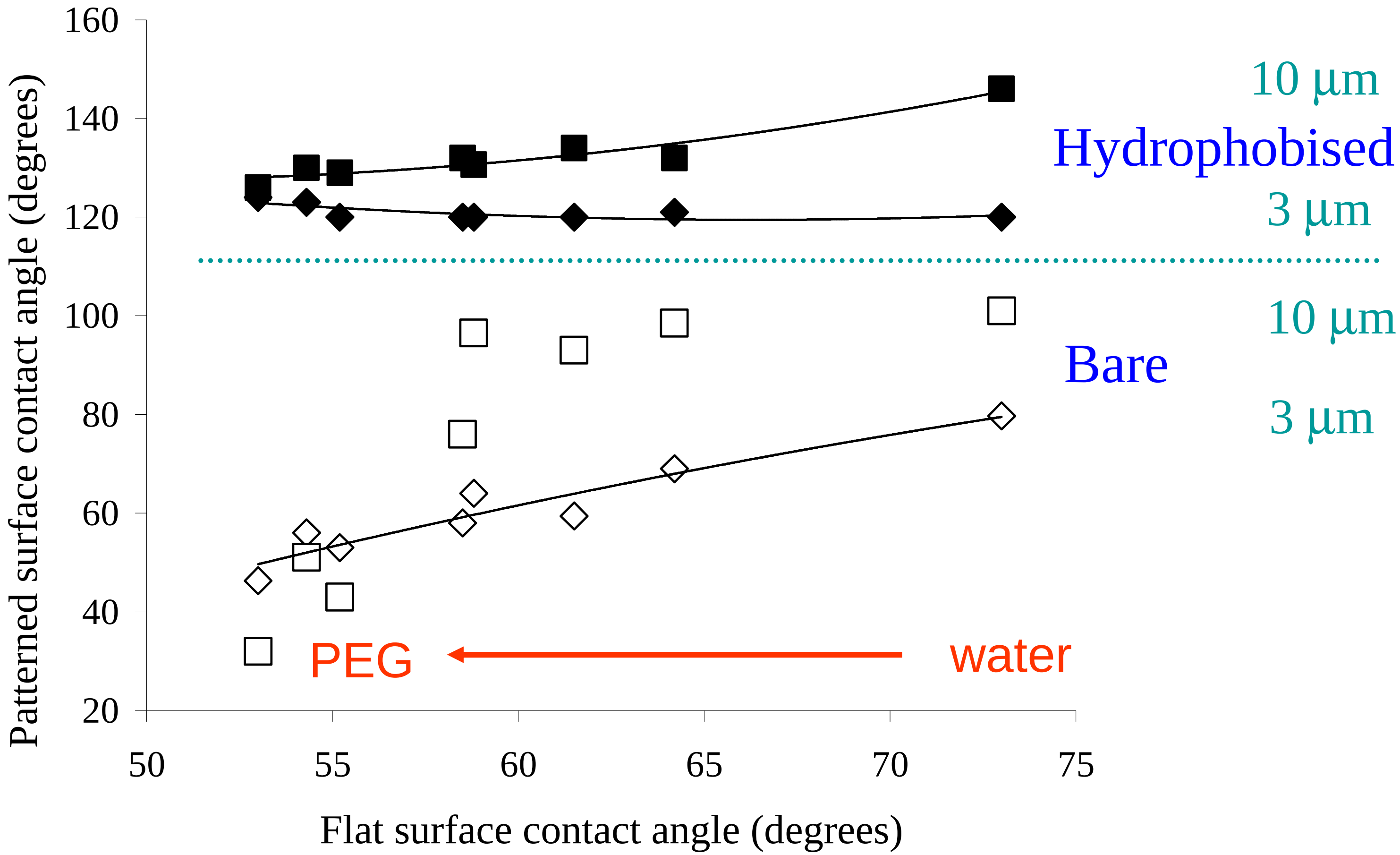
Flat and patterned layers

Bare (70-80°) & hydrophobised (110-120°)

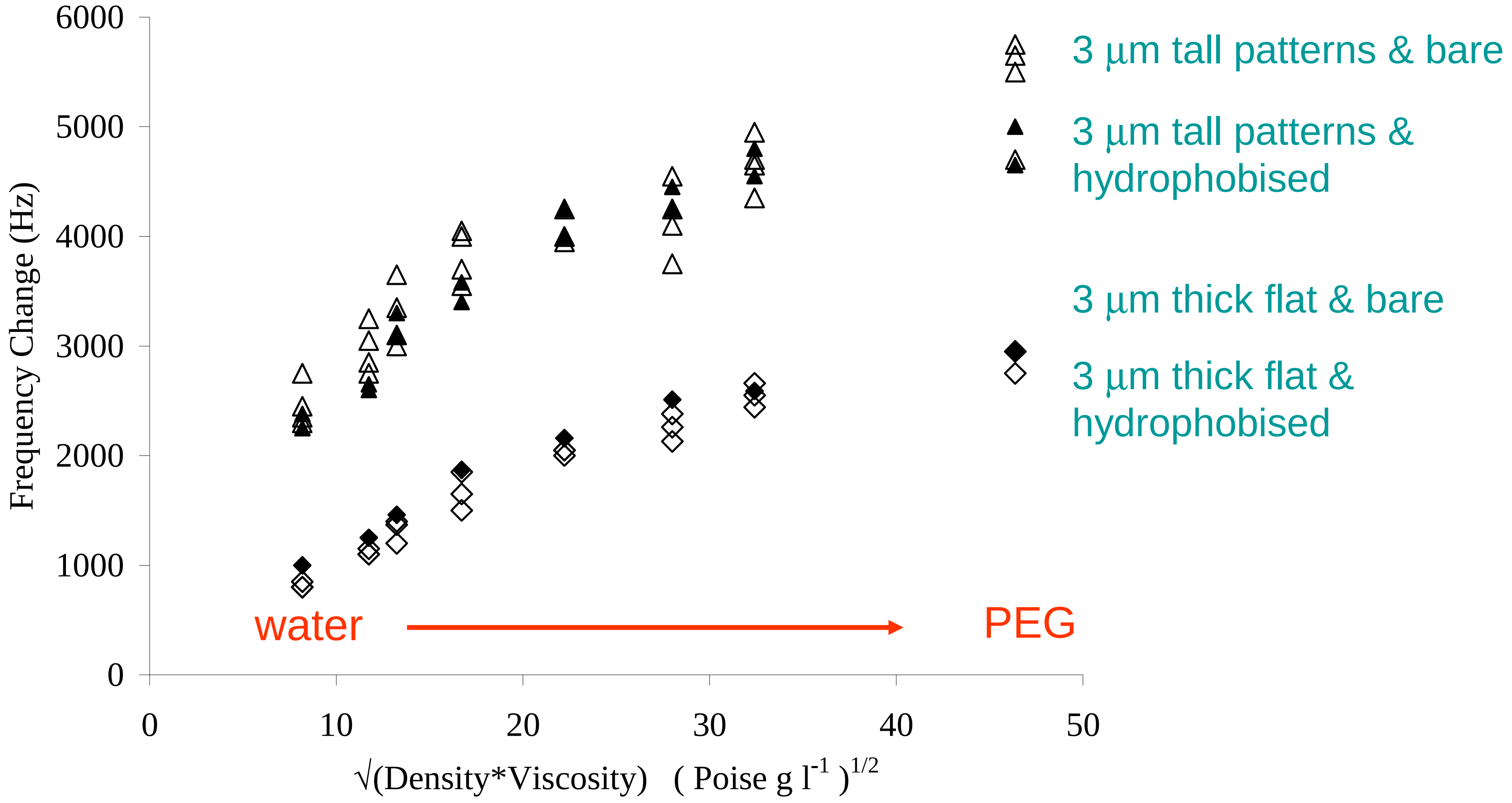
3350 MW PEG solutions 678-20000 mPa s



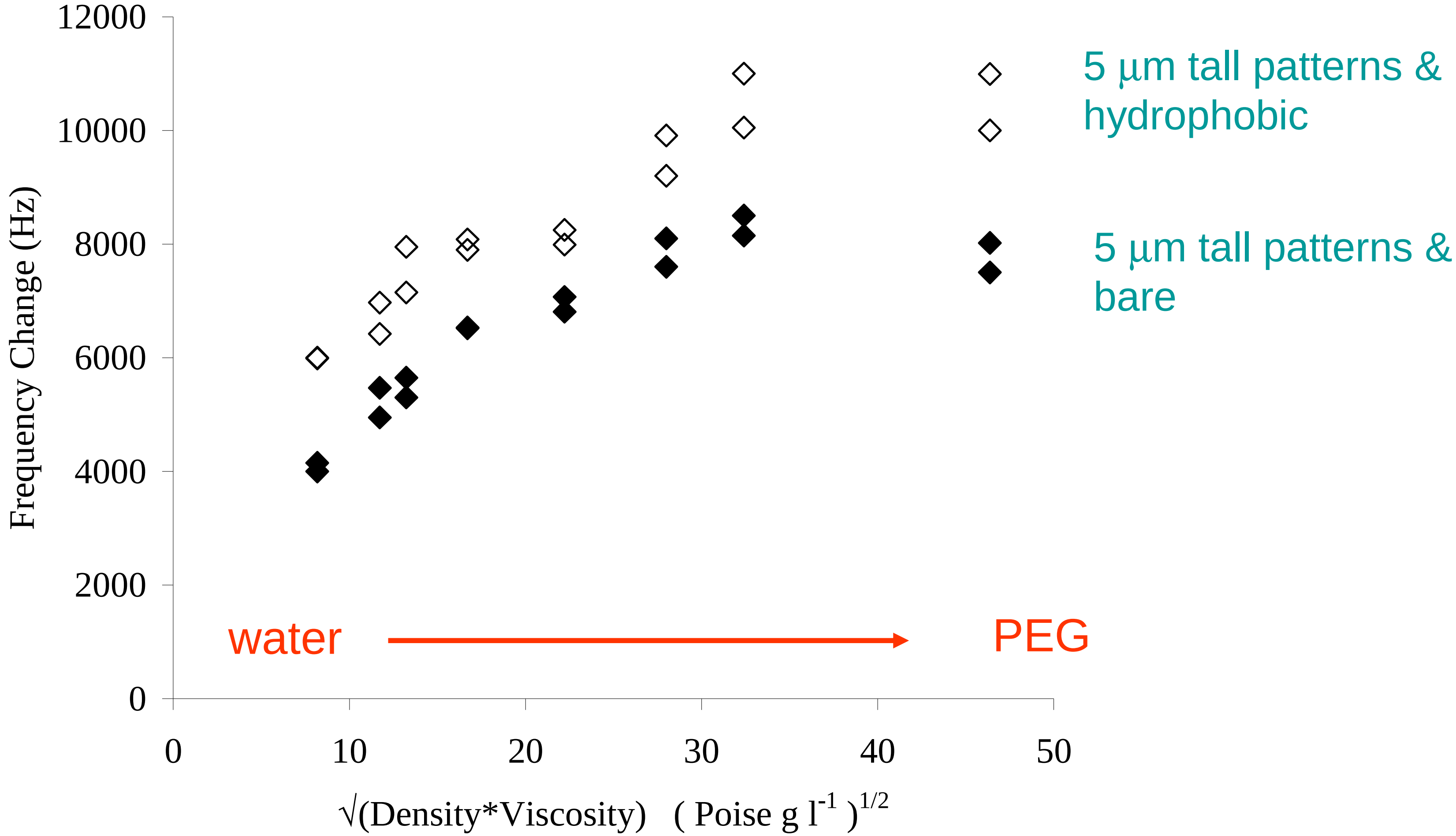




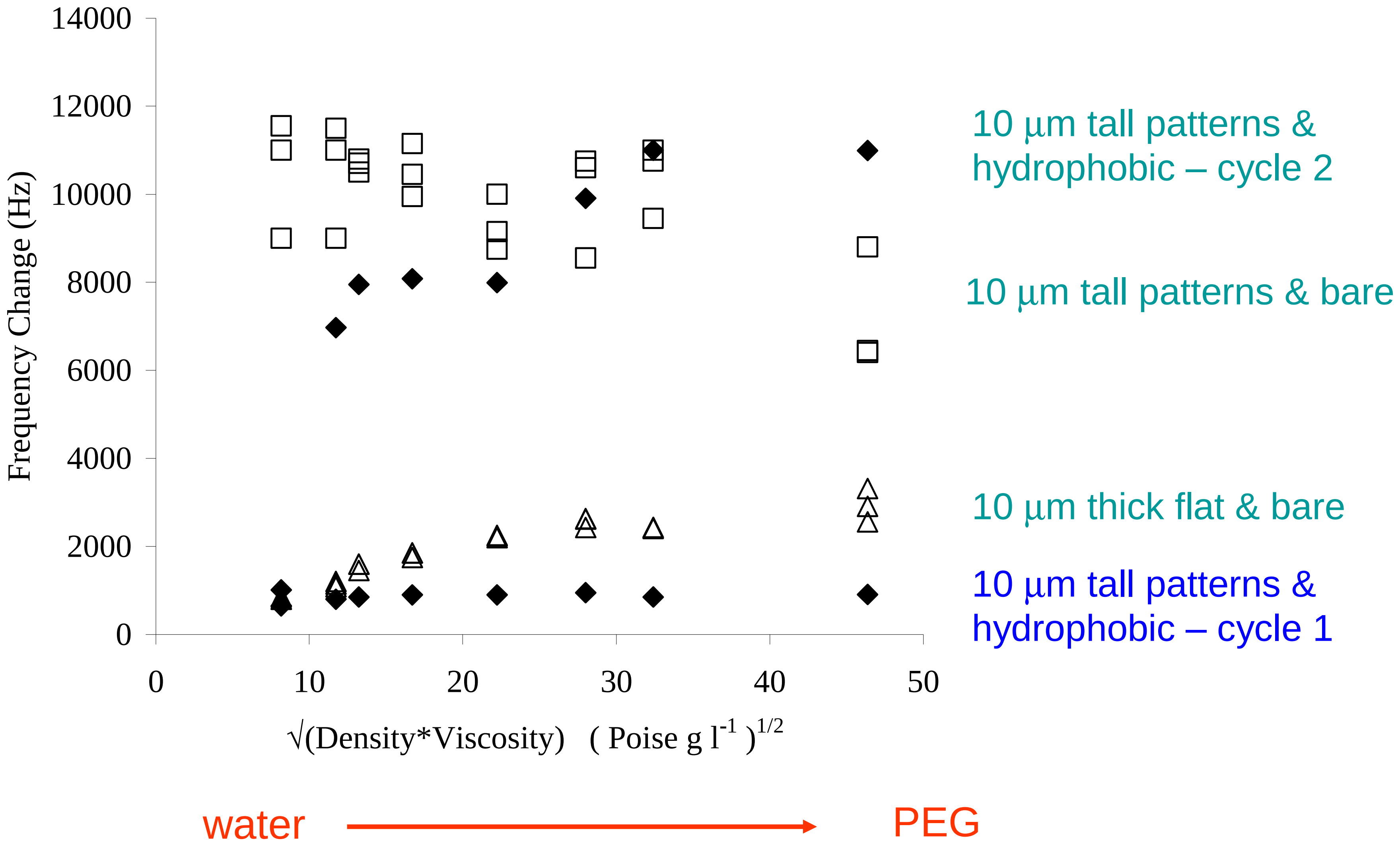
Low Pillar Height QCR Frequency Decrease



Medium Pillar Height Hydrophobic Dependence



Tall Pillar Height Hydrophobic Dependence



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- Mike Thompson, Gordon Hayward and Jon Ellis

  Wetting/Super-hydrophobic QCM, slip and diffuse interface concepts

  Matching slip length to slip parameter in boundary condition

- Richard Cernosek and Lisa Thiesen

  Air trapping and wetting

- Ralf Lücklum

  Slip parameter in boundary condition and wetting concepts

- Mike Newton, Carl Evans and Neil Shirtcliffe

  Super-hydrophobicity

Key References

G. McHale & M.I. Newton, *Surface roughness and interfacial slip boundary condition for quartz crystal microbalances*, J APPL PHYS 95 373-380 (2004)

J.S. Ellis, G. McHale, G.L. Hayward & M. Thompson, *Contact angle-based predictive model for slip at the solid-liquid interface of a transverse-shear mode acoustic wave device*, J APPL PHYS 94 6201-6207 (2003)

G. McHale, R. Lücklum, M.I. Newton, *et al.*, *Influence of viscoelasticity and interfacial slip on acoustic wave sensors*, J APPL PHYS 88, 7304-7312 (2000)

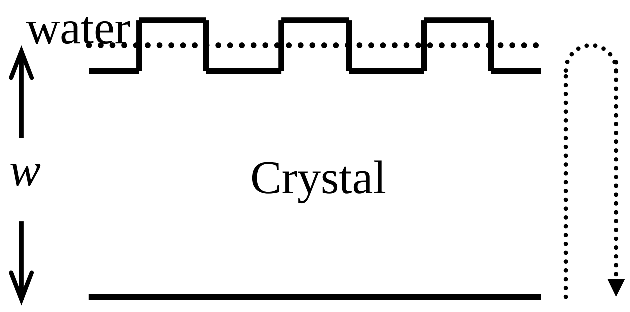
The End

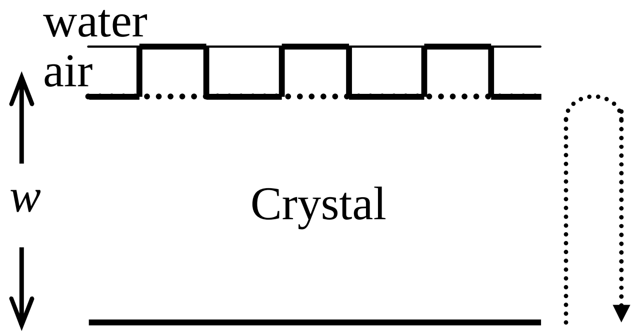
Order of Magnitude Estimates – QCMs

Is Positive Δf Possible?

Possibly, if effective cavity length decreases due to changes in reflectivity

Incomplete liquid penetration versus liquid penetration?





Effective QCM Cavity Lengths, w

$$v = f\lambda \quad \Rightarrow \quad \Delta w/w = -\Delta f/f$$

(v approx constant)

f = 5 MHz and 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

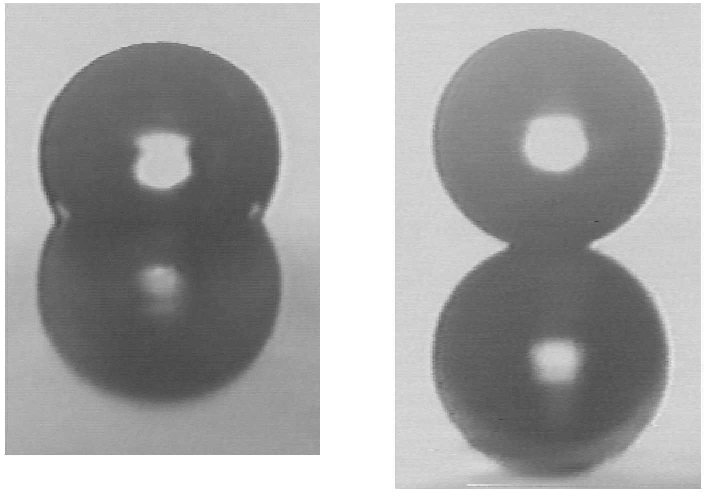
Super-Hydrophobic Surfaces

Contact Angle

Side view images of droplet

Identical chemical functionality

Different topography

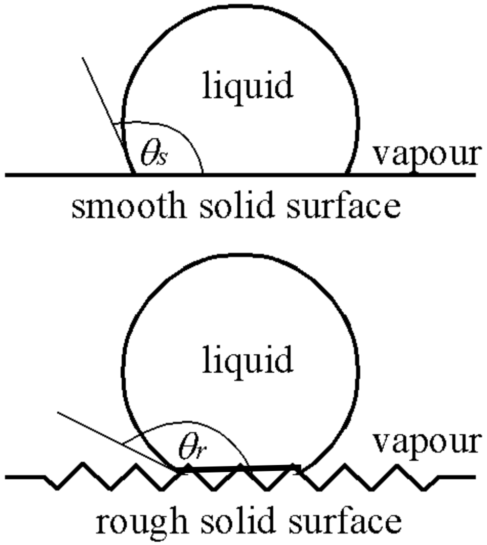


Physical Cause

Surface roughness/ topography

Incomplete liquid penetration (or)

Greater solid-liquid interfacial area



New Sensor Principle

Change hydrophobicity to cause super-hydrophobic transition

Response of QCM/SAW may alter by far more than due to mass change