Hydrophobic Effects and Acoustic Wave Response

Glen McHale
Nottingham Trent University
Nottingham NG11 8NS, UK
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
Hydrophobic Effects

Key Ideas
Liquids Response and Modelling

Shear Mode Vibration

-Entrains liquid
- Liquid oscillation decays
- Penetration depth

\[ \delta = \left( \frac{\eta}{\pi f \rho} \right)^{1/2} \]

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

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 $\lambda/2$
Added mass moves effective boundary
Added liquid moves effective boundary by ~
penetration depth
Sauerbrey and Kanazawa-Gordon Eqns follow

$\theta_e$

Effective cavity smaller $\Rightarrow$ higher frequency
Effective cavity larger $\Rightarrow$ 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 \( b \)

**Wetting Case \( \theta=0^o \)**

Bulk and surface mobility's identical
Slip length vanishes
Friction coefficient \( k = \eta / b \) infinite

**Non-Wetting Case \( \theta=180^o \)**

Surface mobility exponentially large
Slip length exists
Friction coefficient \( k = \eta / b \) reduces

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** $\theta=0^\circ$
- Reflectivity's at all places equivalent
- Effective cavity length is an average
- Defines slip length $b=0$

**Non-Wetting Case** $\theta=180^\circ$
- 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
Hydrophobic Effects

Models & Interpretations
Mathematical Formulation of Wall Slip

Flow Profile

With Slip length

Equations

Match speeds

Expand

Force exerted on wall divided by viscosity

Slip length, $b$, models effective position of interface
Negative $b$, effective interface moves to liquid side of boundary

Slip Length

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

**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 \(b/\delta\)

\[
\left( \frac{\Delta \omega}{\omega} \right)_{\text{slip}} \approx \left( \frac{\Delta \omega}{\omega} \right)_{\text{no slip}} \left( 1 - \frac{2b}{\delta} \right)
\]

Slip length to penetration depth ratio

**Negative Slip Length**
Define a liquid mass as \(\Delta m_f = b \rho_f\)

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

**Sauerbrey result for additional trapped “rigid liquid mass”**


Pictorial Interpretation

**Negative Slip Length**

\[
\text{slip boundary condition} = \text{no-slip boundary condition} + \text{rigid “water” mass layer}
\]

(Kanazawa liquid response) \quad \text{(Sauerbrey “liquid mass” response)}
Acoustic Reflection View

Substrate Supports Standing Waves

Cavity length increases $\Rightarrow$ 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

\[ \sqrt{\text{Density} \times \text{Viscosity}} \quad \text{(Poise g l}^{-1})^{1/2} \]

- 3 \( \mu \)m tall patterns & bare
- 3 \( \mu \)m tall patterns & hydrophobised
- 3 \( \mu \)m thick flat & bare
- 3 \( \mu \)m thick flat & hydrophobised

Water

PEG
Medium Pillar Height Hydrophobic Dependence

\[ \sqrt{\text{Density} \times \text{Viscosity}} \quad (\text{Poise} \text{ g l}^{-1})^{1/2} \]

- 5 \(\mu\)m tall patterns & hydrophobic
- 5 \(\mu\)m tall patterns & bare

**Graph:***
- Frequency Change (Hz) on the y-axis,
- \(\sqrt{\text{Density} \times \text{Viscosity}}\) on the x-axis,
- Two types of patterns: 5 \(\mu\)m tall & hydrophobic, 5 \(\mu\)m tall & bare,
- Water and PEG indicated.
Tall Pillar Height Hydrophobic Dependence

Frequency Change (Hz) vs. \( \sqrt{(\text{Density} \times \text{Viscosity}) \ (\text{Poise g l}^{-1})^{1/2}} \)

- 10 µm tall patterns & hydrophobic – cycle 2
- 10 µm tall patterns & bare
- 10 µm thick flat & bare
- 10 µm tall patterns & hydrophobic – cycle 1

Water → PEG
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  Slip parameter in boundary condition and wetting concepts

• Mike Newton, Carl Evans and Neil Shirtcliffe
  Super-hydrophobicity

Key References


The End
**Is Positive $\Delta f$ Possible?**

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

Incomplete liquid penetration versus liquid penetration?

**Effective QCM Cavity Lengths, $w$**

$$v = f \lambda \quad \Rightarrow \quad \frac{\Delta w}{w} = -\frac{\Delta f}{f}$$

($v$ approx constant)

| $\Delta w$   | $| \Delta f |$       |
|--------------|----------------------|
| 100 Å        | 150 Hz               |
| 100 nm       | 1.5 kHz              |
| 1 \( \mu m \) | 15 kHz               |
| 10 \( \mu m \)| 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