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Rippling, Structuring and Wrinkling Solid and Liquid Surfaces

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Overview

1. Rippling Surfaces: Layer-Guided Acoustic Waves
    - Sensing principles, modes and devices
    - Love waves and acoustic plate modes
    - Sensor research examples
2. Structuring Surfaces: Topography and Wetting
    - Hydrophobicity and superhydrophobicity
    - Anti-adhesive surfaces and adhesive liquids
    - Superspreading and hemi-wicking
3. Wrinkling Surfaces: Films and Liquid-based Optics
    - Liquid-based diffractive optics

Rippling Surfaces

Basics of Acoustic Waves

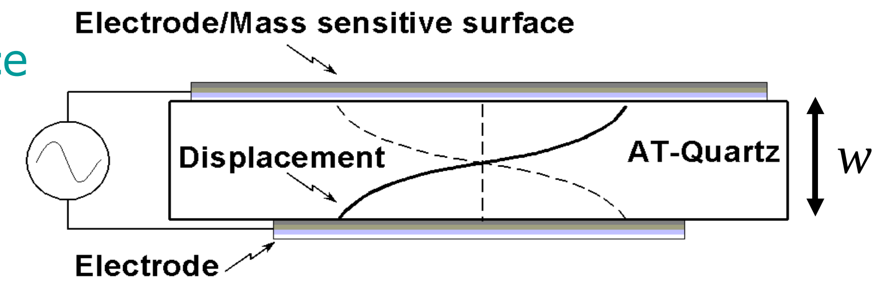
QCM Sensing Principles

Thickness Shear Mode Vibration

Quartz **C**rystal **M**icrobalance - sharp resonance

Frequency given by quartz thickness, w

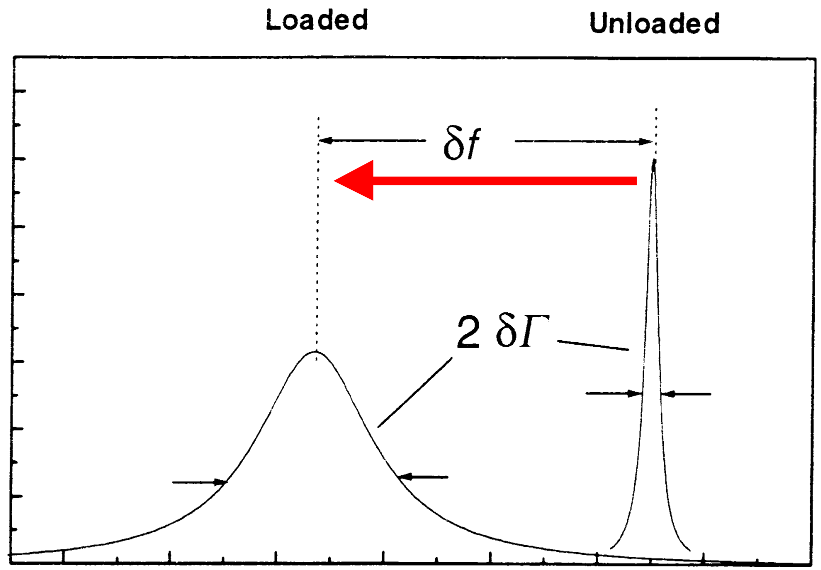
$v_s = f\lambda \quad \Rightarrow \quad f = 2v_s/w$



Mass Loading or Immersion

Frequency reduces due to mass

Resonance broadens due to polymer/liquid



Sauerbrey equation $\Rightarrow \Delta f \propto -f^2 \Delta m/A$

Kanazawa & Gordon $\Rightarrow \Delta f \propto -\sqrt{(\eta\rho)}\, f^{3/2}$

Sensitivity to mass or viscosity-density product increases with frequency

Liquids and Penetration Depth

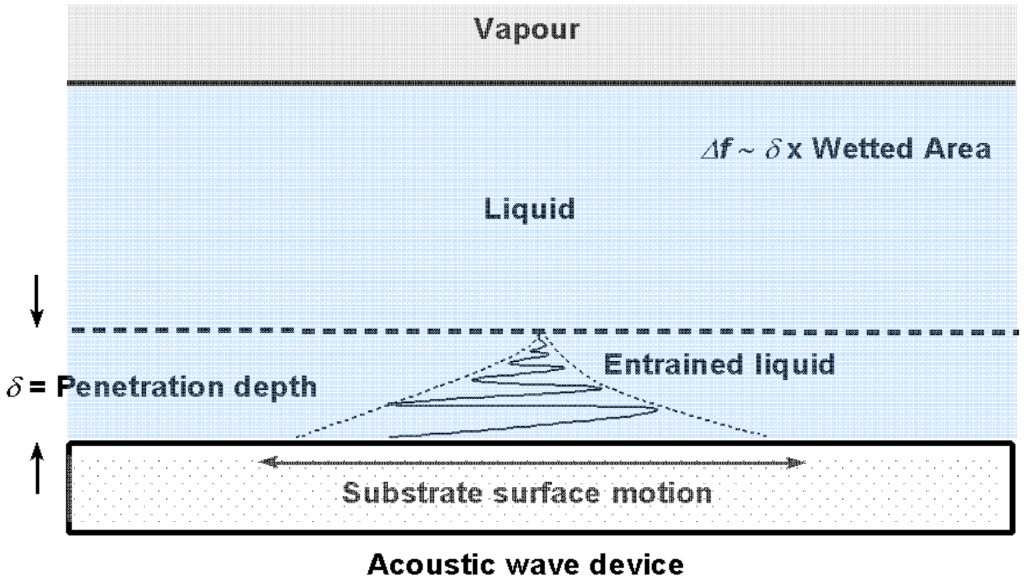
Shear Mode Vibration

Entrains liquid

Liquid oscillation decays

Penetration depth

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



Liquid Sensing

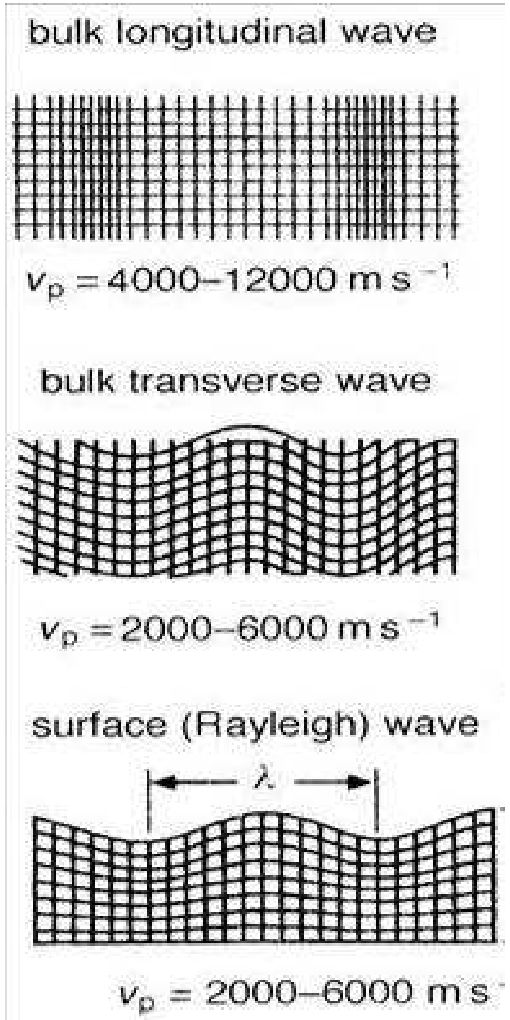
Sense liquid mass (via viscosity-density product) within penetration depth

	QCM		SAW	
For water	5 MHz	$\delta \sim$ 250 nm	500 MHz	$\delta \sim$ 25 nm

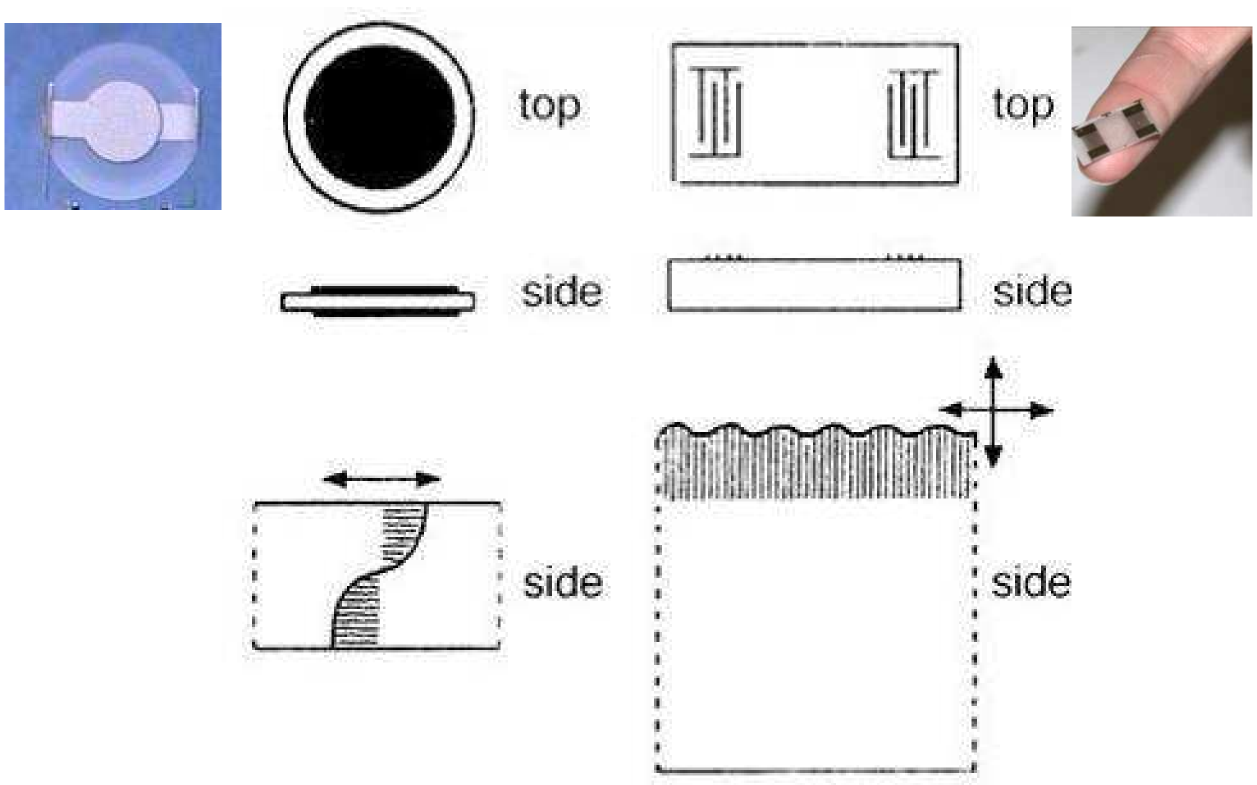
Penetration depth/sensing zone decreases with increasing frequency

Surface Acoustic Waves

Vibrations



QCM versus SAW

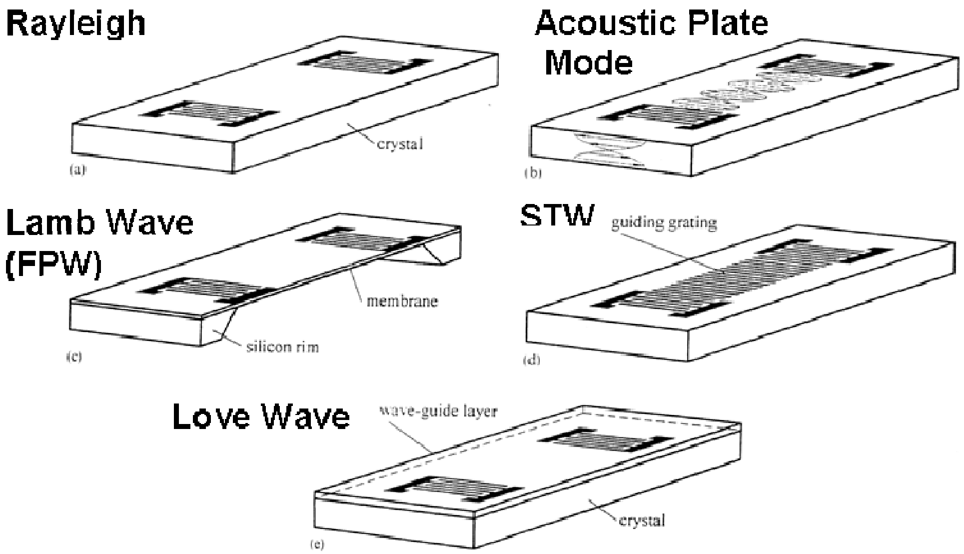


QCM – frequency determined by crystal thickness

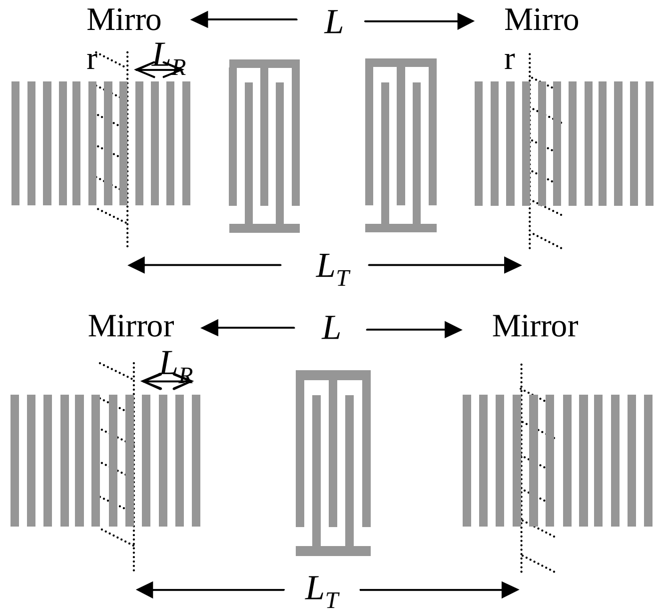
SAW – frequency determined by finger spacing

Acoustic Wave Modes

Delay Lines



Resonators



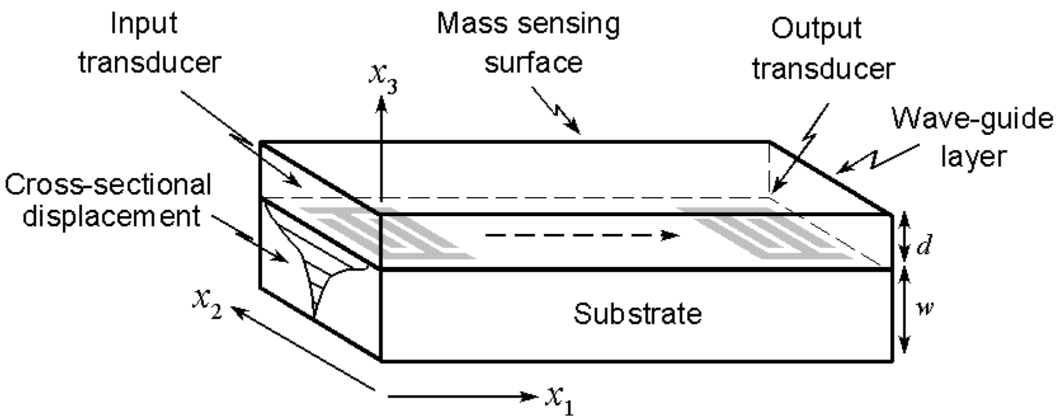
Comparisons

Mode	Rel. Sens.	Complexity	Robustness	Gas/Liquid
QCM	Low	Low/Xtal	Med	g+l
SAW	High	Med/metal on Xtal	High	g
Love	High	Med/film+metal+Xtal	High	g+l
STW	High	Med/metal on Xtal	High	g+l
Lamb	High	High/membrane	Low	g+l
APM	Med	Med/metal on Xtal	Med	g+l

Layer-guided Acoustic Waves

Love Waves versus SH-Acoustic Plate Modes

Love Wave

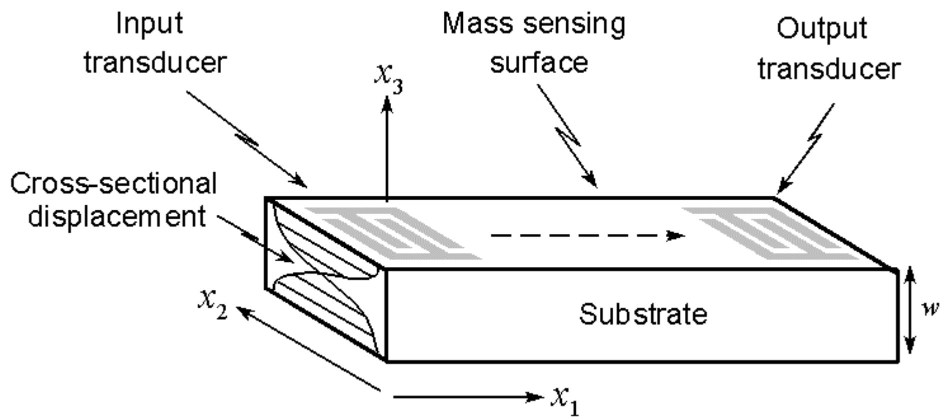


Layer guided SH-SAW with $v_l < v_s$

Surface localised wave

Increased sensitivity

SH-APM



"QCM with propagation"

Substrate resonance

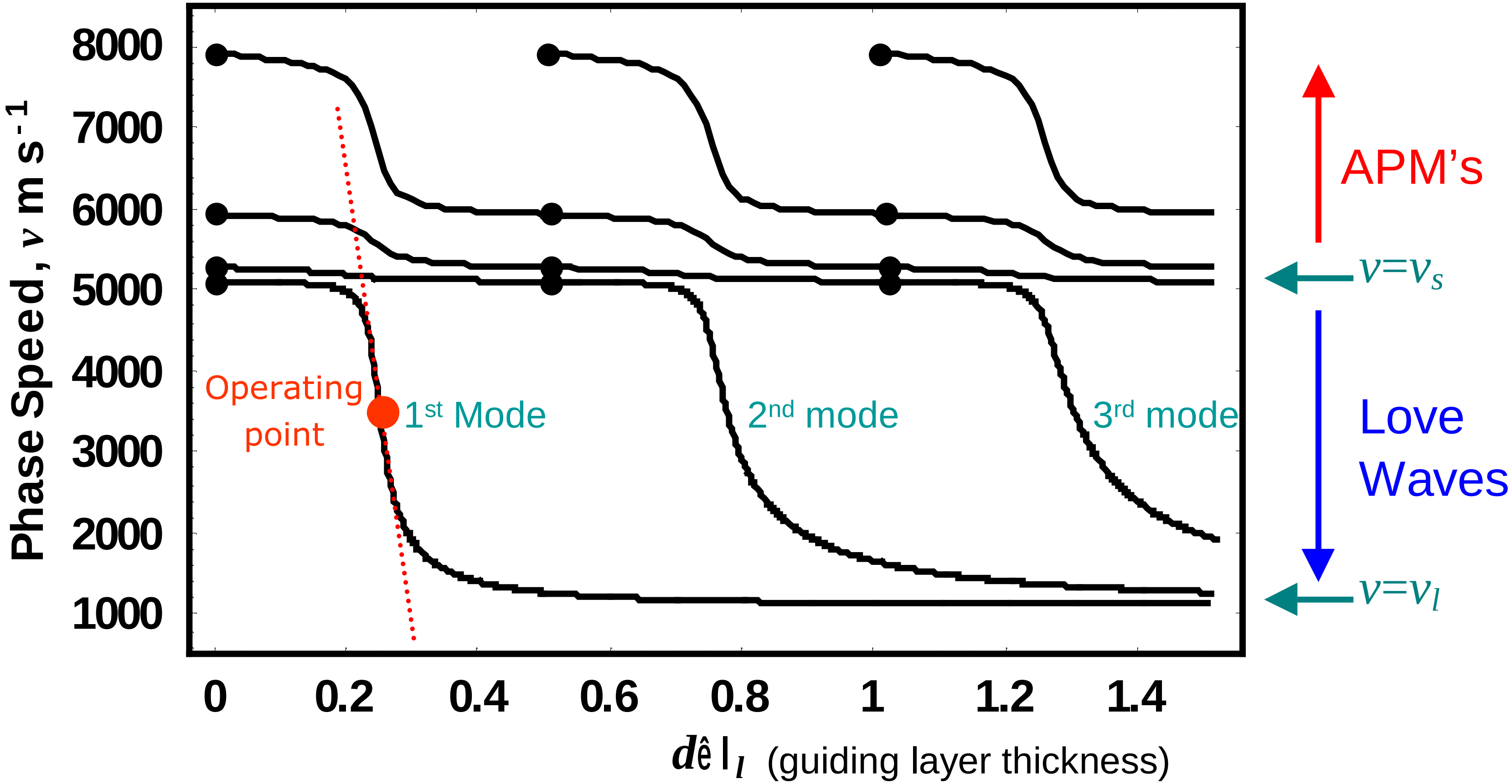
Sensing via both faces

Increased sensitivity <u>versus</u> isolation between sensing and transduction faces

What happens when a wave-guide layer is put on a SH-APM device?

McHale, *et al, J. Appl. Phys.* **93** (2003) 675-690; *MST* **14** (2003) 1847-1853.

Generalized Love Waves – Operating Point



Love wave = Shear mode in substrate-to-shear mode in layer transition

Plate modes = Switch in order of resonance induced by layer

Increased mass/liquid sensitivity related to slope of dispersion curve

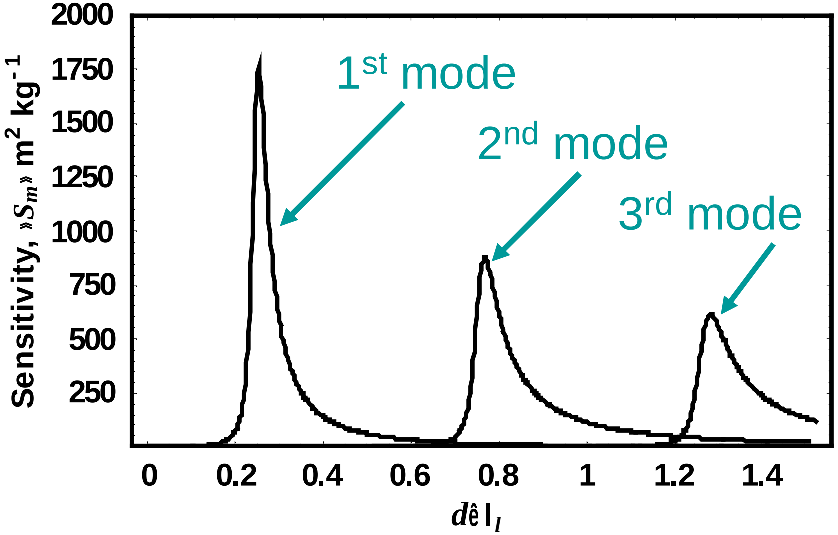
Phase Speed Mass Sensitivity

$$S_m = \lim_{\Delta m \to 0} \frac{1}{\Delta m}\left(\frac{\Delta v}{v_o}\right) \approx \frac{f_o}{\rho_l v_l}\left(\frac{d \log_e v}{dz}\right)_{z_0}$$

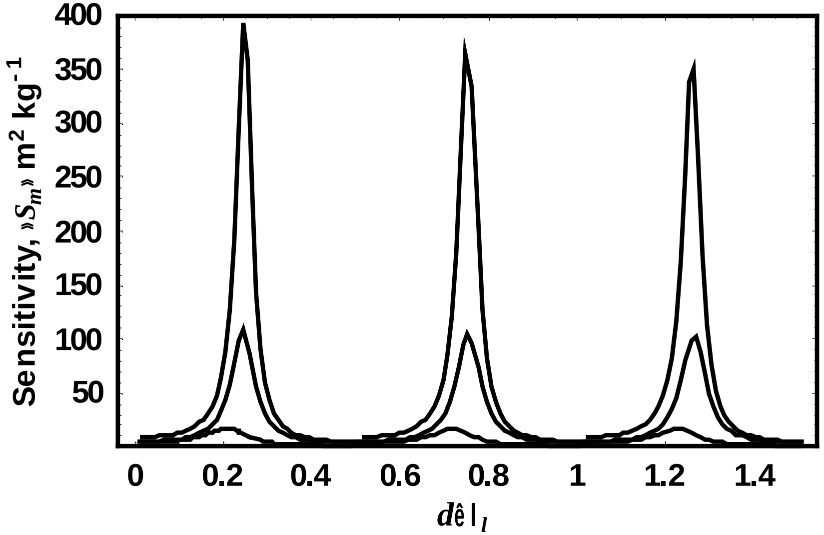
Δm is mass per unit area being sensed, $z = df/v_l$ is the normalized thickness

"Rigid" mass $\Rightarrow$ Mass sensitivity is slope of dispersion curve

Love Waves



Layer-Guided SH-APMs



Generalized Sauerbrey/Kanazawa & Gordon

Polymer Waveguide on Polymer Substrate

Complex velocity shift

$$\frac{\Delta v}{v_o} \approx \left(\frac{1-v_f^2/v_o^2}{1-v_l^2/v_o^2}\right)\left(\frac{d\log_e v}{dz}\right)_{z=z_o}\left(\frac{\tan\left(T_f^o h\right)}{T_f^o h}\right)\frac{\omega\rho_f h}{2\pi v_l^\infty \rho_l}$$

$\omega\Delta m/A$

$(\rho\eta\omega)^{1/2}$

Complex slope factor
from polymer waveguide $\Rightarrow$
Enhanced sensitivity

tan$x$/x factor gives mass/liquid loading limits

$$\left(\frac{\tan\left(T_f^o h\right)}{T_f^o h}\right) \rightarrow \begin{cases} 1 & h \rightarrow 0 \\ \dfrac{-\sqrt{-2j}}{2h\left(1-v_f^2/v_o^2\right)}\sqrt{\dfrac{2\eta_f}{\omega\rho_f}} & h \rightarrow \infty \quad \text{and} \quad \omega\tau \rightarrow 0 \end{cases}$$

Sauerbrey/
solid limit

Kanazawa &
Gordon/liquid limit

McHale, *et al, J. Appl. Phys.* **93** (2003) 675-690; *MST* **14** (2003) 1847-1853.

NTU

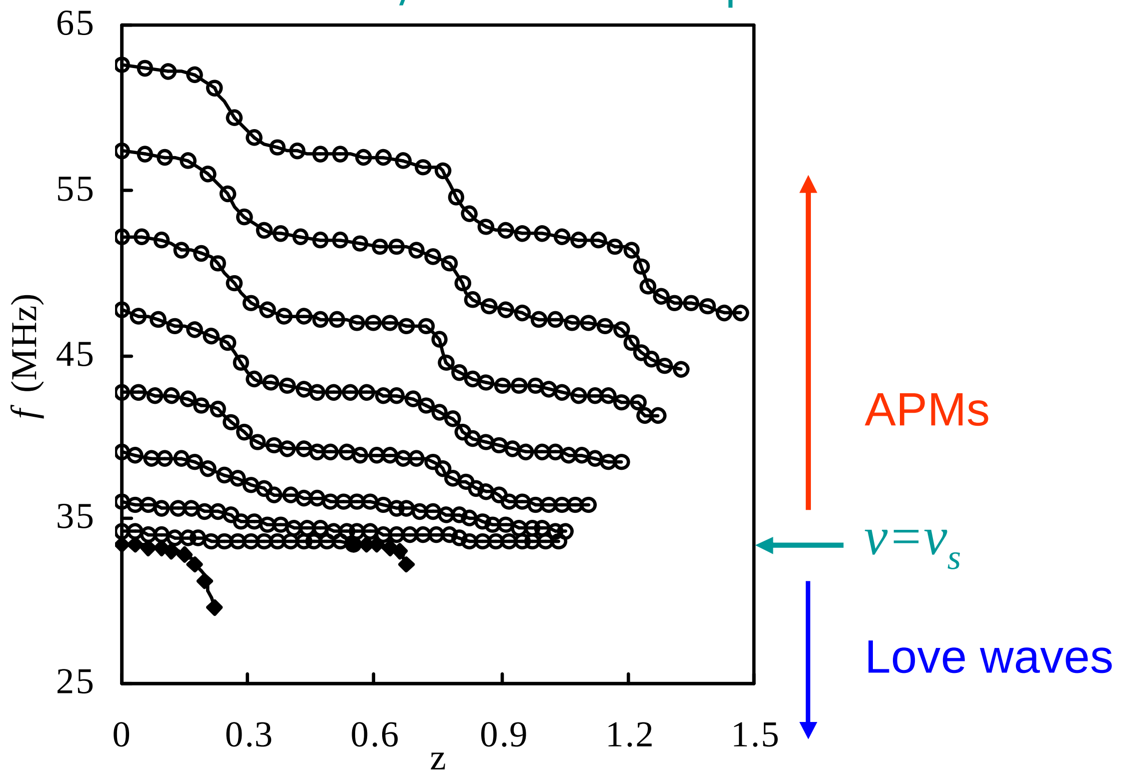
Experimental Data for Layer-Guided SH-APMs

25 MHz surface skimming bulk wave (SSBW)

Propagation orthogonal to x-axis of thinned (200 μm) ST-Q substrate

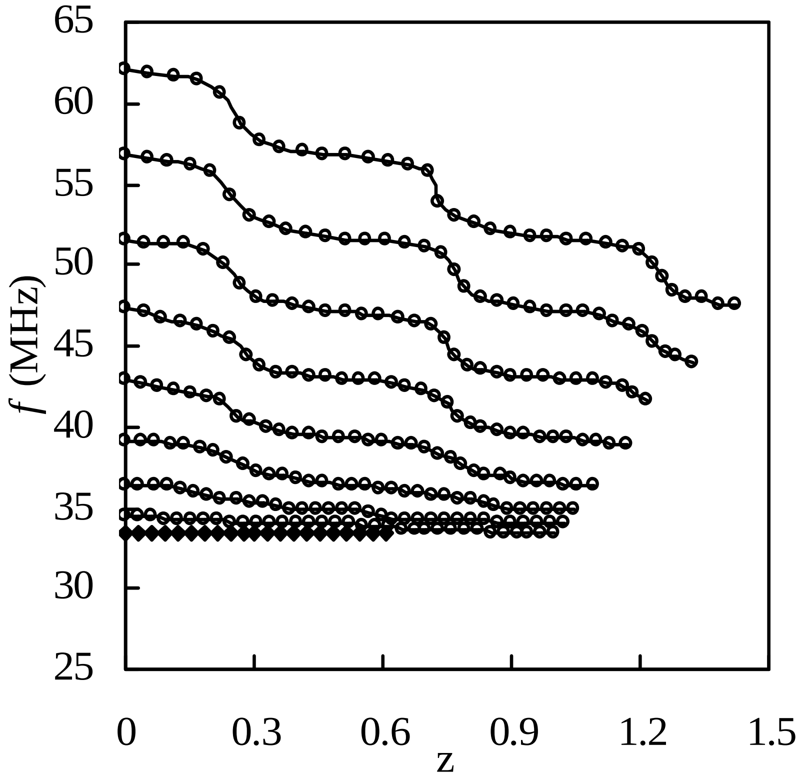
IDT Face Coated

Love wave and SH-APM
are both sensitive
x-axis is d/λ with λ=IDT period



Opposing Face to IDTs Coated

SH-APM changes
Love wave insensitive
x-axis is d/λ with λ=IDT period

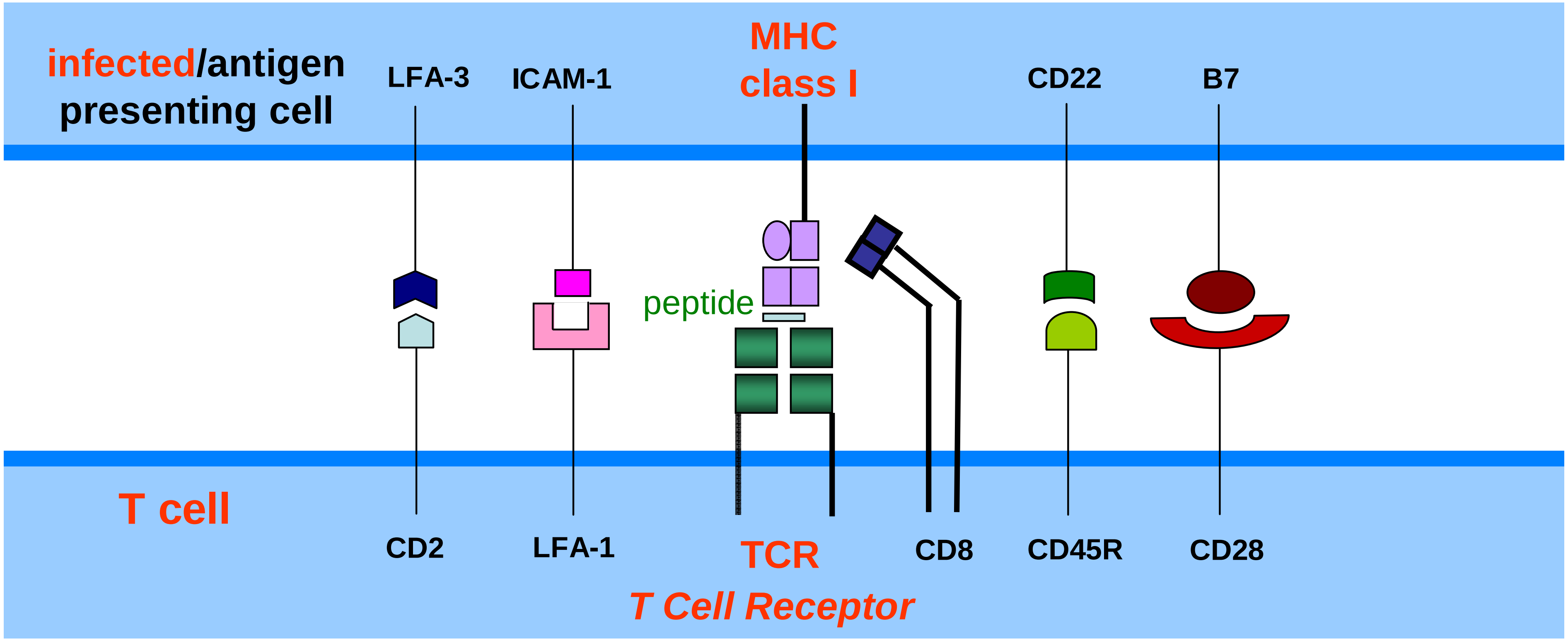


McHale, *et al, Appl. Phys. Lett.* **82** (2003) 2181-2183. Newton, *et al*, *Sens. Act.* **A109** (2004) 180-185. F. Martin, PhD Thesis, Nottingham Trent University (2002).

Sensor Research Examples

Example 1: Peptides and T-Cells

1. Infection/virus broken into peptide fragments and presented on cell surface
2. Cytotoxic T-cells attach to peptides and "read" peptide sequence
3. If foreign, cell is killed by release of a cytotoxic chemical
4. Major histocompatability complex (MHC) antigens are responsible for the expression of peptides on the infected cell
5. Vaccine introduces peptide to the T-cell – Aim is to find suitable peptides



Peptides and T-Cells

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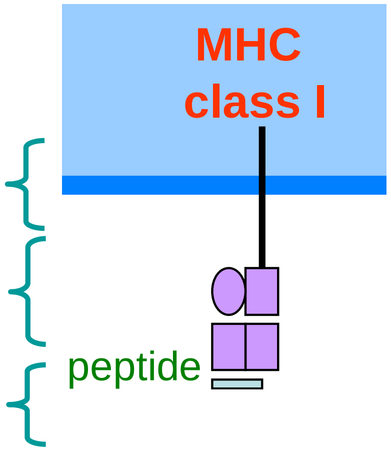
Sensor Strategy

Make this the acoustic wave sensor

Recognition layer is MHC protein

Detect peptide specific binding



Screen for suitable peptides (from the 1000's that exist) with specificity and strong affinity for the MHC

Current State-of-Art

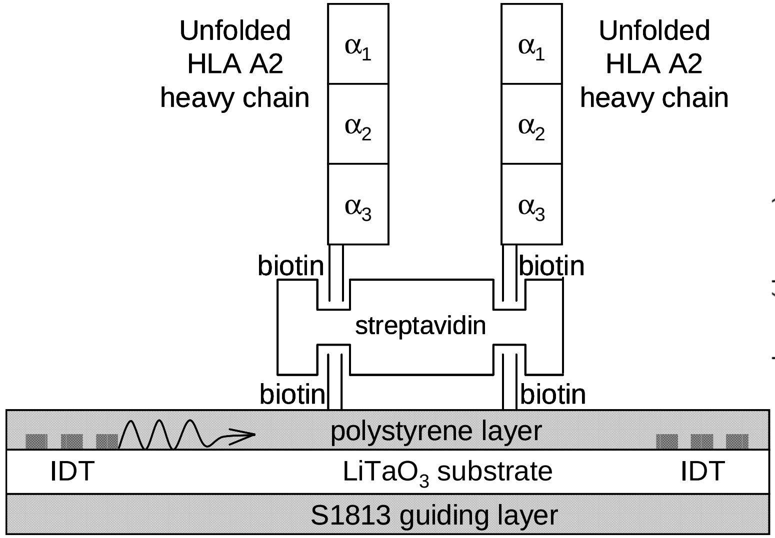
Cellular peptide-MHC assays

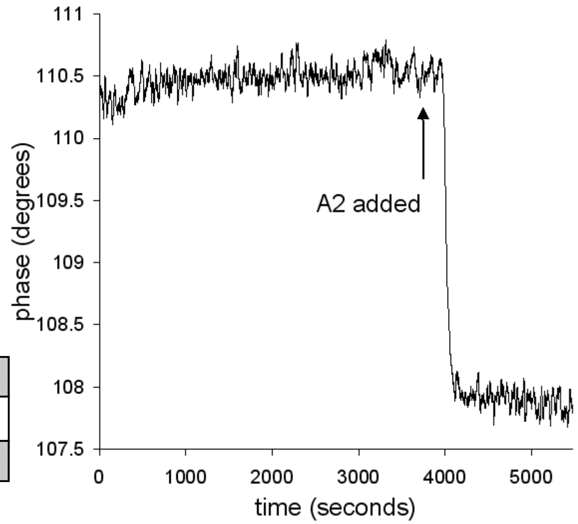
→ yes/no and not real-time

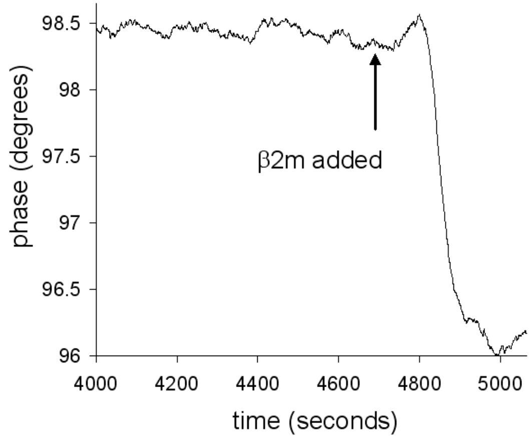
Sensitive, real-time and non-cellular based assay would assist vaccine development

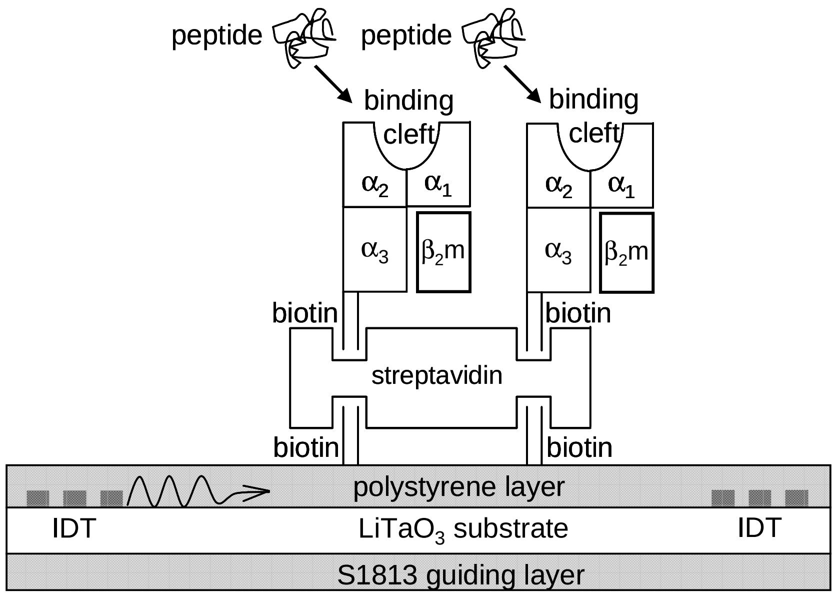
Flow Cell with SH-APM Screening Device

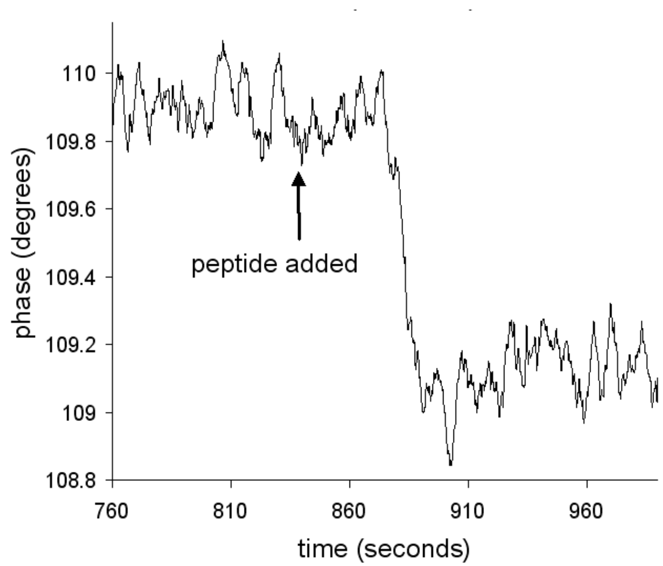
β_{2m} protein binds to A2 and folds to create peptide specific binding cleft









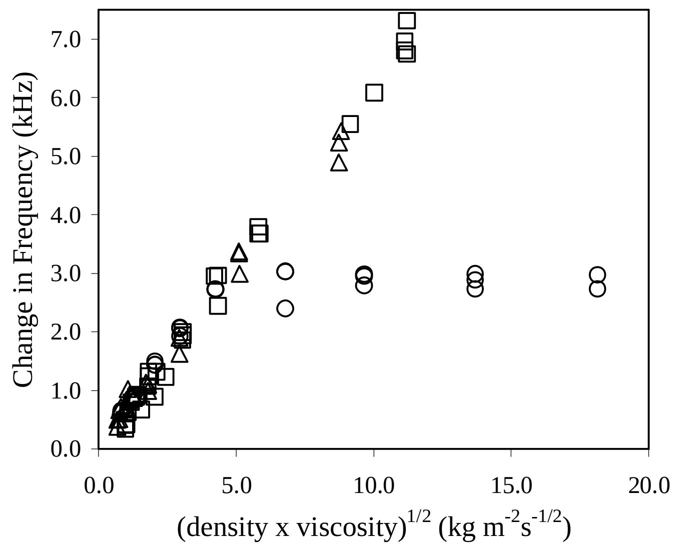


Stanley, *et al, Analyst* **136** (2006) 892-894.

Example 2: Ionic Liquids

Determining Physical Properties

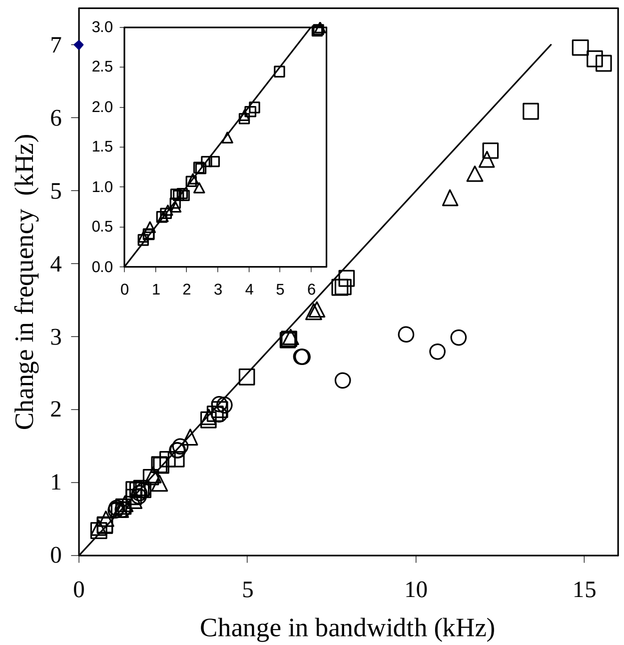
Room temperature ionic liquids (RTIL's)
Green solvents because non-volatile
Millions of simple IL's, billions of binary ILs, …
Designer solvents
Poorly characterised



QCM

Can measure density-viscosity product, but can also determine whether Newtonian via coupled frequency shift-bandwidth increase

$$\Delta f = -\Delta B/2$$



Data

Polydimethylsiloxane oil - known non-Newtonian at higher molecular weights (ooo)
Two ionic liquids [C_4mim][OTf] (□□□) and [C4mim][NTf_2] (ΔΔΔ)

McHale, *et al*, *Anal. Chem.* **80** (2008) 5806-5811.

Overview of NTU Acoustic Wave Sensors

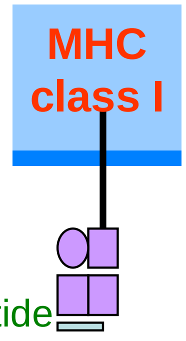
1. MHC-peptide screening	Cancer Vaccines
2. Microfluidic chip for properties of ionic liquids	Green Chemistry
3. Particulates/PAHs/Terpenes	Pollution Monitoring
4. Steroid detection (nandrolone, testosterone via MIPS)	Drug Detection
5. Sperm quality and detection device	Vet AI

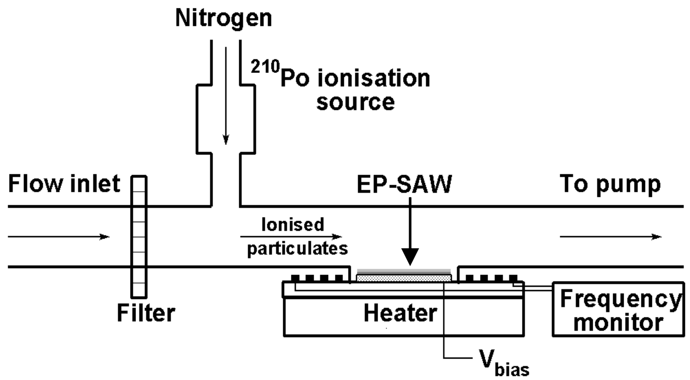
<u>Sensor Strategy</u>

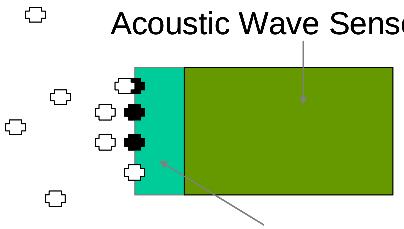
Make this the acoustic wave sensor

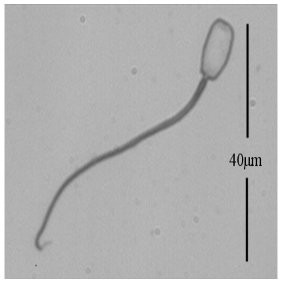
Recognition layer is MHC protein

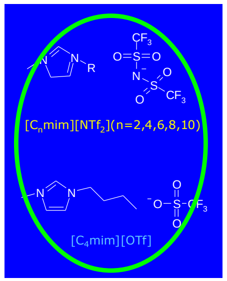
Detect peptide specific binding











Almost all involve the solid-liquid interface

Structuring Surfaces
Topography and Wetting

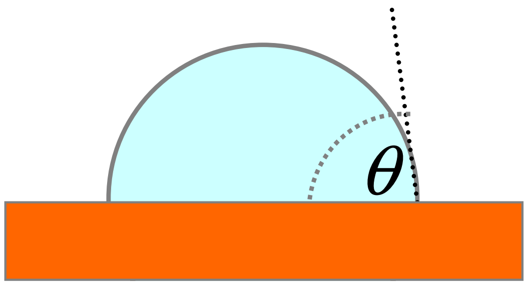
Hydrophobicity and Superhydrophobicity

Surface Chemistry

Terminal group determines whether surface is water hating

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

Contact Angles on Teflon

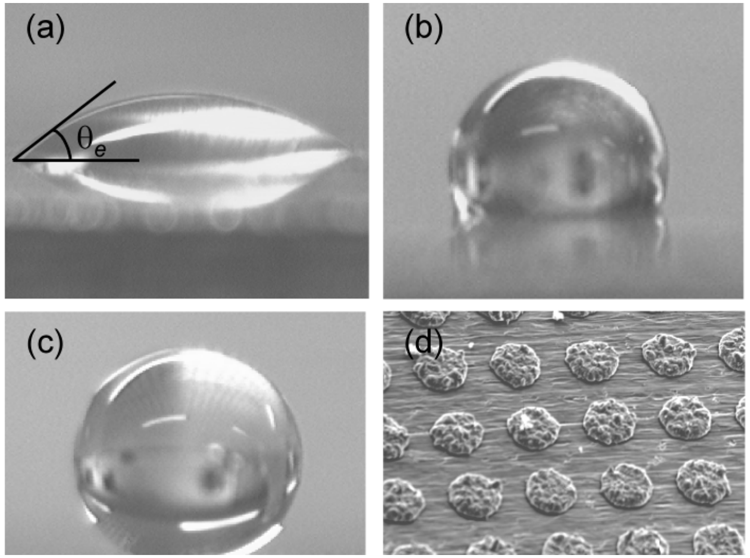


Characterize hydrophobicity

Water-on-Teflon gives ~ 115^o

The best that *chemistry* can do

Enhancement by Topography



(a) is water-on-copper

(b) is water-on-fluorine coated copper

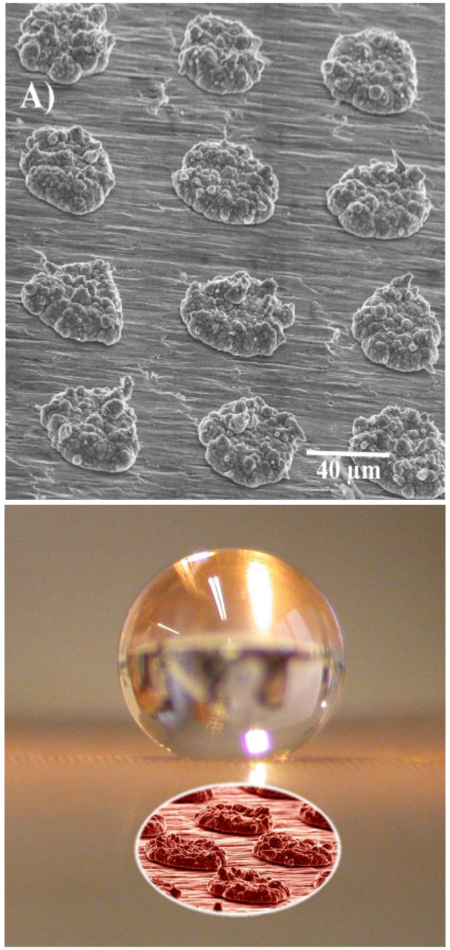
(c) is a super-hydrophobic surface

(d) "chocolate-chip-cookie" surface

Superhydrophobicity is when θ>150^o
and a droplet easily rolls off the surface
(low contact angle hysteresis)

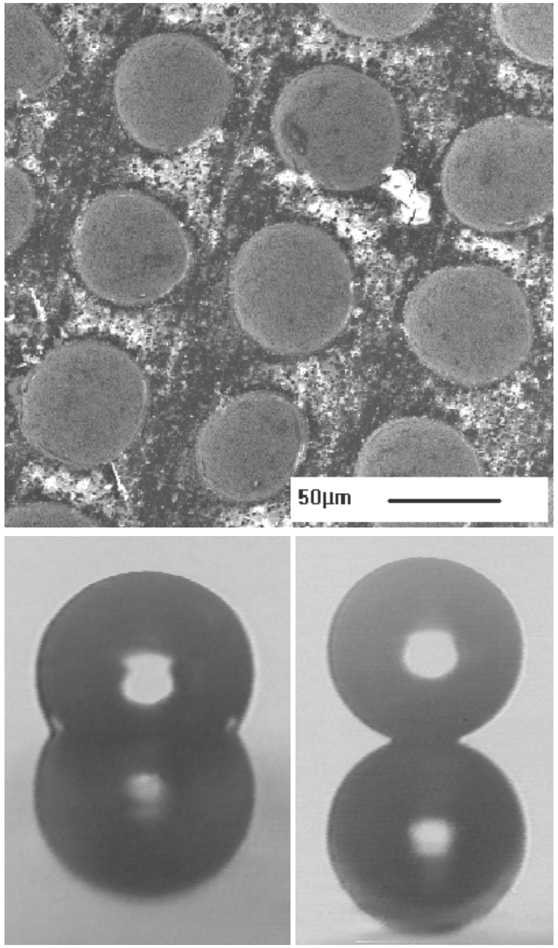
Superhydrophobicity – NTU Examples

Deposited Metal



Patterned & hydrophobic

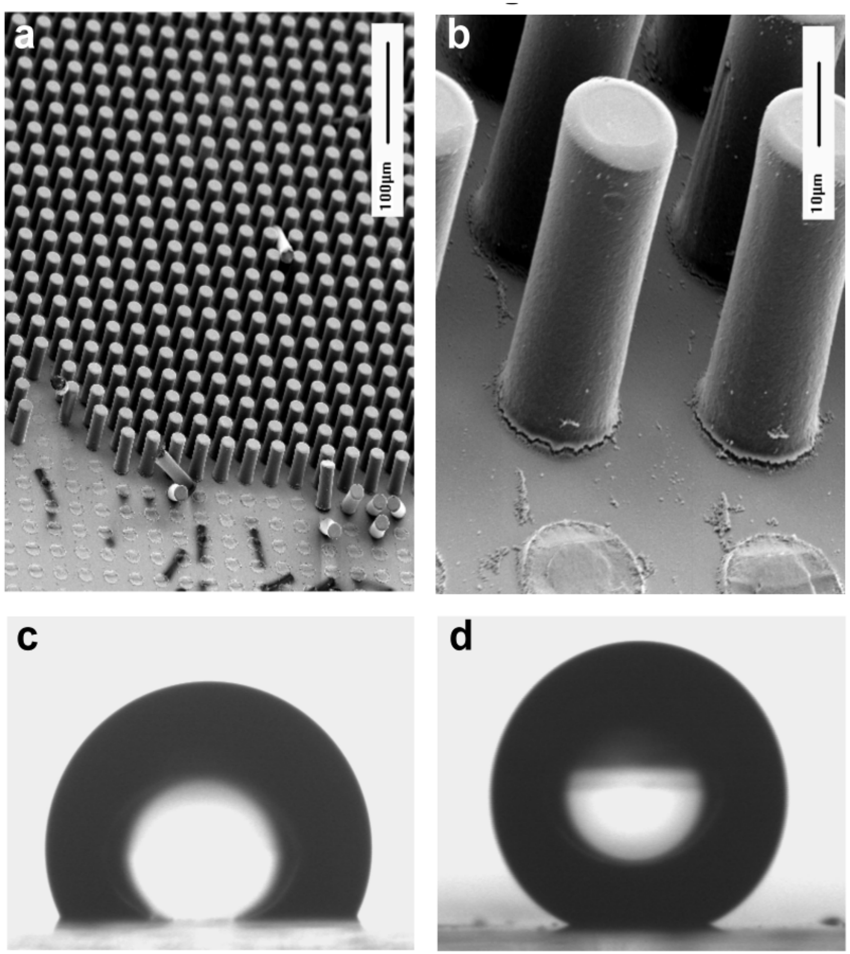
Etched Metal



Flat & hydrophobic

Patterned & hydrophobic

Polymer Microposts

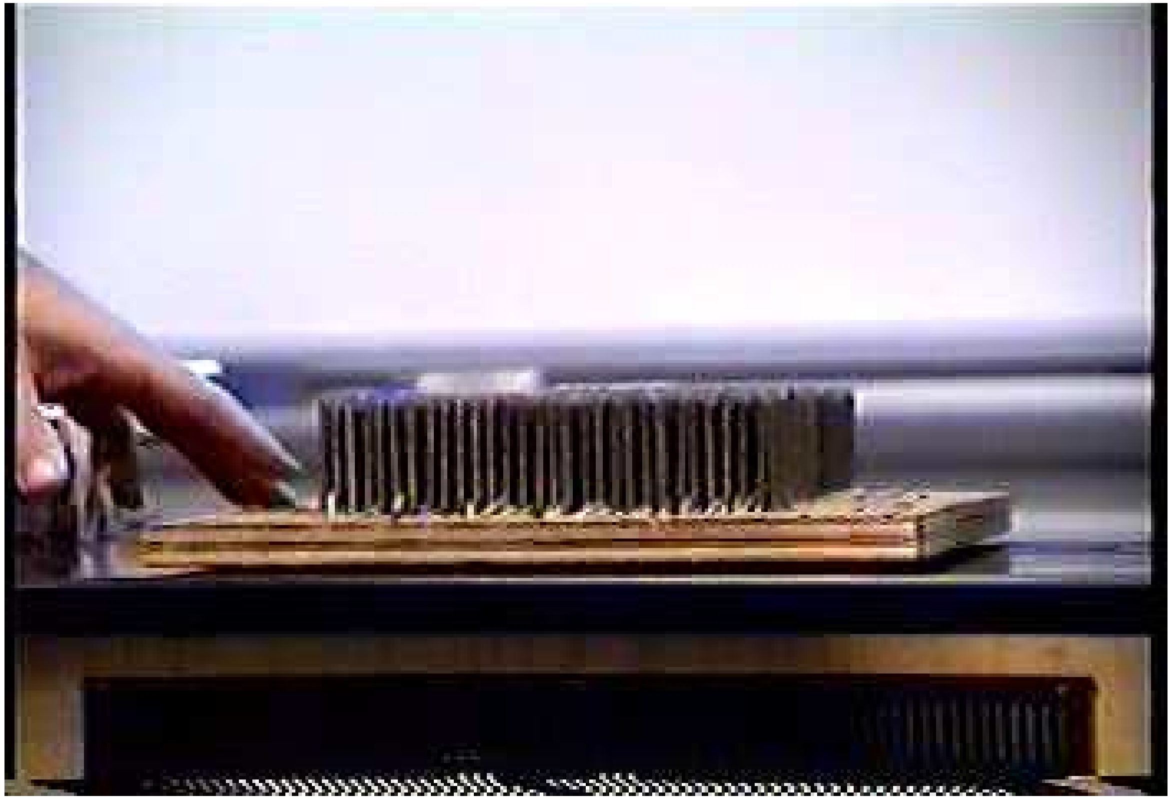


Flat & hydrophobic

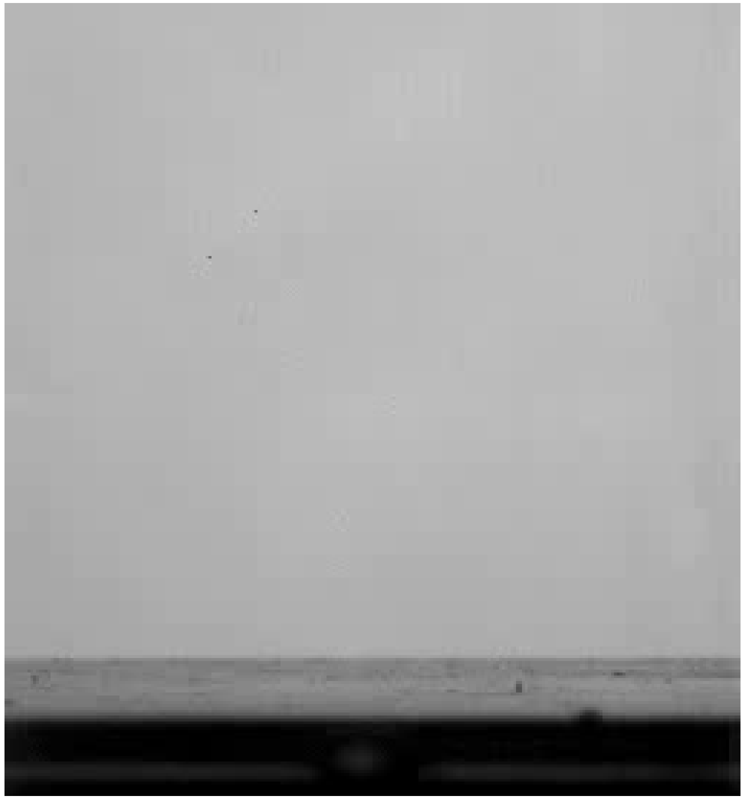
Patterned & hydrophobic

Shirtcliffe, *et al*., *Langmuir* **21** (2005) 937-943; *Adv. Maters.* **16** (2004) 1929-1932; J. Micromech. Microeng. **14** (2004) 1384-1389.

Fakir's Carpet (and Bouncing Droplets)



Acknowledgement: Wake Forest University



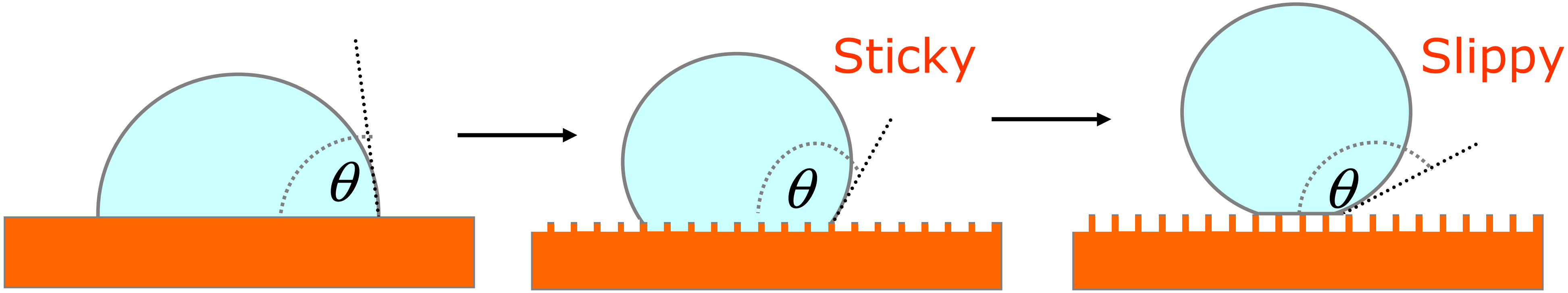
Courtesy: Prof. David Quéré, ESPCI

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.

Topography & Wetting

Droplets that Impale and those that Skate

What contact angle does a droplet adopt on a "rough" surface?



Young's Law	Wenzel Eq.	Cassie-Baxter Eq
$\cos\theta_e = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$	$\cos\theta_W(x) = r(x)\cos\theta_e$	$\cos\theta_{CB}(x) = f_s(x)\cos\theta_e - (1 - f_s(x))$

Chemistry

Roughness — $r(x)$= true area/planar projection at edge

Chemistry — Young's Law θ_e

Topography — $f_s(x)$= solid surface fraction at edge

Cassie & Baxter, *Trans. Faraday Soc.* **40** (1944) 546-551. Wenzel, *Ind. Eng. Chem.* **28** (1936) 988-994; *J. Phys. Colloid Chem.* **53** (1949) 1466-1467. McHale, *Langmuir* **23** (2007) 8200-8205.

Anti-Adhesive and Adhesive Surfaces

1. Reducing Biofouling via S/H Channels

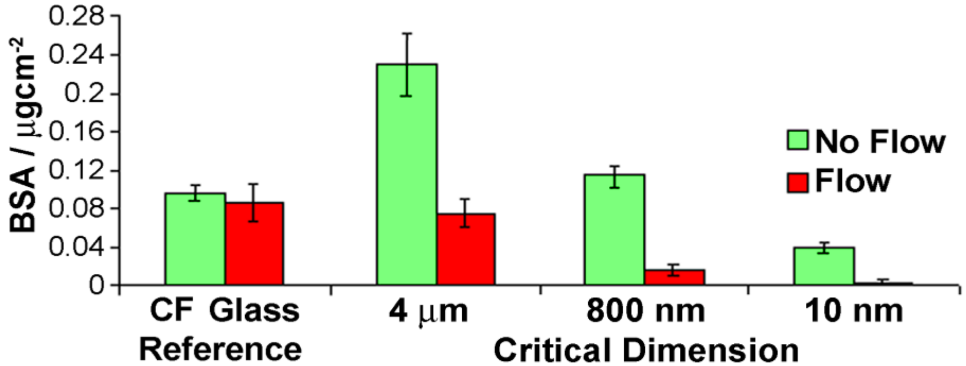
Superhydrophobic Surfaces Used

1. Glass slides
2. Sputter coated 200 nm Cu on 5 nm Ti on slides
3. Large grained (4 μm particles, 20 μm pores) superhydrophobic sol-gel on slides
4. Small grained (800 nm particles, 4 μm pores) superhydrophobic sol-gel on slides
5. CuO nanoneedles (10 nm) on Cu sheet

Proteins on Superhydrophobic Surfaces

1. Substrates incubated in BSA protein (15 nm in size) in phosphate buffer
2. Flow cell 1500μm x 650μm x 65mm using buffer solution
3. Fluorimetric assay to quantify protein removal

Fluorinated nanoscale superhydrophobic surfaces showed almost complete removal of protein under shear flow

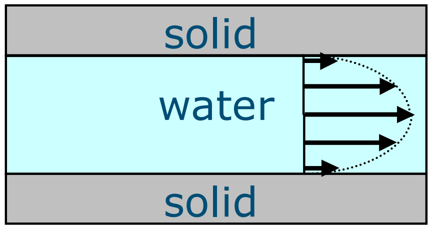


Koc, *et al.*, *Lab on a Chip* **81** (2008) 582-586.

2. Reducing Drag in Pipes via S/H Walls

Concept

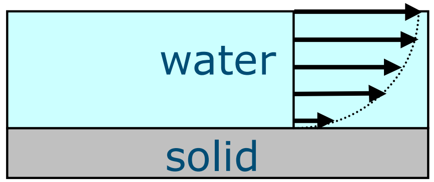
Closed-channel



Two walls cause frictional drag

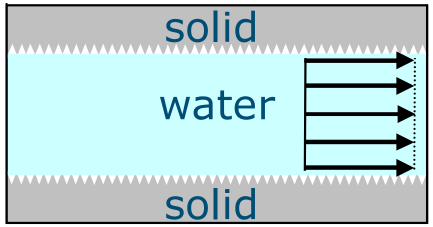
Open-channel

Low frictional drag to air



High frictional drag to solid

Super-channel



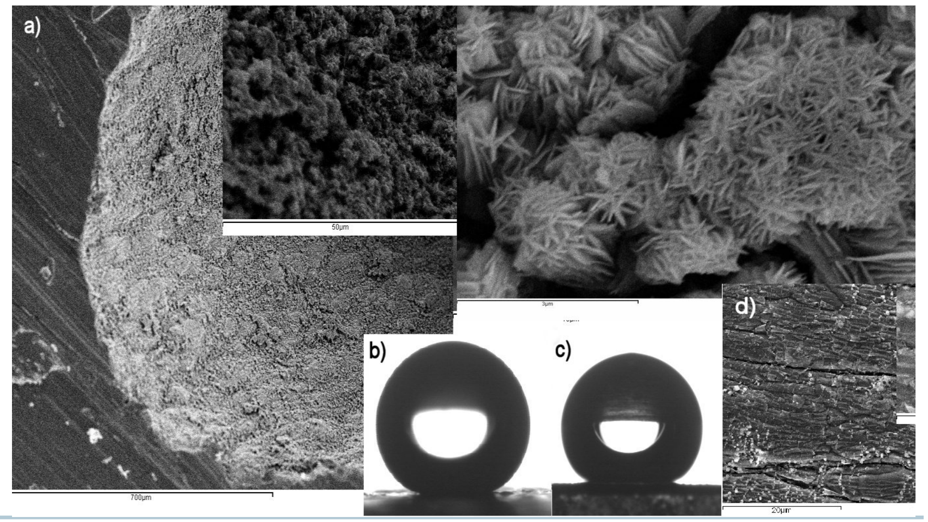
Walls appear as cushions of air

Experiment

Forced flow through small-bore Cu tubes

Electron microscope images of hydrophobic nano-ribbon (1µm x 100nm x 6nm) decorated internal copper surfaces of tubes (0.876 mm radii).

Side-profile optical images of droplets of b) water, and c) glycerol on surface shown in a) the original surface is shown in d)

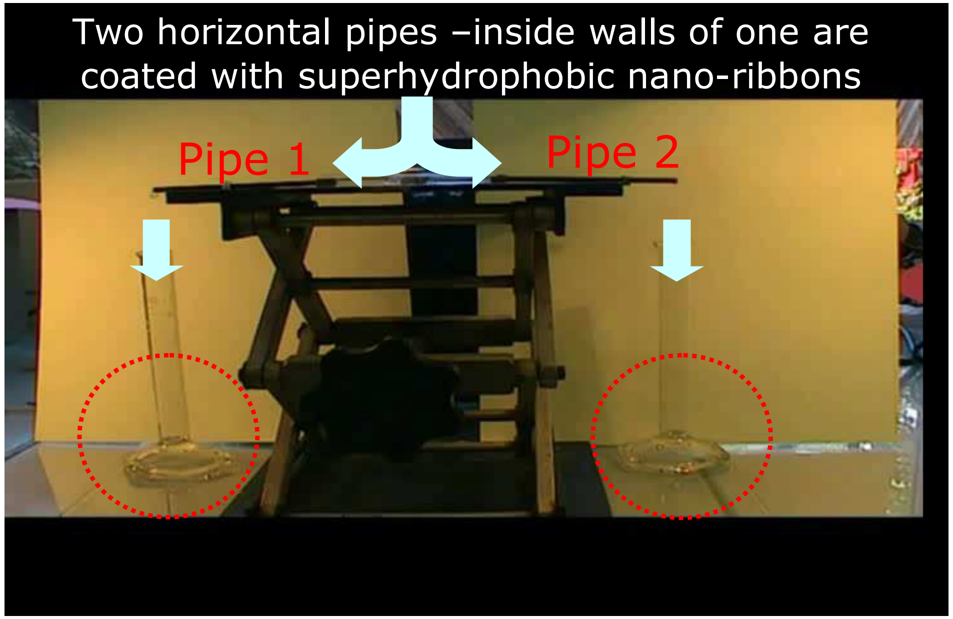


2. Reducing Drag in Pipes via S/H Walls

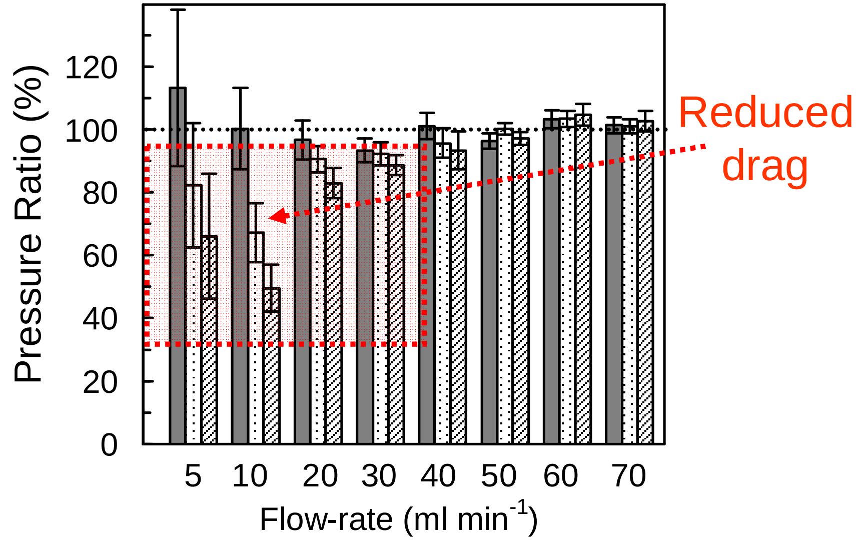
Quantitative Experiment

1. 4 parallel tubes with 4 surface finishes
2. Cu, hydrophobic Cu, nanoribbon Cu, hydrophobic nanoribbon Cu
3. Peristaltic pump to force flow in all 4
4. Measure pressure drop across each

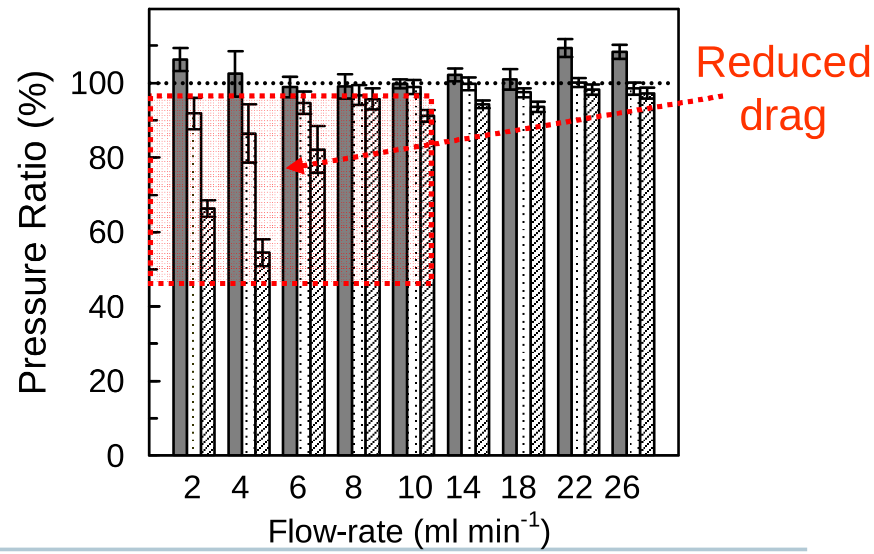
Supporting Visualization Experiment



Water

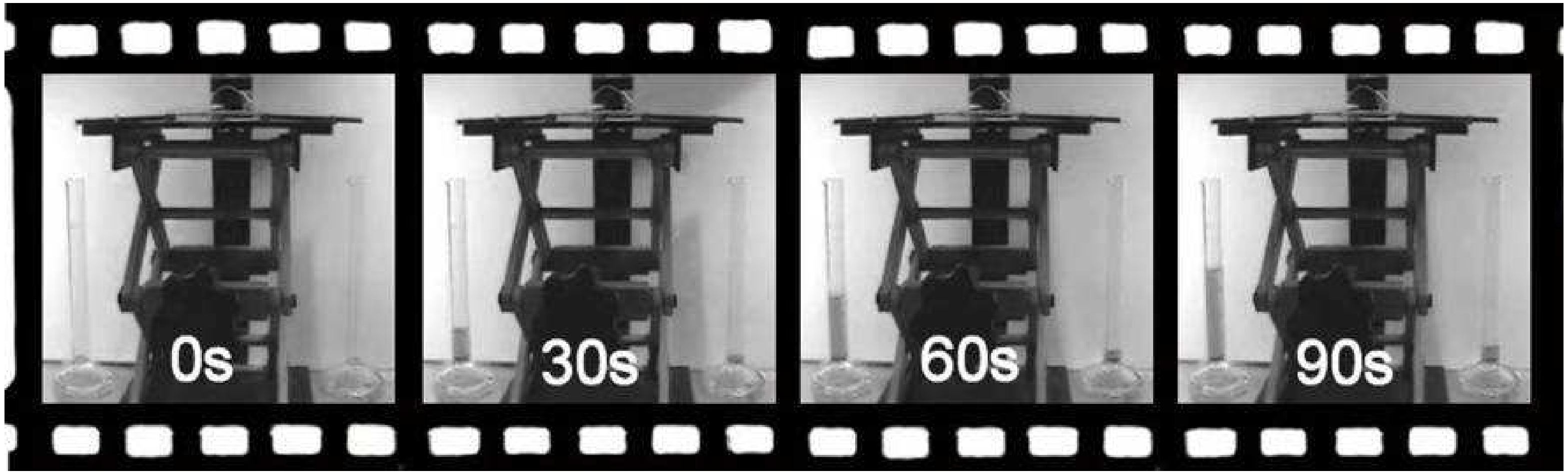


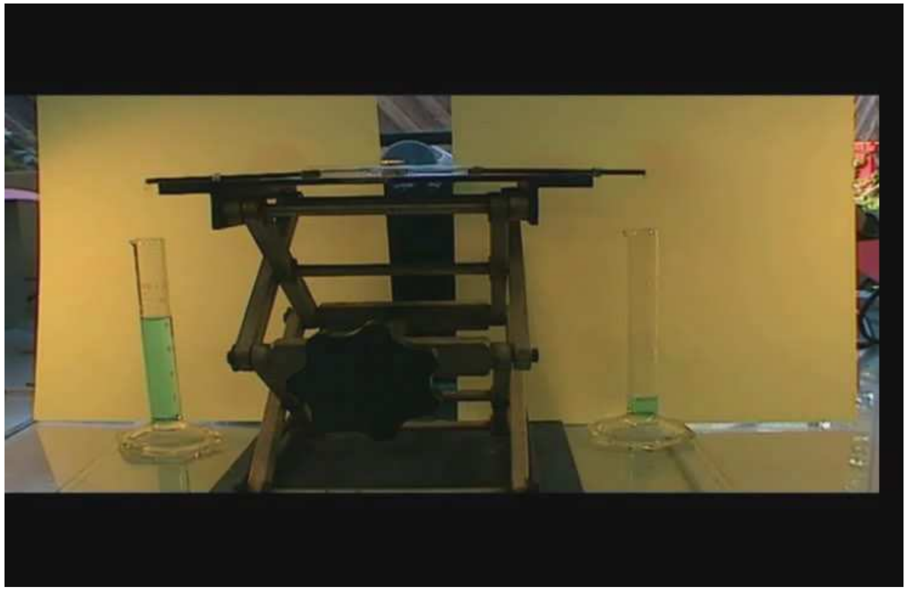
Water-Glycerol (50%)



Shirtcliffe *et al.*, ACS Appl. Maters. Interf. **1** (2009) 1316-1323.

Visualization Results – Extracted Frames





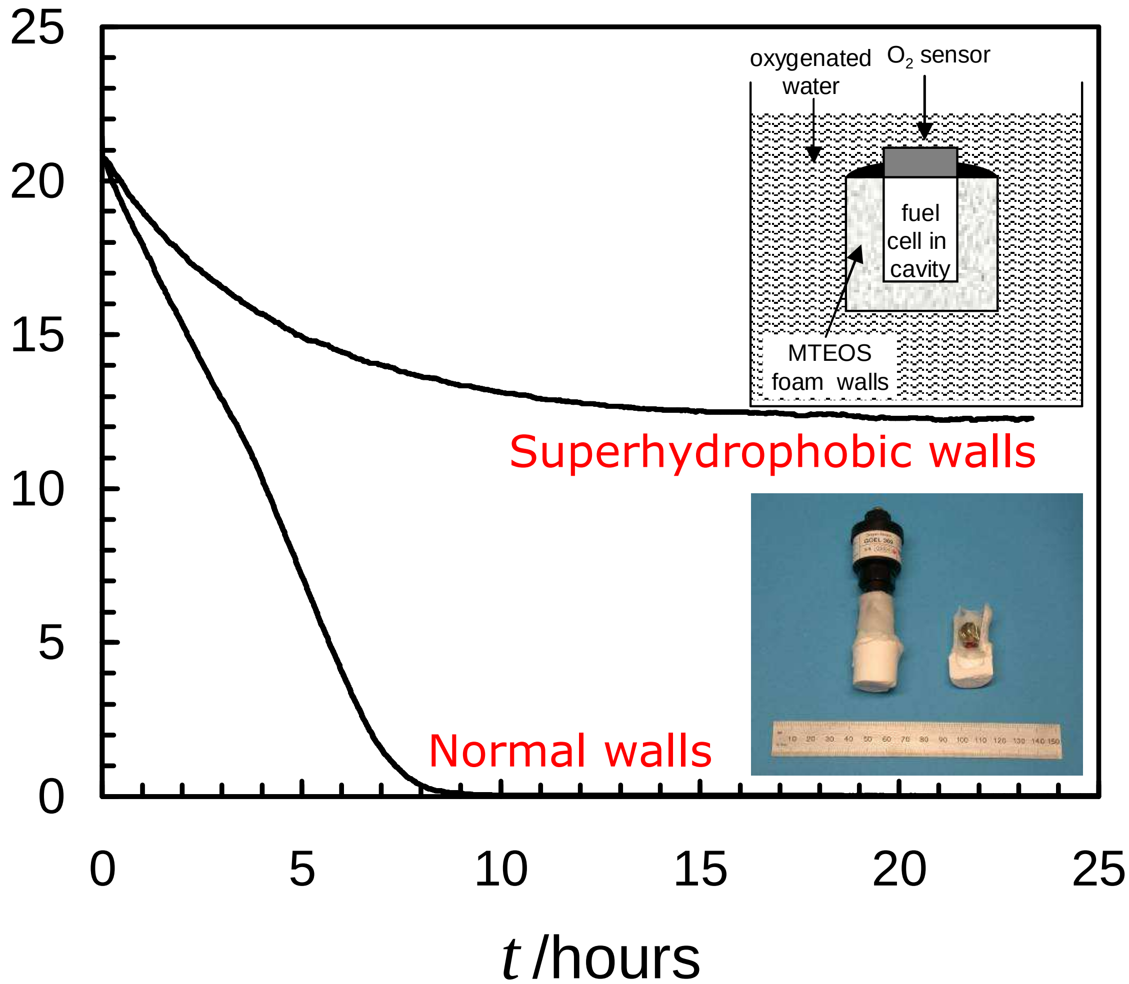
Shirtcliffe *et al*., *ACS Appl. Maters. Interf*. **1** (2009) 1316-1323.

3. Plastrons: Lubricating the Interface

Superhydrophobic surfaces have a silvery sheen when immersed – due to surface retained layer of air. Plastrons for breathing without gills have been known about in insect physiology for since the 1940's.

Water ("Diving Bell") Spider – but not bubble respiration

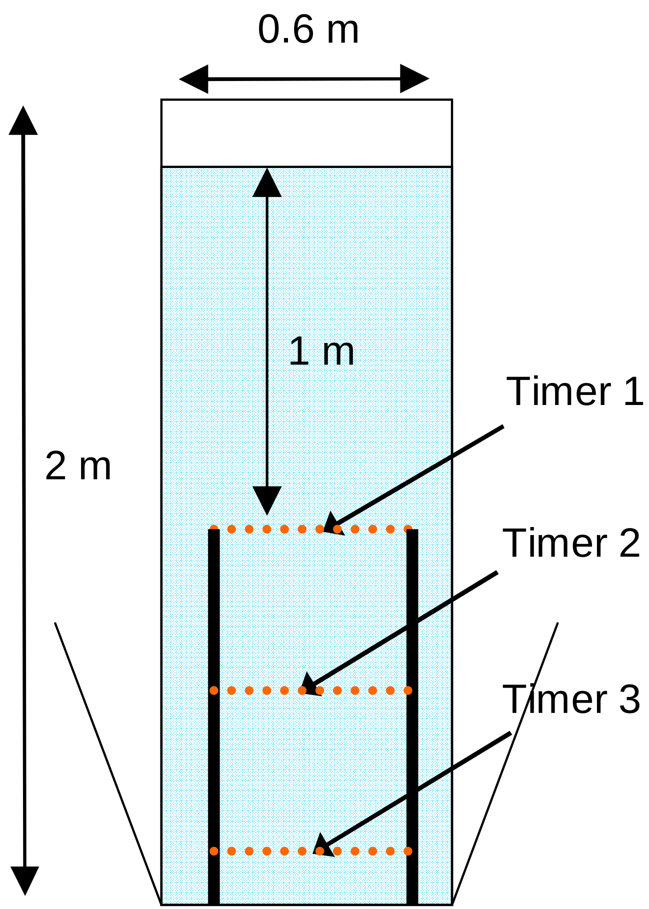
The Movie – Microcosmos



Thorpe & Crisp, J. Exp. Biol. 24 (1947) 227. Shirtcliffe *et al*., Appl. Phys. Lett. 89 (2006) art. 104106.

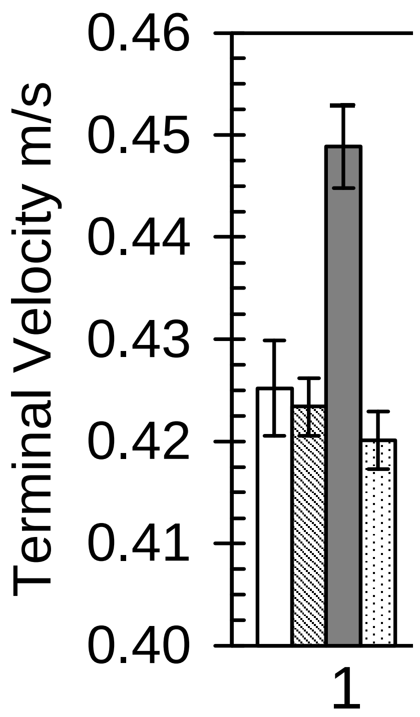
3. Plastrons: Terminal Velocity

In the presence of a fluid, a falling object eventually reaches a terminal velocity. Textbooks tell us that in water the terminal velocity does not depend on the surface chemistry …. But is that true?



3. Plastrons: Terminal Velocity Results

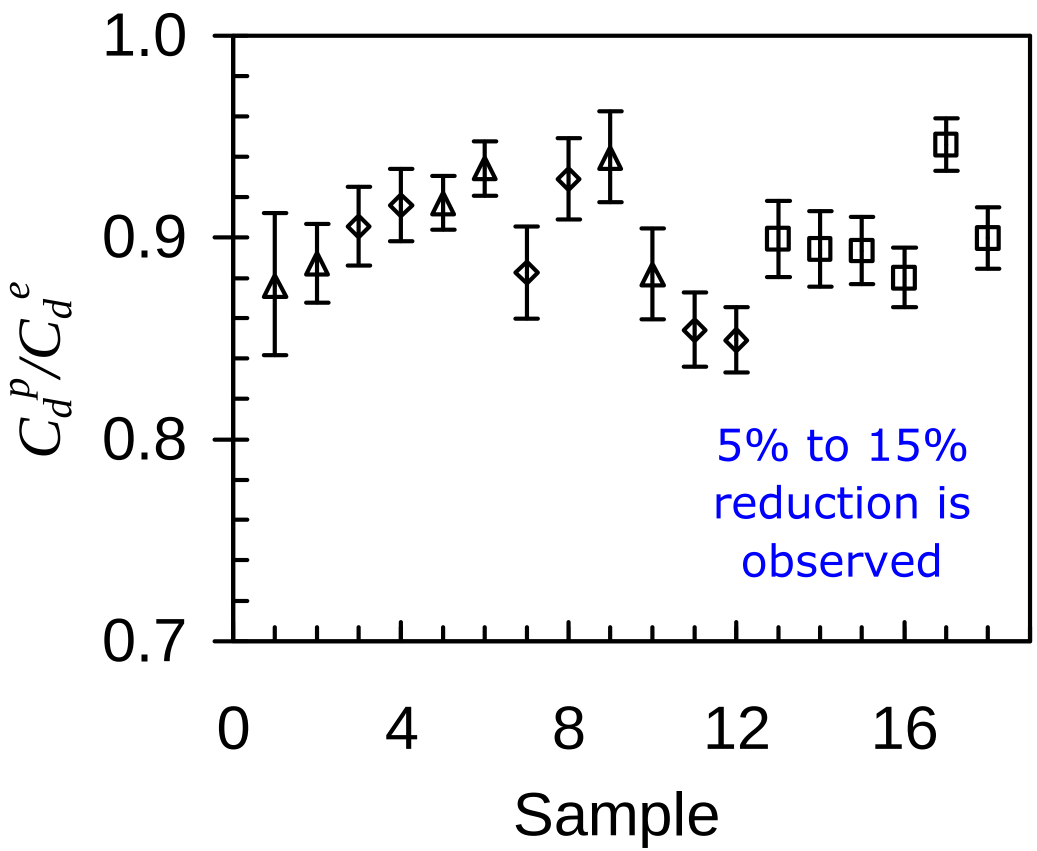
Results for 1-inch Diameter Sphere



Sequence of Four Bars

1. Blank surface
2. Sieved sand surface
3. (Super) Hydrophobic sand
4. Hydrophobic sand with ethanol pre-treatment to prevent plastron

Reduction in Drag Coefficient



Superhydrophobicity alone is not enough. Also need a plastron to persist to achieve drag reduction

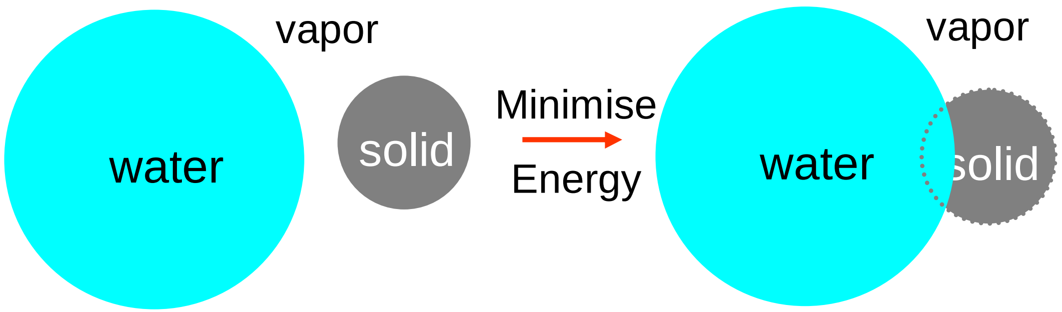
McHale *et al.*, *Appl. Phys. Lett.* **94** (2009) art. 064104.

4. Increasing Droplet Mobility - Liquid Marbles

Loose Surfaces

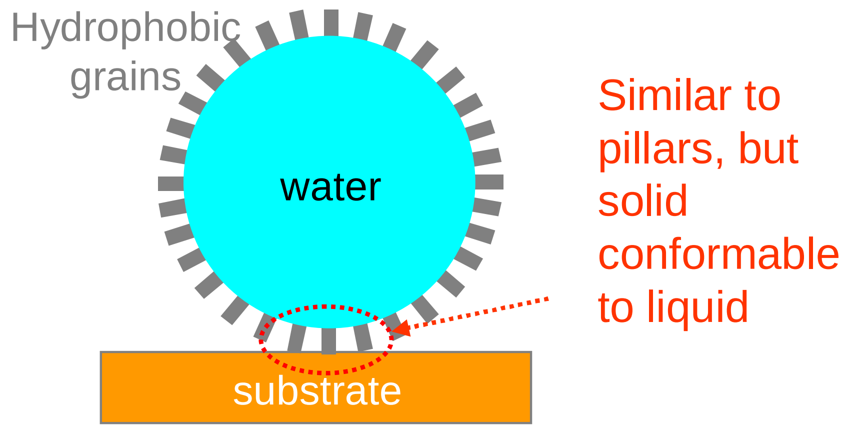
1. Grains are not fixed, but can be lifted by the liquid
2. Surface free energy favors solid grains attaching to liquid-vapor interface
3. A water droplet rolling on a hydrophobic lycopodium (or other grain/powder) becomes coated and forms a liquid marble

Hydrophobic Grains and Water



$$\Delta F = -\pi R_g^2 \gamma_{LV} (1 + \cos\theta_e)(1 + r \cos\theta_e)$$

Energy is always reduced on grain attachment assuming grain is smooth (r=1)

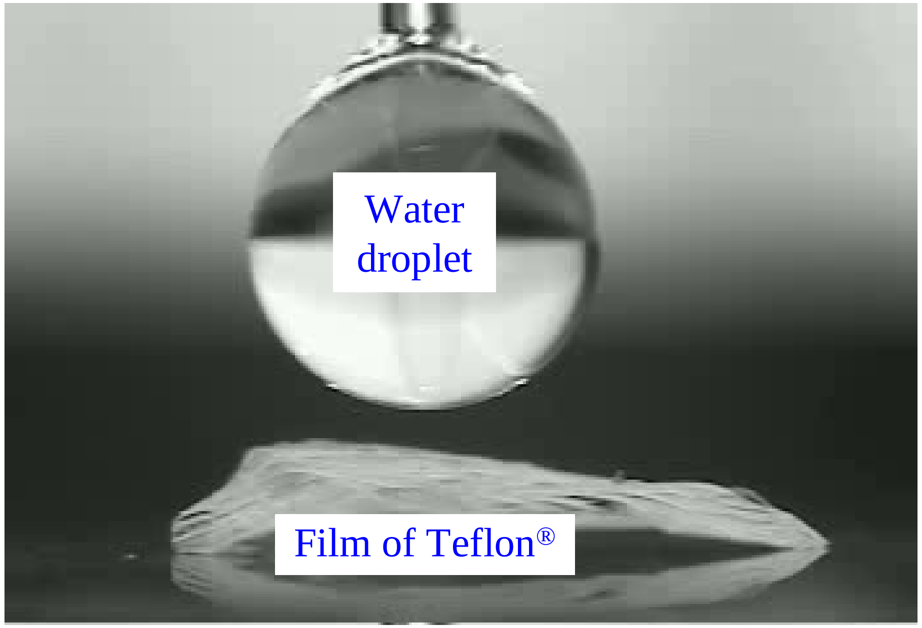


Aussillous & Quéré, *Nature* **411** (2001) 924-927.; McHale, *et al*., Langmuir **23** (2007) 918-924; Newton *et al*., *J. Phys. D. Appl. Phys.* **40** (2007) 20-24.

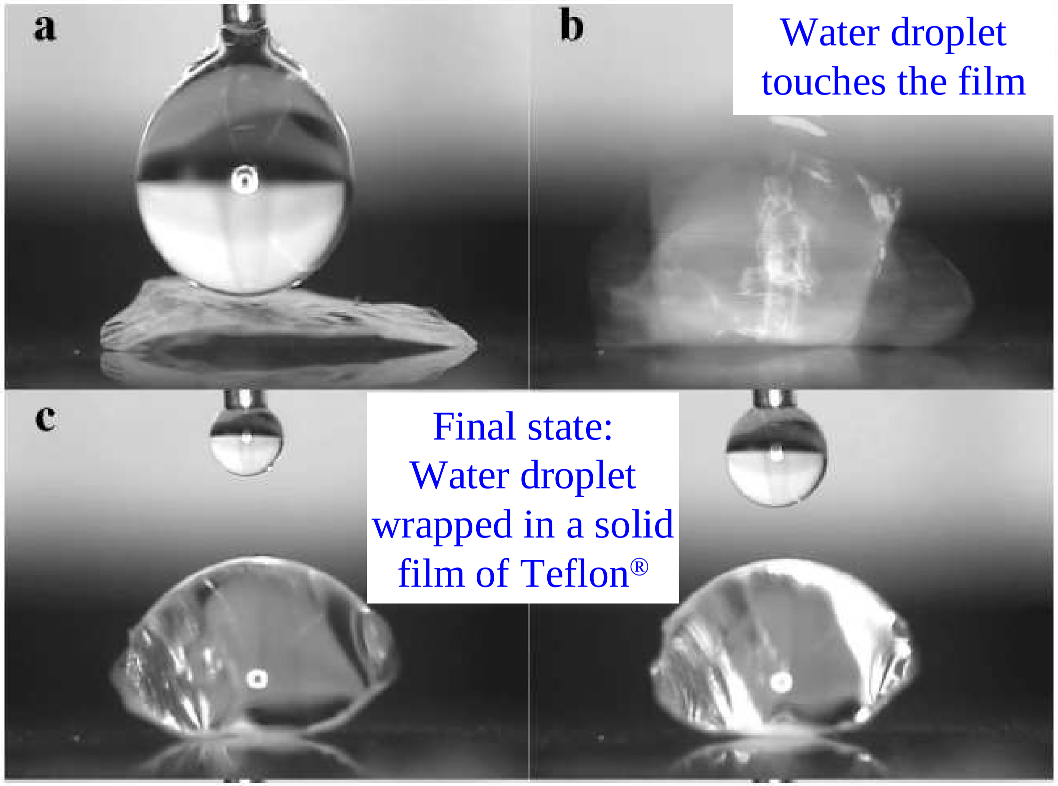
5. Liquid Adhesion – Teflon is Hydrophilic?

1. We all know Teflon® is a hydrophobic solid and gives a non-stick surface …..
2. Consider a thin, 3.7 μm, film of Teflon® AF2400 contacted by a droplet of water

Droplet Wrapping Video



Stills from Video



Courtesy: Prof. Tom McCarthy (UMass, Amherst)

If a droplet wraps itself up in Teflon® … is this consistent with Teflon® being hydrophobic?

Gao & McCarthy, *Langmuir* **24** (2008) 9183-9188. McHale, *Langmuir* **25** (2009) 7185-7187. Py, *et al.*, *Phys. Lett.* **98** (2007) art. 156103; *Eur. Phys. J.* **166** (2009) 67-71.

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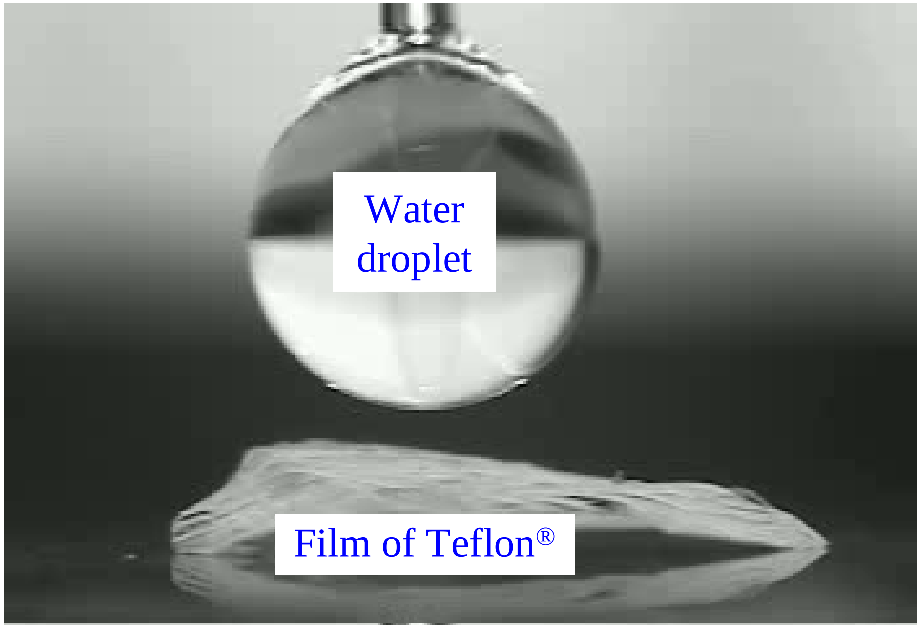
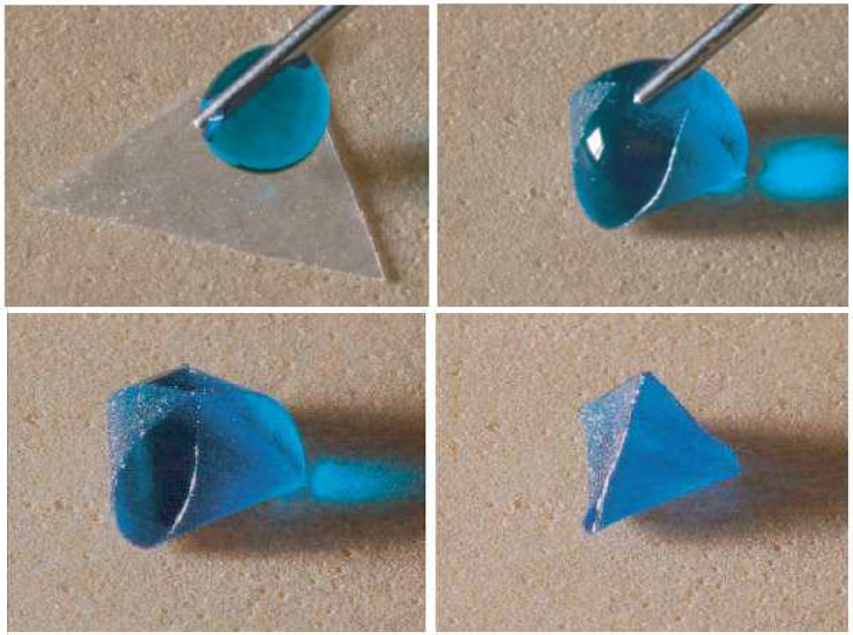


Py *et al's* "Capillary Origami"



Droplet contacting triangular sheet of PDMS

Courtesy: Prof. Tom McCarthy (UMass, Amherst)

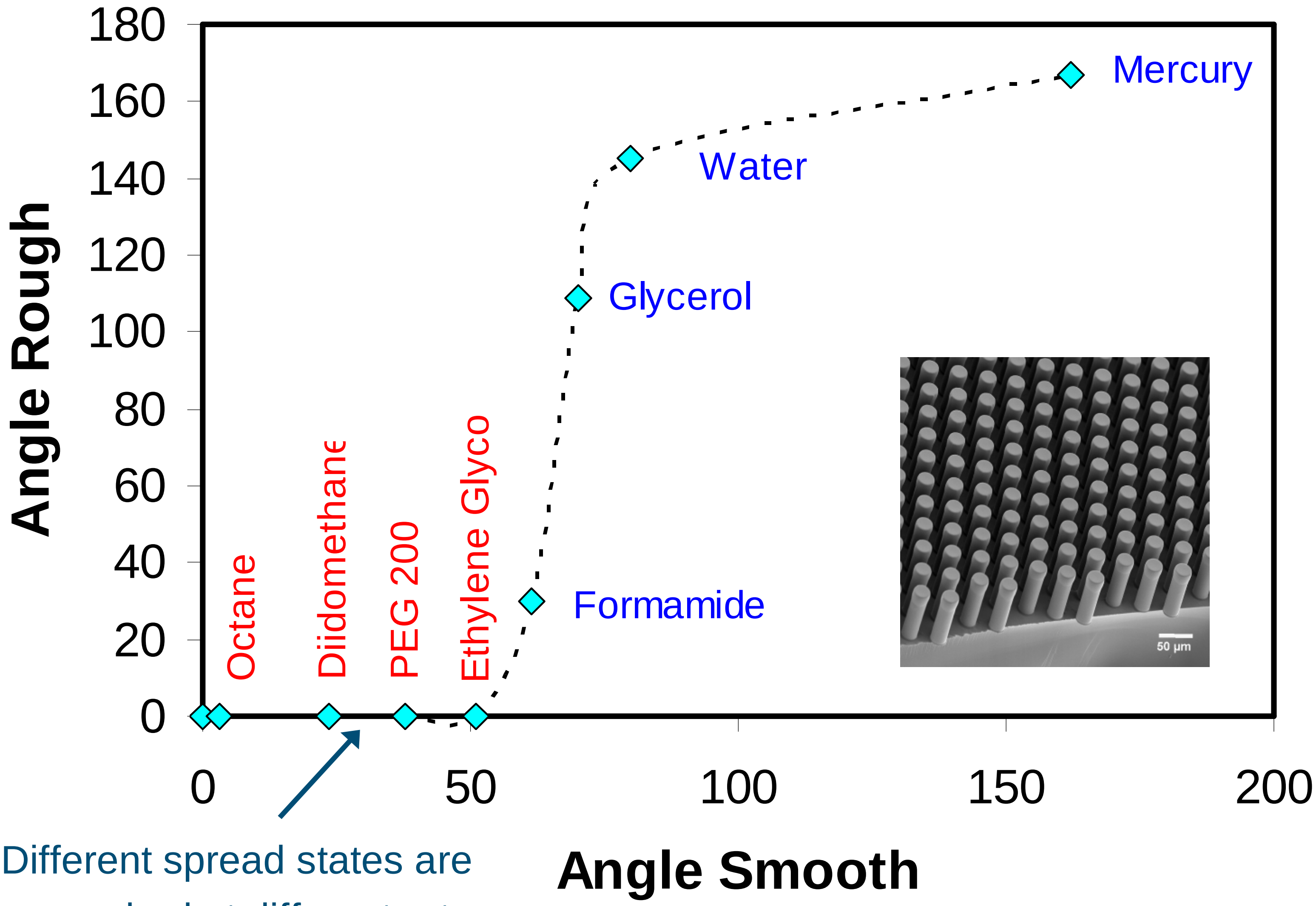
Acknowledgement: Py *et al.* Eur. Phys. J.

If a droplet wraps itself up in Teflon® … is this consistent with Teflon® being hydrophobic?

Gao & McCarthy, *Langmuir* **24** (2008) 9183-9188. McHale, *Langmuir* **25** (2009) 7185-7187. Py, *et al.*, *Phys. Lett.* **98** (2007) art. 156103; *Eur. Phys. J.* **166** (2009) 67-71.

Superspreading and hemi-wicking

Super-spreading on Structured Surfaces



Different spread states are approached at different rates

McHale *et al.*, *Analyst* **129** (2004) 284-287; *Phys. Rev. Lett.* **93** (2004) art. 036102.

Superspreading of PDMS on Pillars

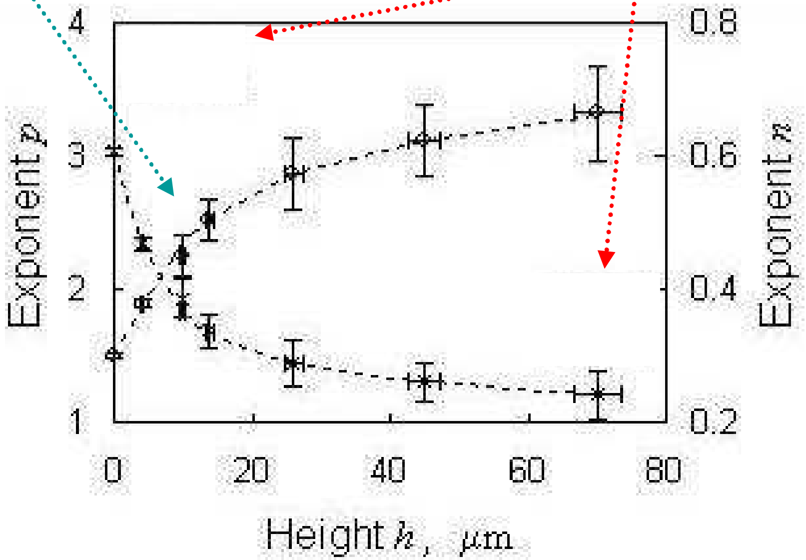
Tanner's Law exponents *p* and *n*

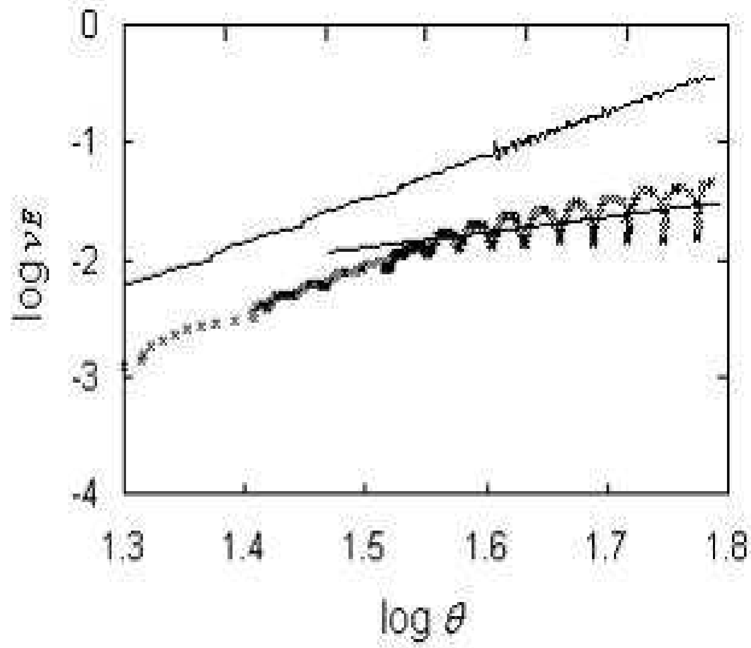
(cubic to linear transition)

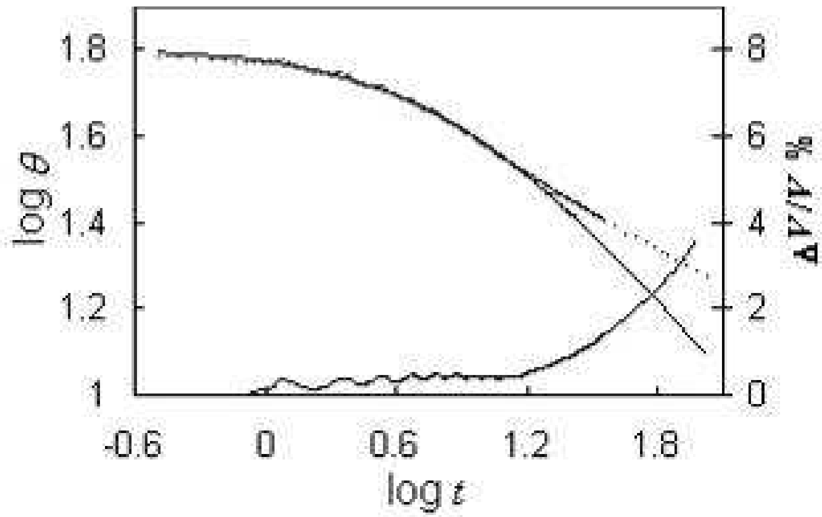
$$v_E \propto v^* \theta^p \qquad \theta \propto \left(\frac{V^{1/3}}{v^*}\right)^n \frac{1}{(t+t_o)^n}$$

Effect of substrate on PDMS

Effect of substrate on water

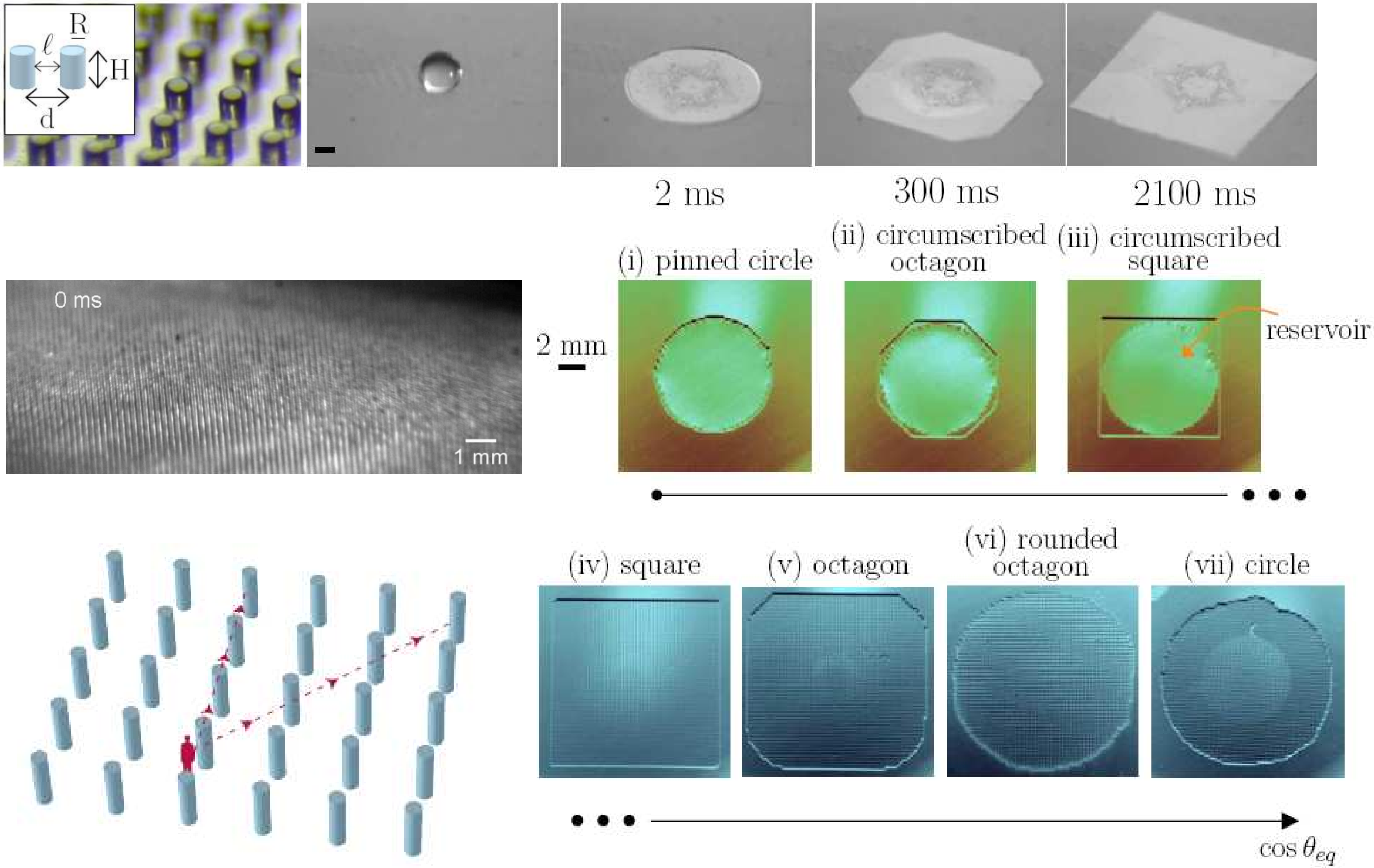






McHale *et al*., *Phys. Rev. Lett.* **93** (2004) art. 036102.

Topography Induced Wetting: Hemi-Wicking



Bico *et al*., *Coll. Surf*. **A206** (2002) 41-46. Quéré, *Physica* **A313** (2002) 32-46.
Courbin *et al*, *Nature Materials*. **6** (2007) 661-664; McHale, **6** (2007) 627-638.

Wrinkling Surfaces

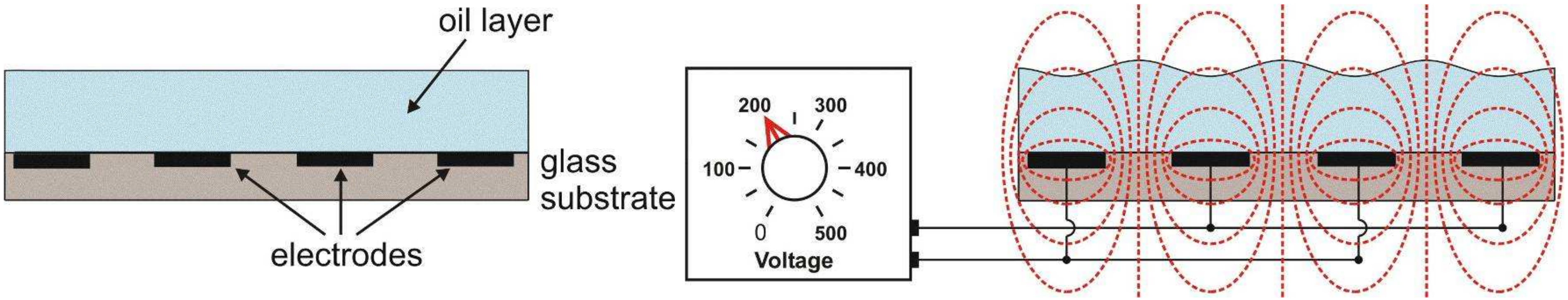
Liquid-based Optics

Liquids for Diffractive Optics

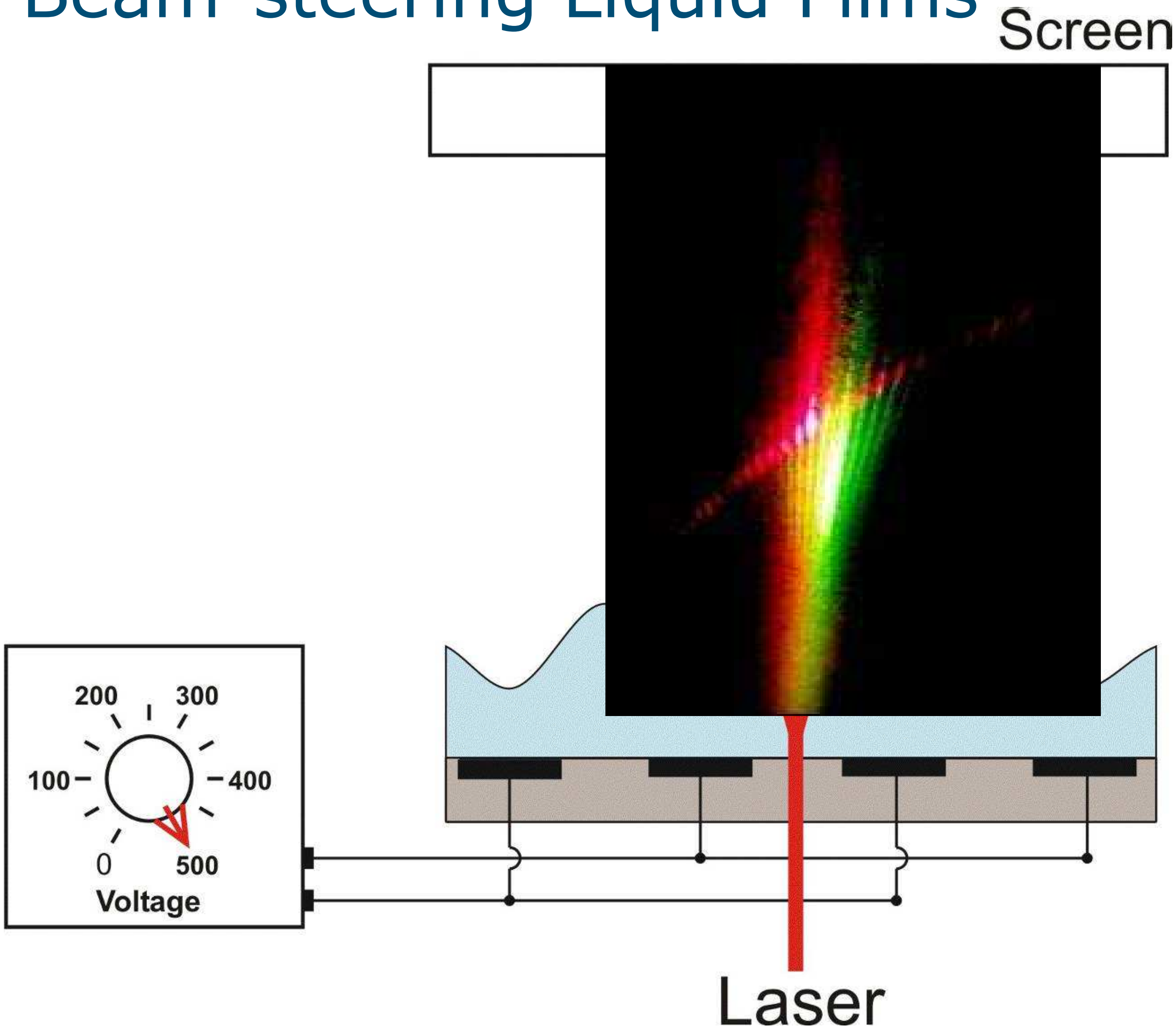
1. A diffraction grating uses surface structure to split light into its constituent colours
2. Can also redirect path of ray of light of a single colour – photonic devices

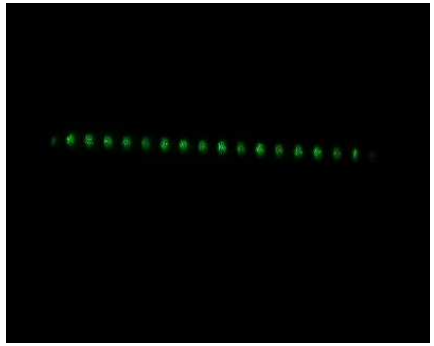
Edge of a CD under white light

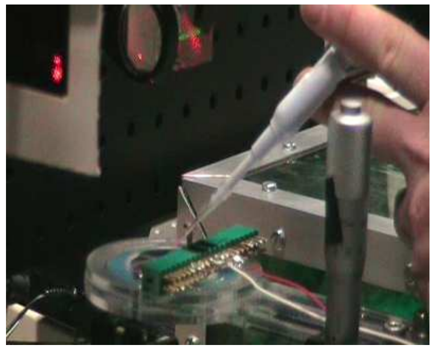
Diffraction using programmable electrical control of oil-air interface



Beam-steering Liquid Films







 Brown, *et al, Nature Photonics* **3** (2009) 403-405; UK Patent Application 0501696.9.

Conclusions

1. Rippling Solid Surfaces
   - Acoustic waves sense interactions at surface and probe liquid properties
   - Simple, low power, sensitive sensors are possible
2. Structuring Solid Surfaces
   - Topography can amplify effect of surface chemistry
   - Superhydrophobic surfaces repel droplets and keep surfaces clean, and can reduce bio-fouling and drag
   - Liquids can be forced to spread or hemi-wick into surfaces
3. Wrinkling Liquid Surfaces
   - Free surface of a spread film of a liquid can be used to create optical effects

The End

EPSRC
Engineering and Physical Sciences Research Council

COST

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Mr Steve Elliott + Mr Jeremy Simons

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Dr Percival	Atmospheric Sciences
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Prof. Carl Brown, Dr Gary Wells, …	Liquid-based Optics