NOTTINGHAM TRENT UNIVERSITY

Water: A tale of two surfaces

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Professorial Lecture 10th November 2008

The Journey's Origin

"The borders between great empires are often populated by the most interesting ethnic groups. Similarly, the interfaces between two forms of bulk matter are responsible for some of the most unexpected actions"

Pierre Gilles de Gennes
(Nobel Laureate in Physics , 1991)
Dirac Memorial Lecture, 1994

Acknowledgement: Le Figaro

A founder of Soft Condensed Matter Physics

"Of course, the border is sometimes frozen (the Great Chinese Wall). But in many areas, the overlap region is mobile, diffuse, and active (the Middle East border of the Roman empire, disputed states between Austria and the Russians, or the Italians, …)"

In The Garden

Surfaces and Materials

plants & leaves

ponds & insects

soil

channels

clothes

windows & roofs

The Natural World

The Man-made World

The Great Empires

The Great Empires of Bulk Matter

solids - organic matter, glass, brick, metal, plastic, ...
liquids - water, oil, …

The Two Surfaces

surface of the solid
surface of the liquid } these are also interfaces (to air)

The Border

solid–to-liquid interface

The border is sometimes frozen. But in many areas, the overlap region is mobile, diffuse, and active.

Insects at the Water's Surface

Walking on Water

Microcosmos (Copyright: Allied Films, 1996)

Winners and Losers: Understanding provides a competitive advantage

Surface Tension

Liquid Surface

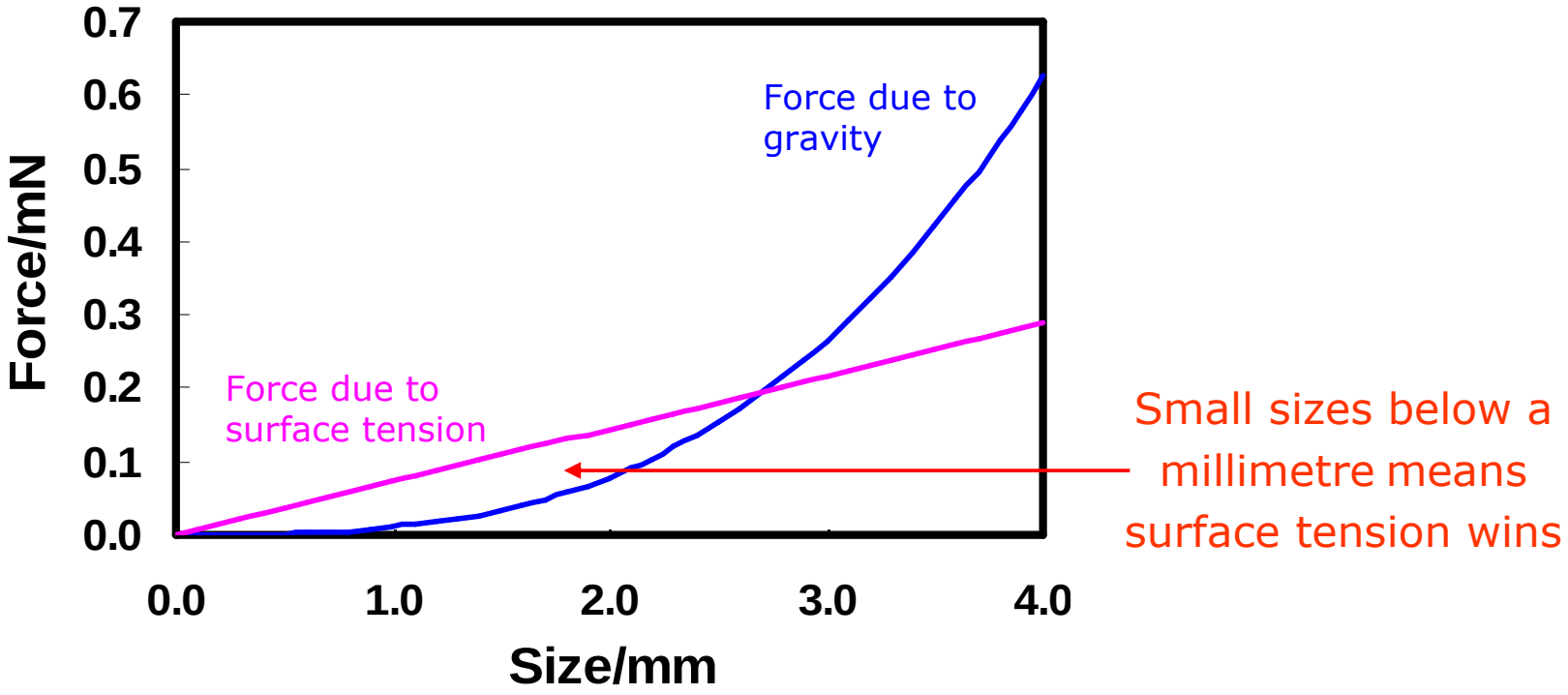
Molecules at a surface have fewer neighbours

Liquid surface ("skin") behaves as if it is in a state of tension

For a free "blob", the smallest area is obtained with a sphere

http://www.brantacan.co.uk

Surface Tension v Gravity



Size Matters: Fiction or Fact?

The Movie – Antz (1998)

Copyright: DreamWorks Animation (1996)

Courtesy: BigWave Productions

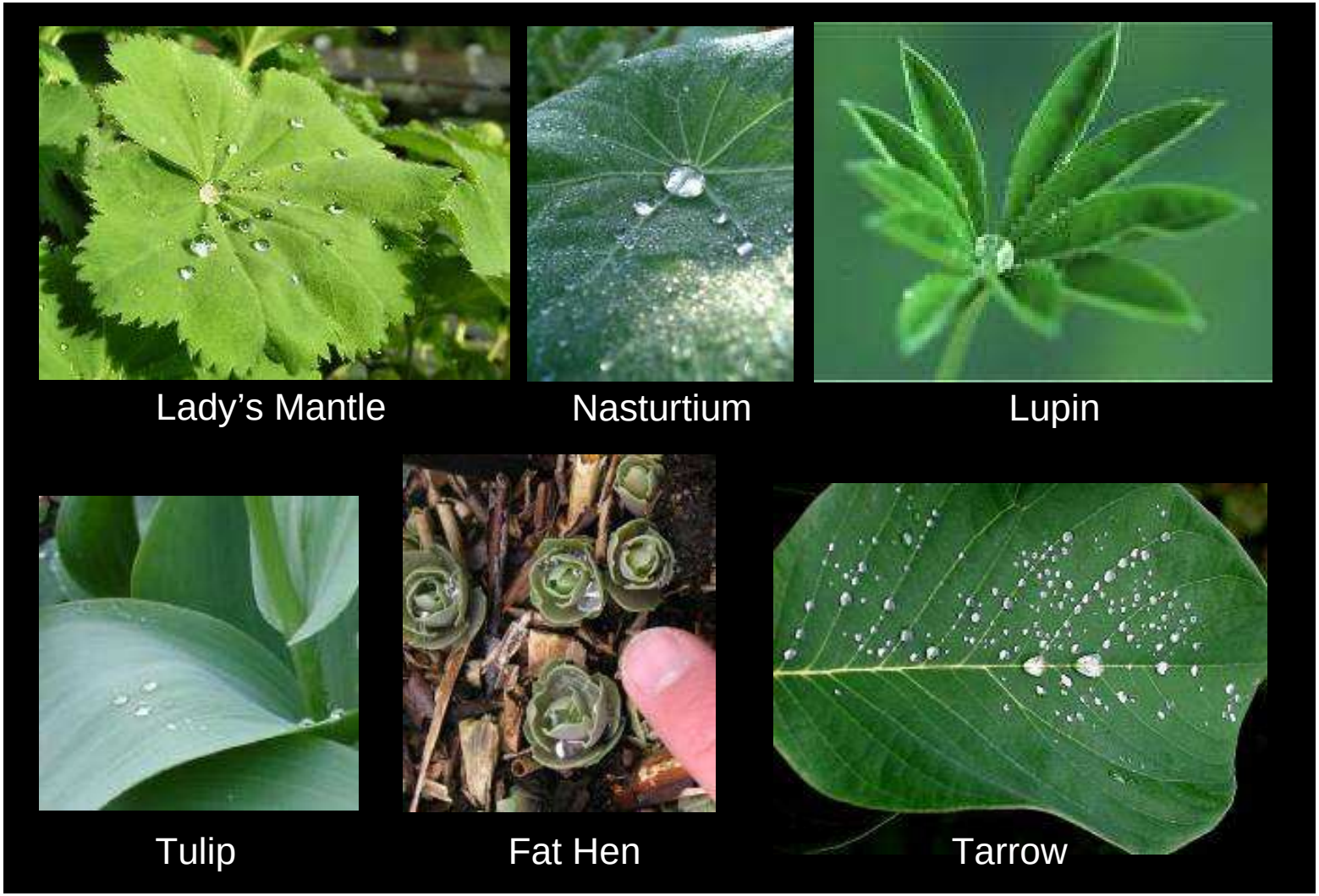
Is it just imagination?

Or could it happen?

Surface Tension “Floating” Paperclip Demonstration

Surfaces of Plants and Leaves

Plants and Leaves



Lady's Mantle, Honeysuckle, Fat Hen, Tulip, Daffodil, Sew thistle (Milkweed), Aquilegia, Nasturtium, Cabbage/Sprout/Broccoli (Image Sources: Various)

The Sacred Lotus Leaf

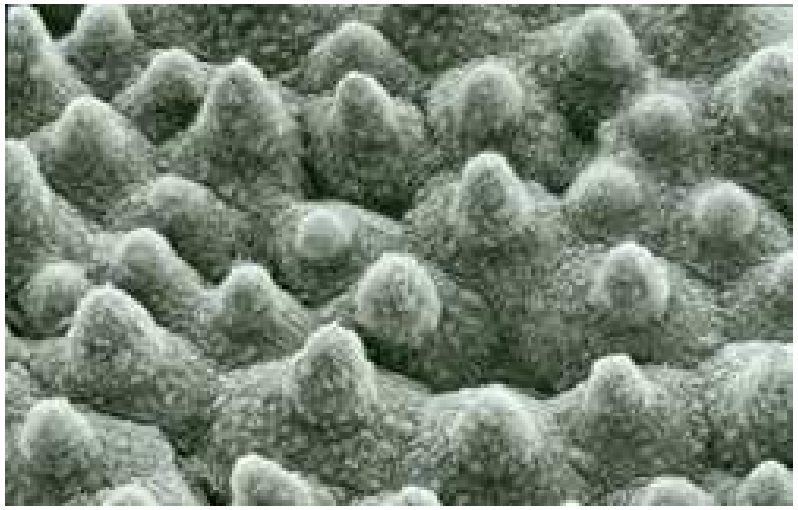
Plants

Many leaves are super-water repellent (i.e. droplets completely ball up and roll off their surface)

The Lotus plant is known for its purity

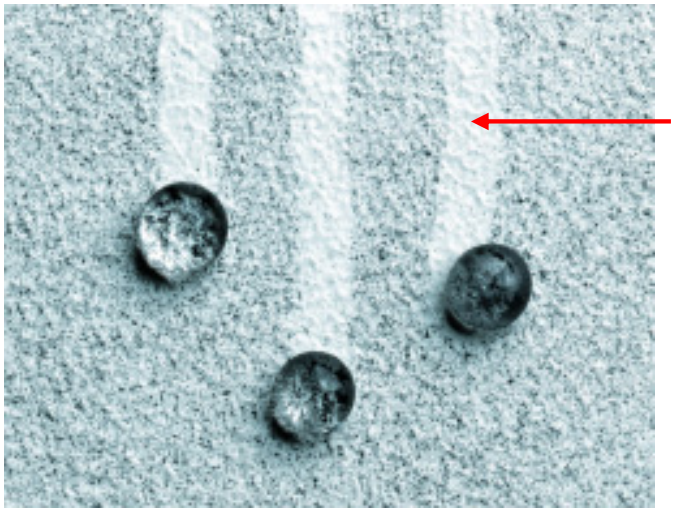
Some leaves are self-cleaning (*under the action of rain*)

Microscope Image of Lotus Leaf



Acknowledgement: Neinhuis and Barthlott

Self-Cleaning Glass



Acknowledgement: BASF

Mimicking the Surfaces in Nature

Hydrophobicity and Superhydrophobicity

Surface Chemistry

Terminal group determines whether surface is water hating

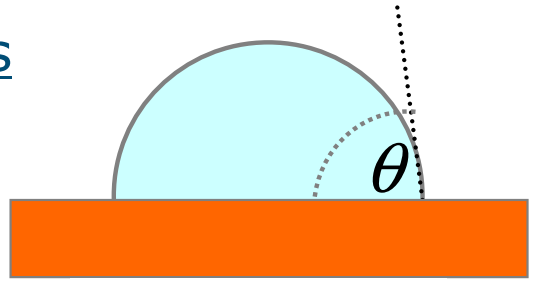
Hydrophobic terminal groups are Fluorine (CF_x) and Methyl (CH_3)

Contact Angles on Teflon Coated Frying Pans

Characterize hydrophobicity

Water-on-Teflon gives ~ 115°

The best that *chemistry* can do



Physical Enhancement

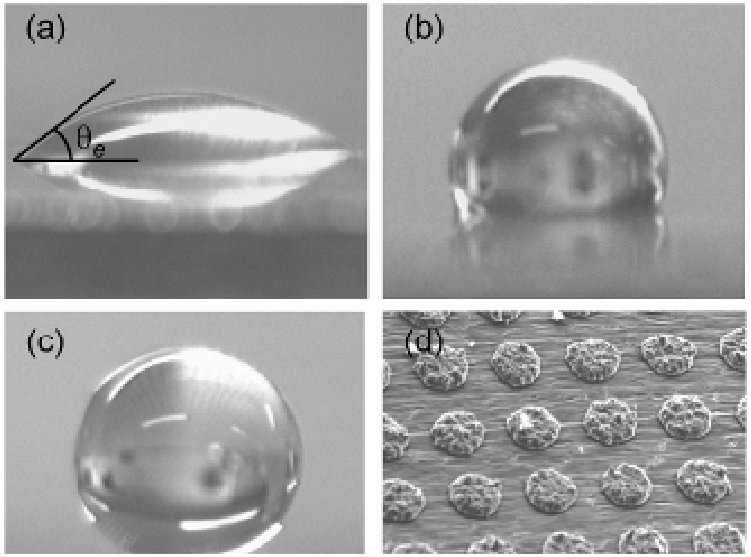
(a) is water-on-copper

(b) is water-on-fluorine coated copper

(c) is a super-hydrophobic surface

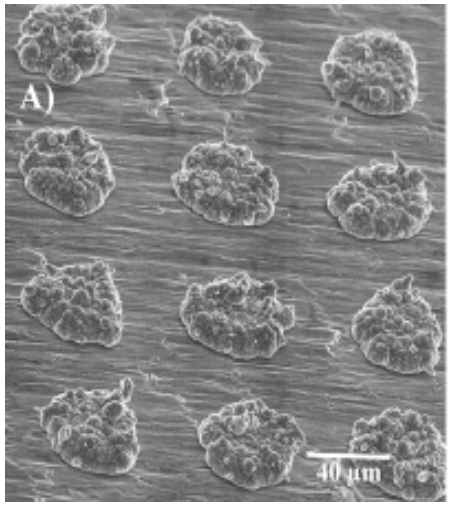
(d) "chocolate-chip-cookie" surface

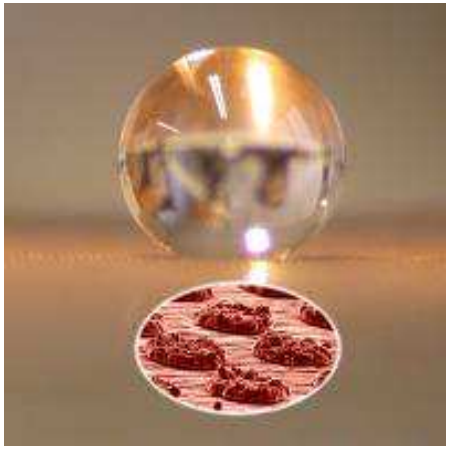
Superhydrophobicity is when θ>150°
and a droplet easily rolls off the surface



Mimicking Superhydrophobic Surfaces

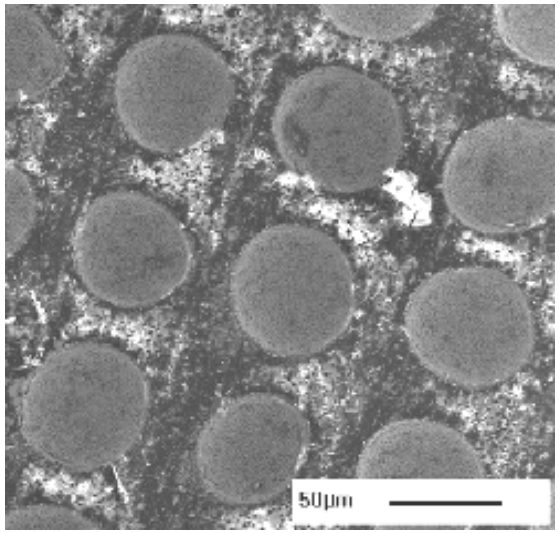
Deposited Metal

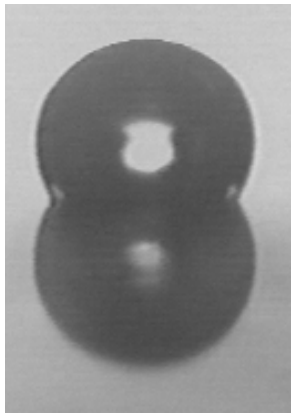




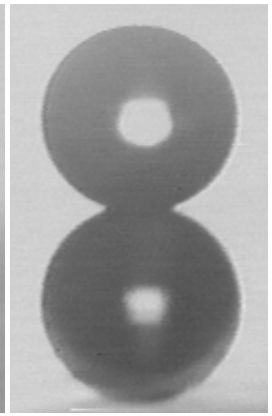
Patterned & hydrophobic

Etched Metal



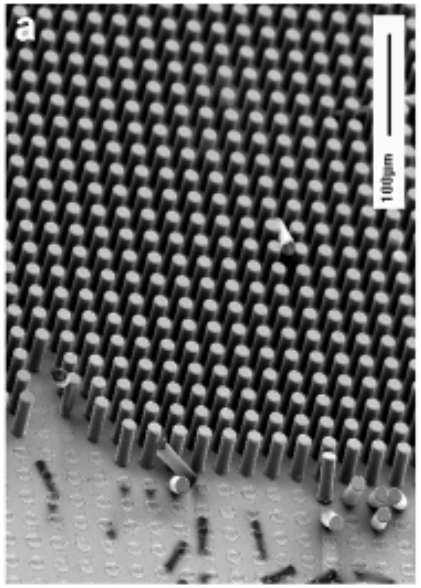


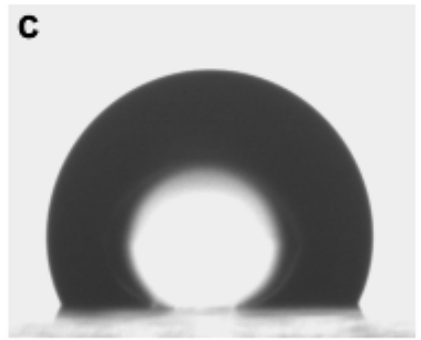
Flat & hydrophobic



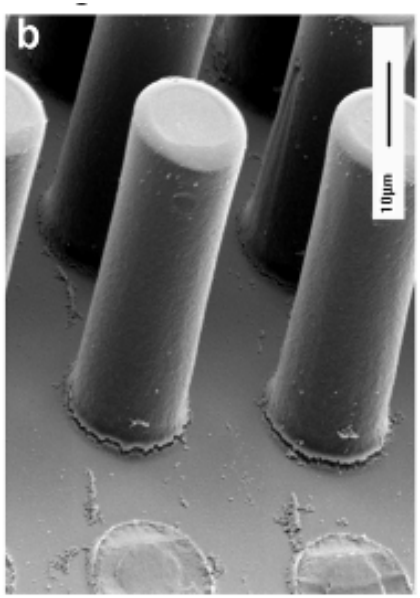
Patterned & hydrophobic

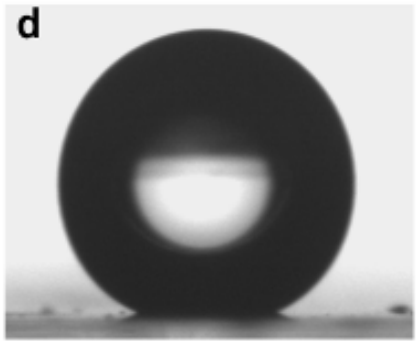
Polymer Microposts





Flat & hydrophobic





Patterned & hydrophobic

NTU Materials Demonstration

Etched and deposited copper
sol-gel and oasis foams
hydrophobic paint, sand and cloth

The Fakir’s Carpet

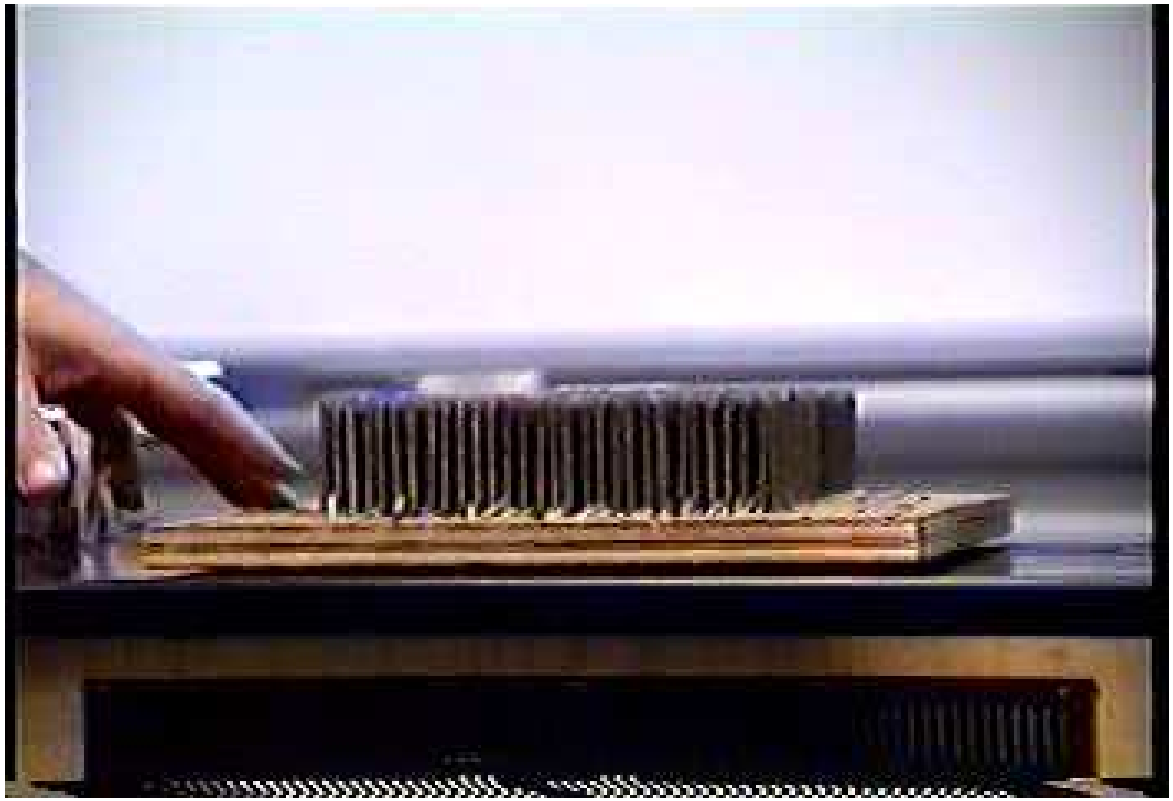
Bed of Nails

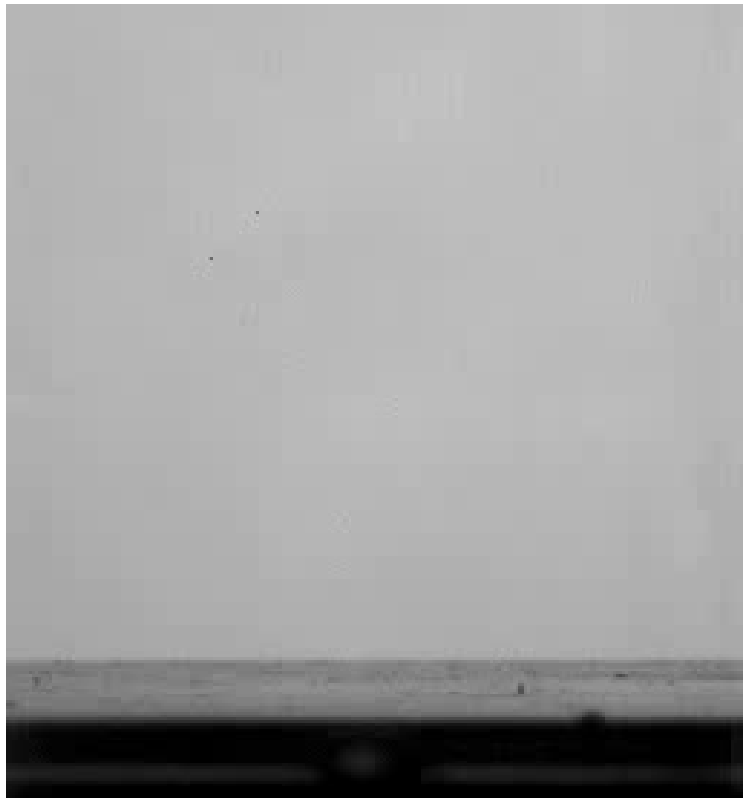
Roman consul Marcus Atilius Regulus is tortured to death by Carthaginians in about 255 BC. The illustration was painted in about 1415 in Paris.

Acknowledgement: Physics, UCLA

Fakir’s Carpet Demonstration
James and Laurice

Fakir's Carpet and Bouncing Droplets

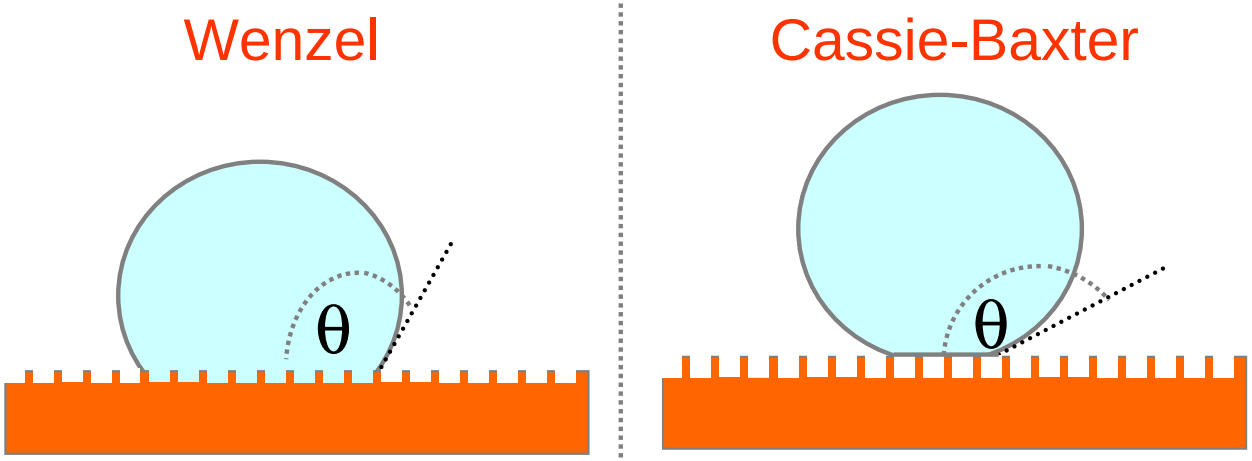




Acknowledgement: Wake Forest University

Courtesy: Prof. David Quéré, ESPCI

Penetrating versus Skating



Surface Chemistry and Surface Structure

Provided our "nails" are tall, thin and close enough and we make them hydrophobic (water-repellent), water can skate across their tips

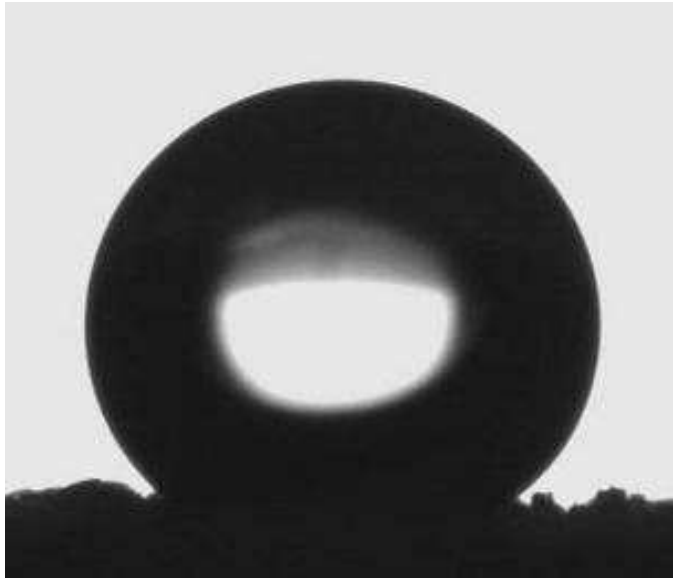
A droplet of water sitting on a composite air-solid interface balls up

The Surface of Hydrophobic Soil

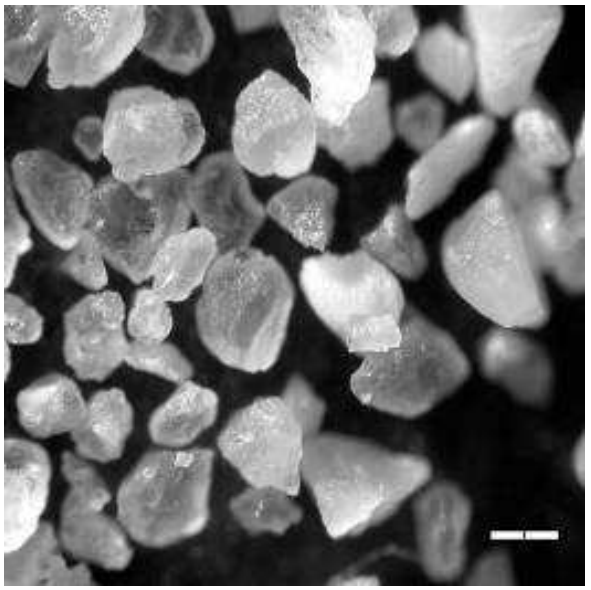
Magic Sand Demonstration

Super Water-Repellent Sand/Soil

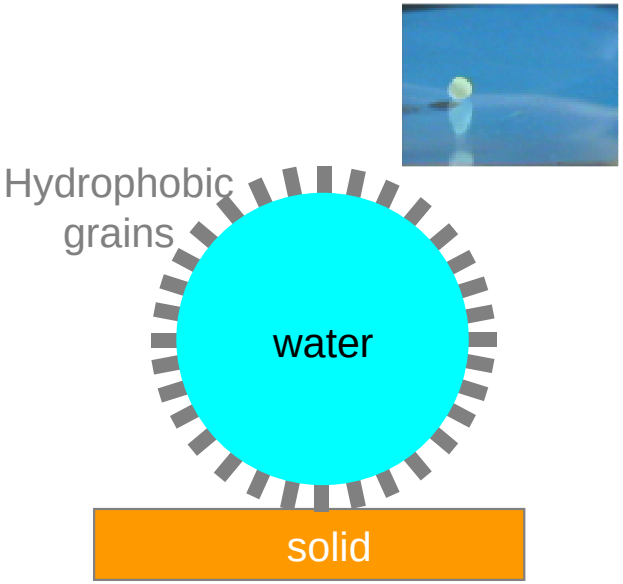
Sand with 139°



Shape and Packing



Liquid Marbles



Hydrophobic sand occurs naturally, but can also be reproduced in the lab

Hydrophobic sand sticks to the surface of water to form a liquid marble

Hydrophobic Soil - Occurrence

Forests

Overland flow, soil erosion and land remediation

Farmland

Gray water and irrigation

Golf courses

Localized dry spots

Courtesy: Dr Stefan Doerr (Swansea), Dr Pete Robinchaud (USDA- Forest Service), Dr Margaret Roper (CSIRO, Australia).

Forest Fire and Debris Slide

Courtesy: Dr P. Robinchaud USDA- Forest Service. Video footage courtesy, Devore resident, Mr. Davis showing Greenwood Ave. Devore CA. 25/12/2003.

Ponds, Plastrons and Pipes

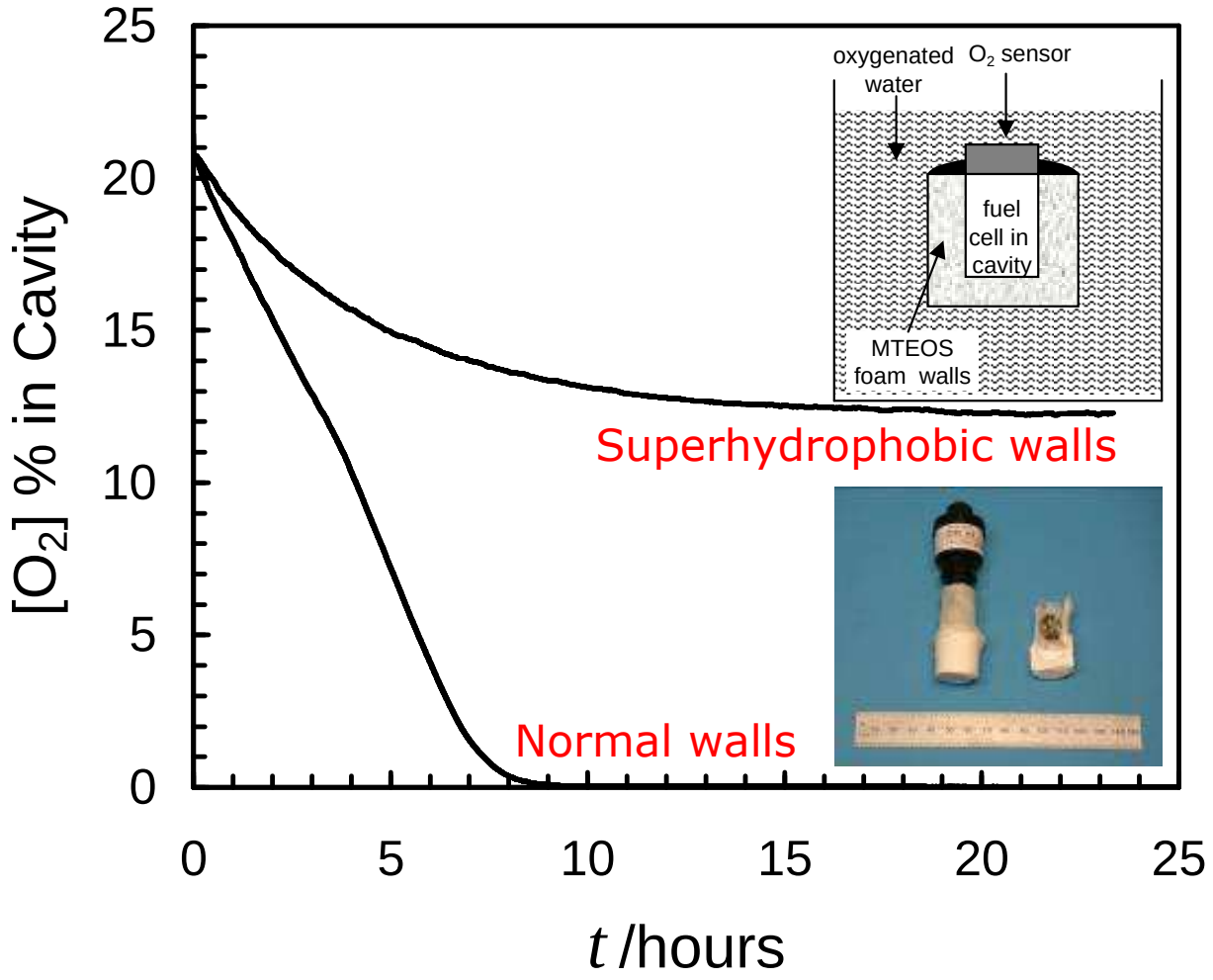
Plastron Demonstration

Breathing without Gills: Plastron Respiration

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

The Movie – Microcosmos

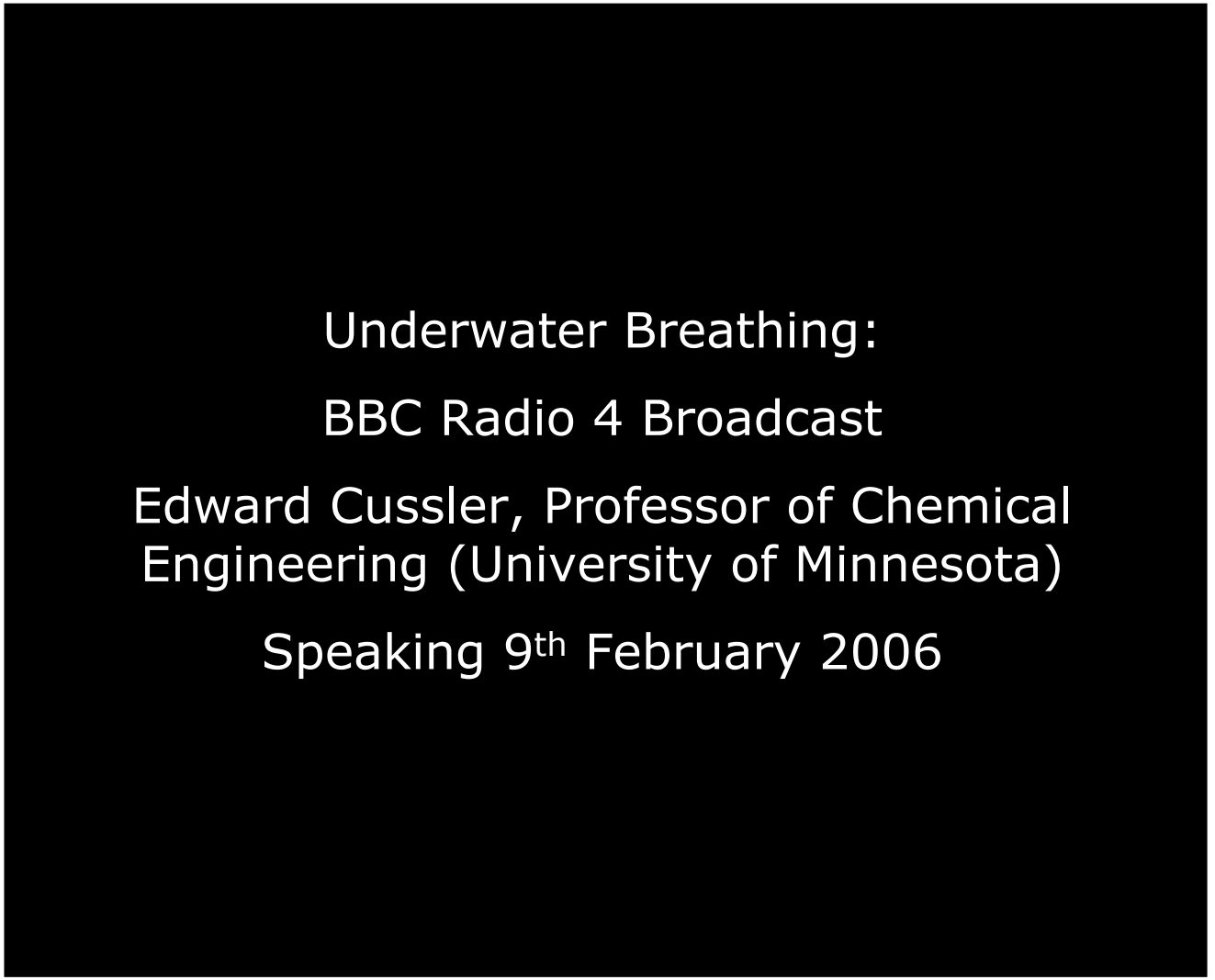
Copyright: Allied Films Ltd (1996)



Superhydrophobicity: Plastron Respiration

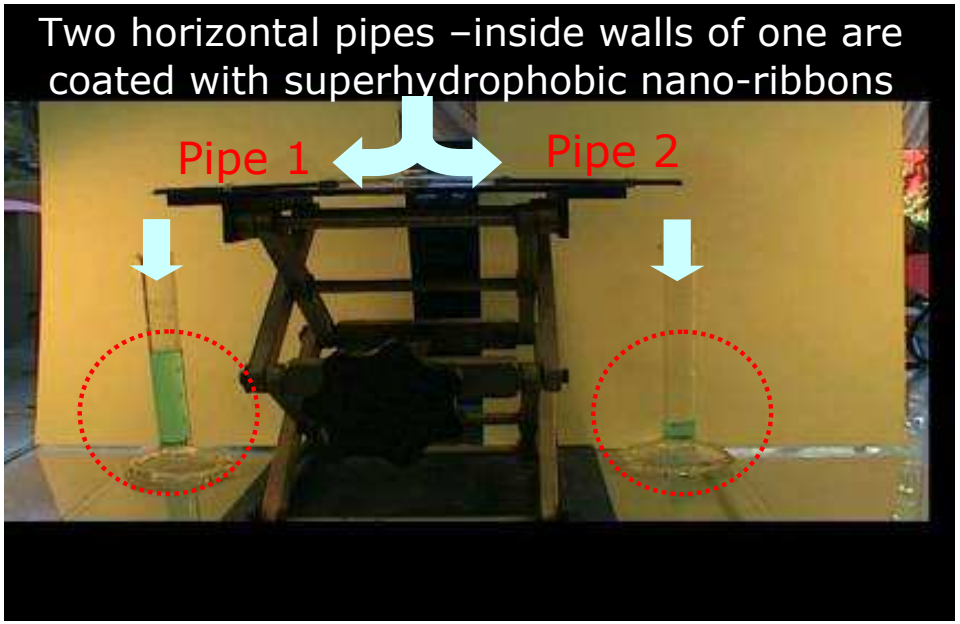
Similar to super gas exchange membranes

Edward Cussler

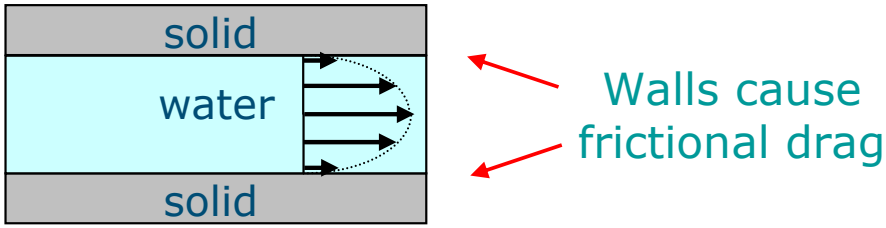


Flow in Pipes with Superhydrophobic Walls

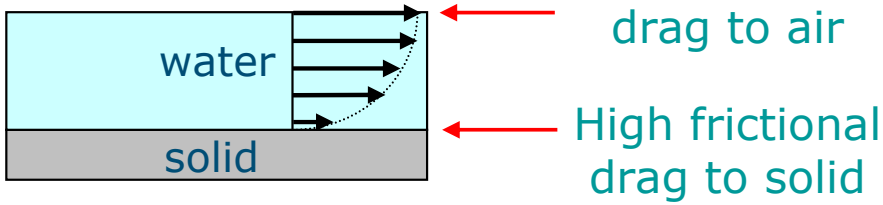
Hosepipe



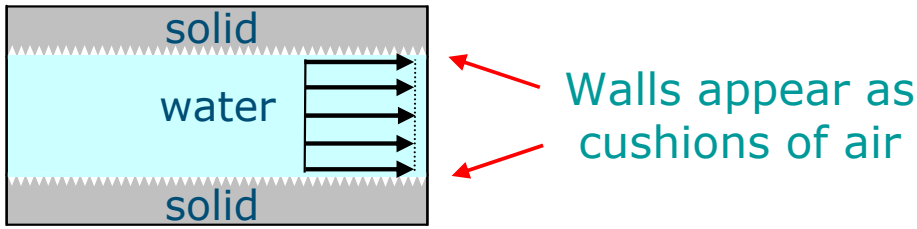
Closed-channel



Open-channel



Super-channel



Falling Objects

Galileo and Apollo 15

In the absence of a fluid, objects of different masses fall under the action of gravity fall at equal rates of acceleration

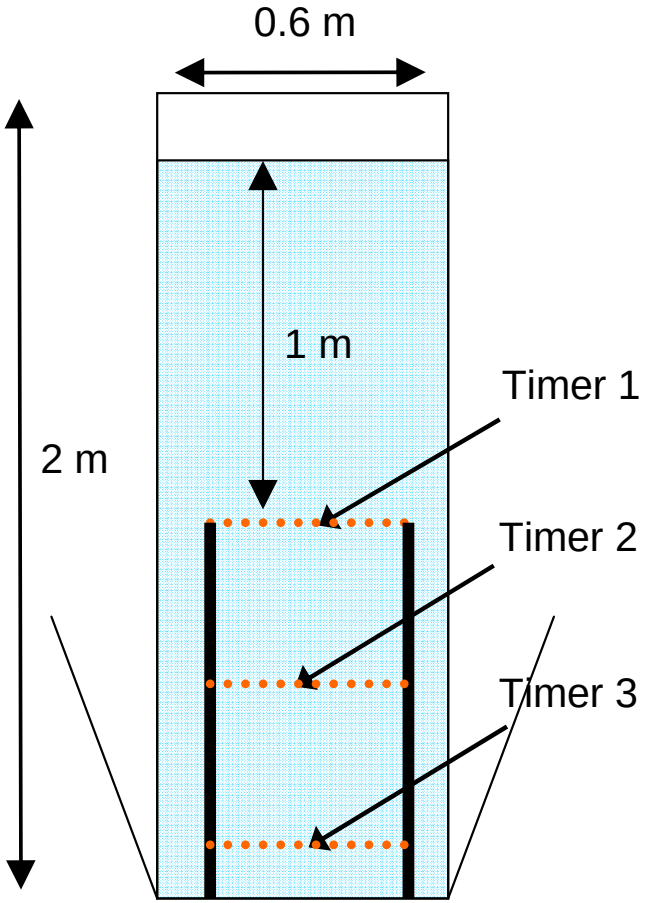
Acknowledgement: Wikipedia

Apollo 15 moon walk, Commander David Scott

Acknowledgement: http://nssdc.gsfc.nasa.gov/planetary/lunar/

Stokes and 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?

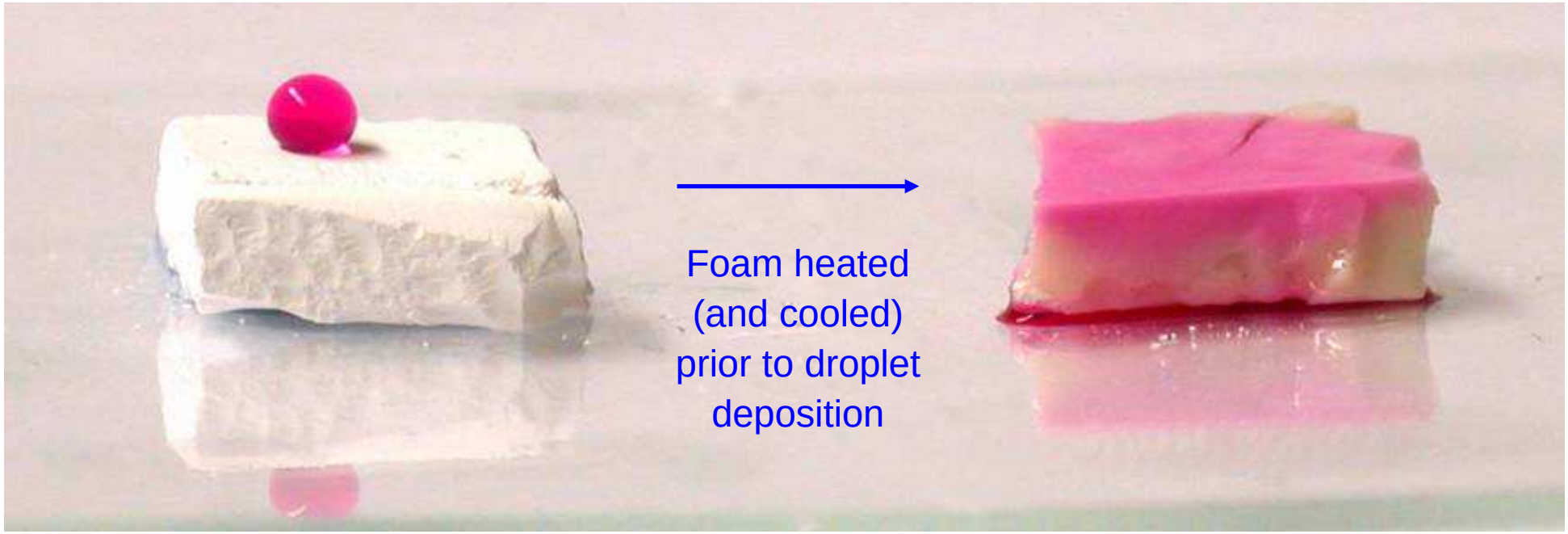


Sensing at Surfaces

Example 1: Triggering Changes

Superhydrophobic Foam

Super-Slurp



Mechanisms for Switching

Temperature history of substrate

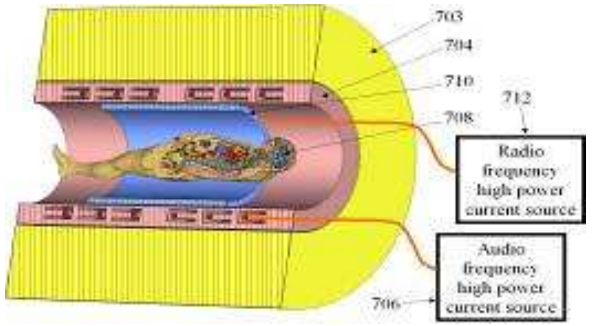
Contamination of a liquid (alcohol content, surfactant, …)

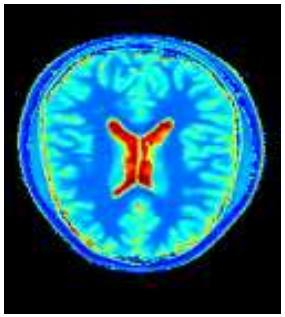
"Operating point" for switch is chosen by intelligent materials design → Sensor

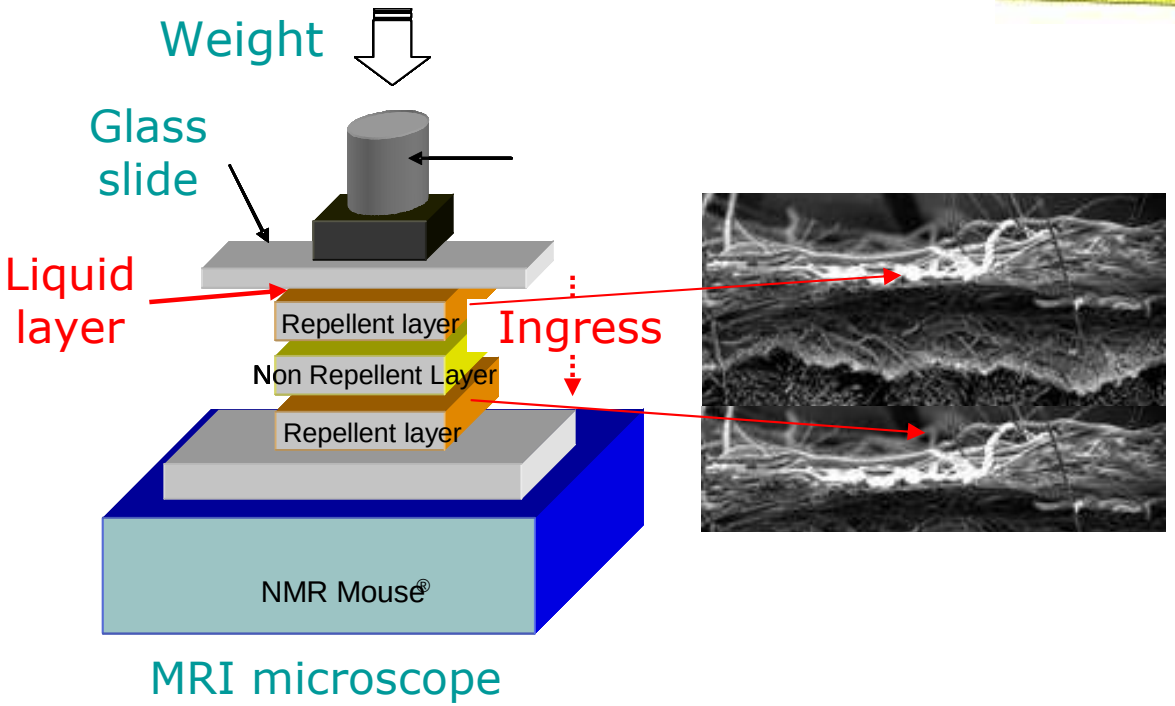
Example 2: MRI of Protective Textiles

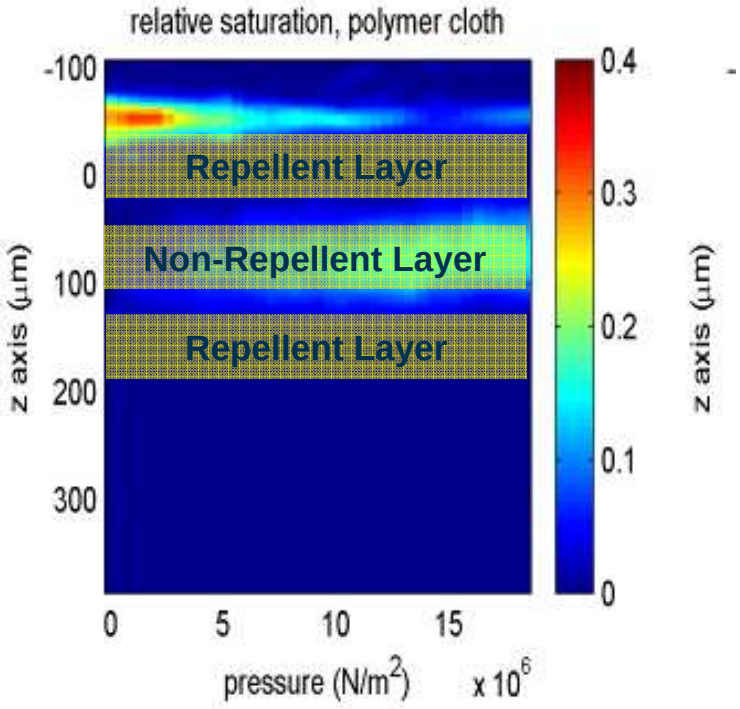
Textiles can be made super-repellent, e.g. two repellent and one wicking layer

How can we know how much pressure is needed to drive liquid into them?









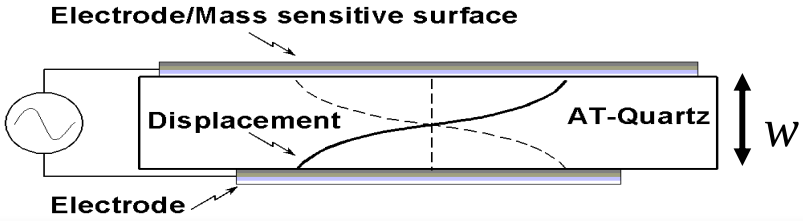
Acknowledgement: Dr Martin Bencsik with Hans Adraiensen and Dr Stuart Brewer

Example 3: Weighing Small Masses

Quartz Crystals and Surface Acoustic Waves

Timing elements in watches,

Filters in TVs, mobile phones, ...



Frequency accuracy to better than 1 part in 10 million

Detects molecular layers less than one monolayer thick

Can also detect changes in liquid properties

Examples of NTU Acoustic Wave Sensors

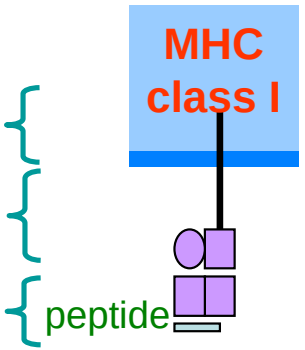
1. Particulates/PAHs/Terpenes	Pollution Monitoring
2. MHC-peptide screening	Cancer Vaccines
3. Steroid detection (nandrolone, testosterone)	Drug Detection
4. Sperm quality and detection device	Vet AI
5. Microfluidic chip for properties of ionic liquids	Green Chemistry

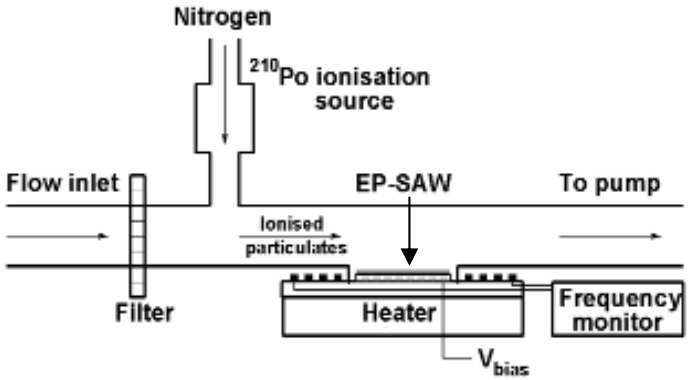
Sensor Strategy

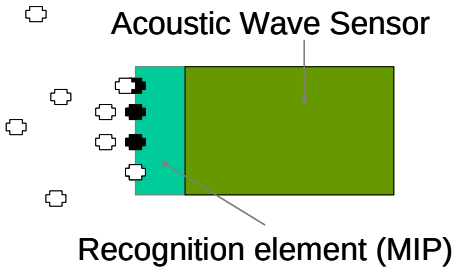
Make this the acoustic wave sensor

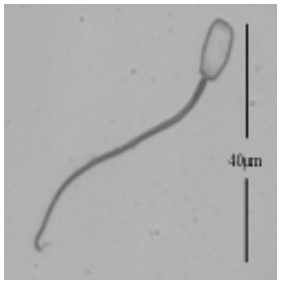
Recognition layer is MHC protein

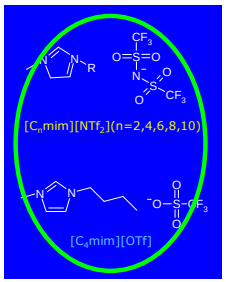
Detect peptide specific binding











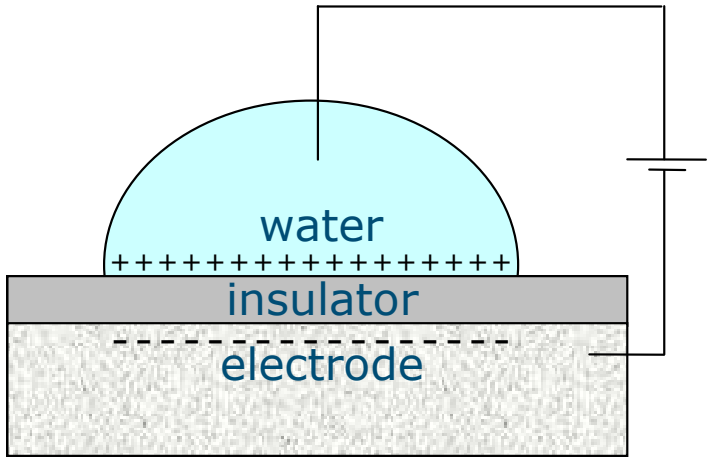
Almost all involve the solid-liquid interface

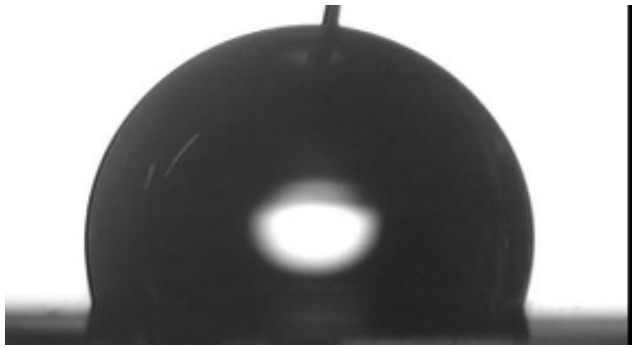
New Liquid Based Devices

The Principle of Electrowetting-on-Dielectric

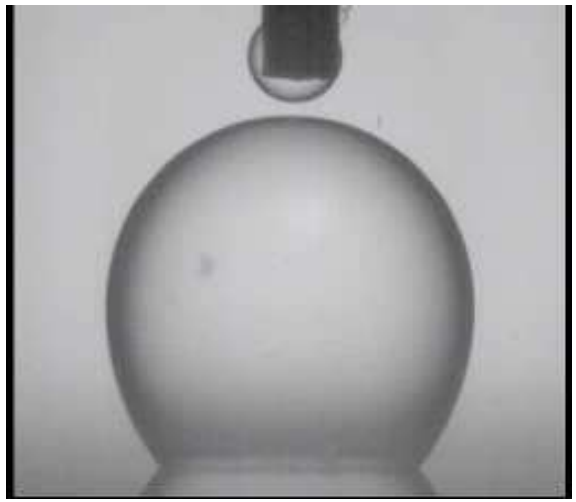
Use a droplet of water as an electrode – charge up water-solid interface

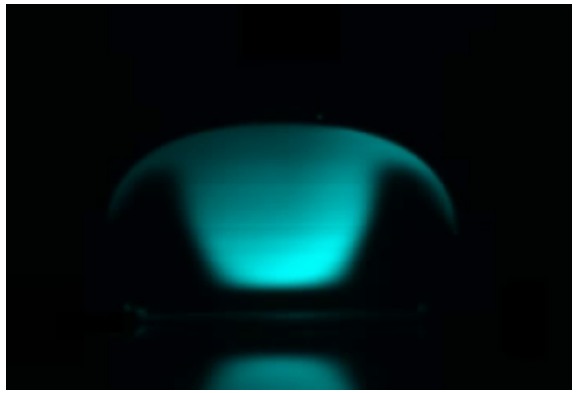
Electrowetting in Air





Electrowetting: Water in Oil



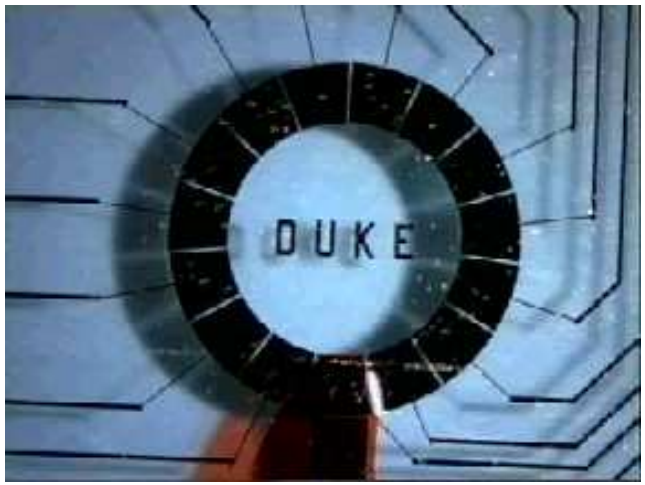


Courtesy: Prof. Frieder Mugele (Univ. Twente)

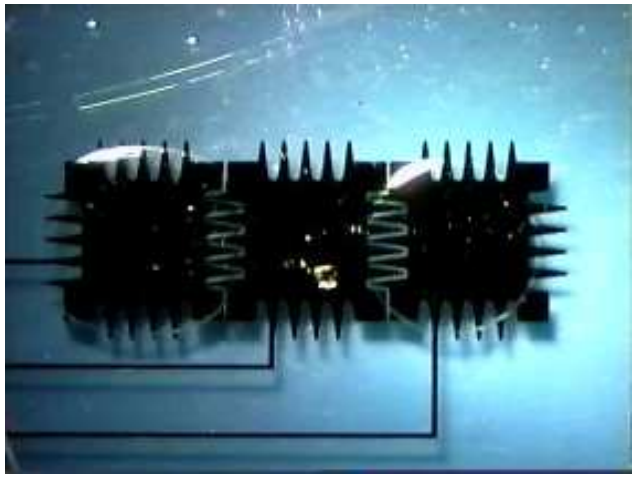
Example 1: Chemical Factories in Droplets

Electrowetting to dispense, merge/split/mix and move

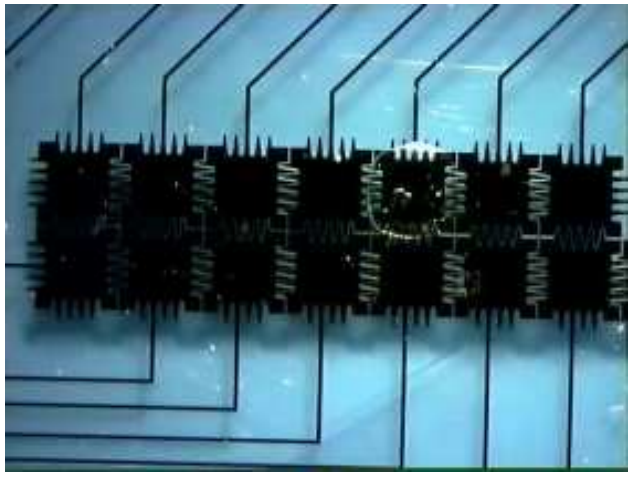
Dispense



Combine/Split



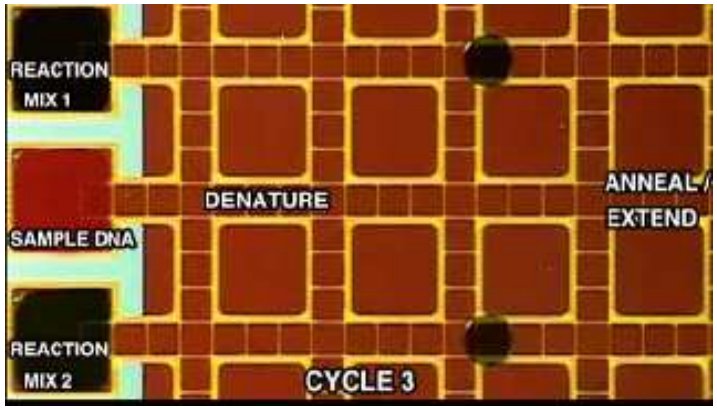
Digital Motion



Courtesy: Dr Mike Pollack (Duke University – co-founder Advanced Liquid Logic, USA)

Assays on the size of a credit card

Immunoassays, clinical chemistry, …

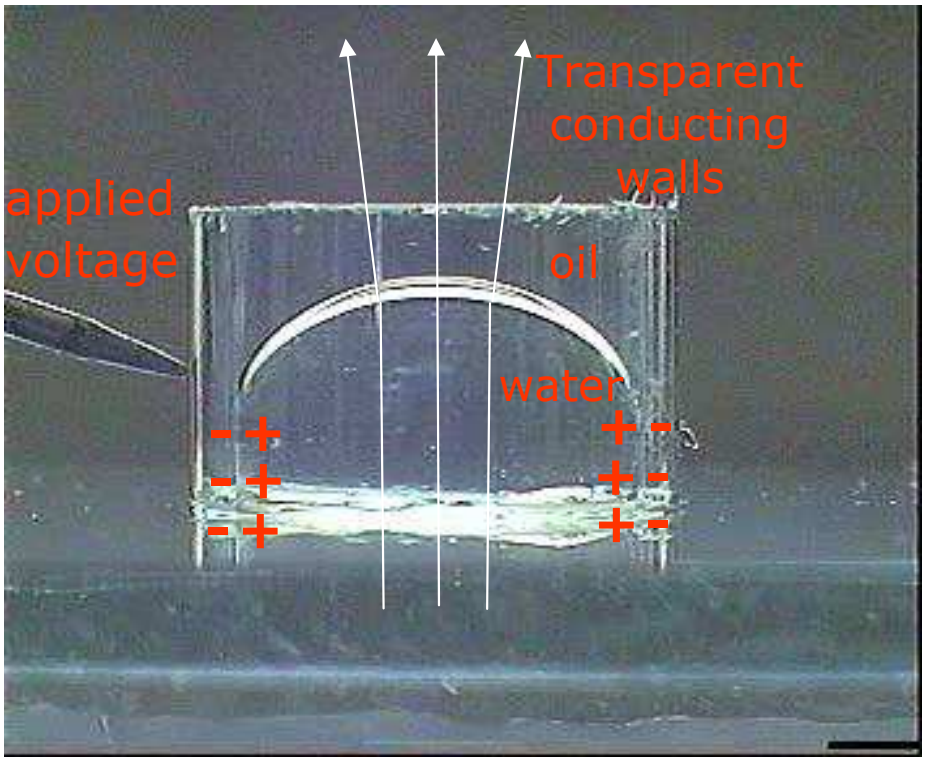


Acknowledgement: Advanced Liquid Logic

Example 2: Liquid Lenses

Voltage Control of Liquid-Oil Interface (Varioptics and Philips)

- Electrically charge the solid-water interface to cause shape changes
- Electrowetting uses capacitance of a liquid-insulator-conducting solid structure



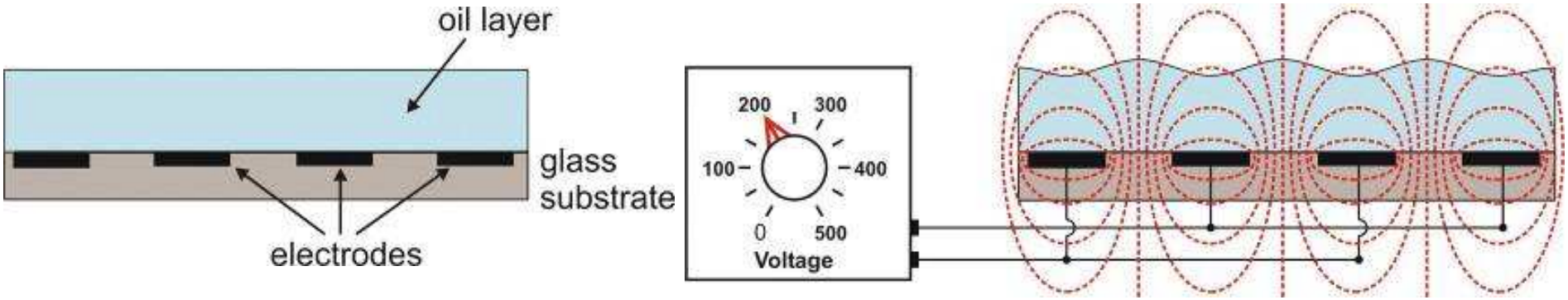
Courtesy: Dr Stein Kuiper (Philips Research Labs, Eindhoven)

Example 3: Liquid Photonics

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

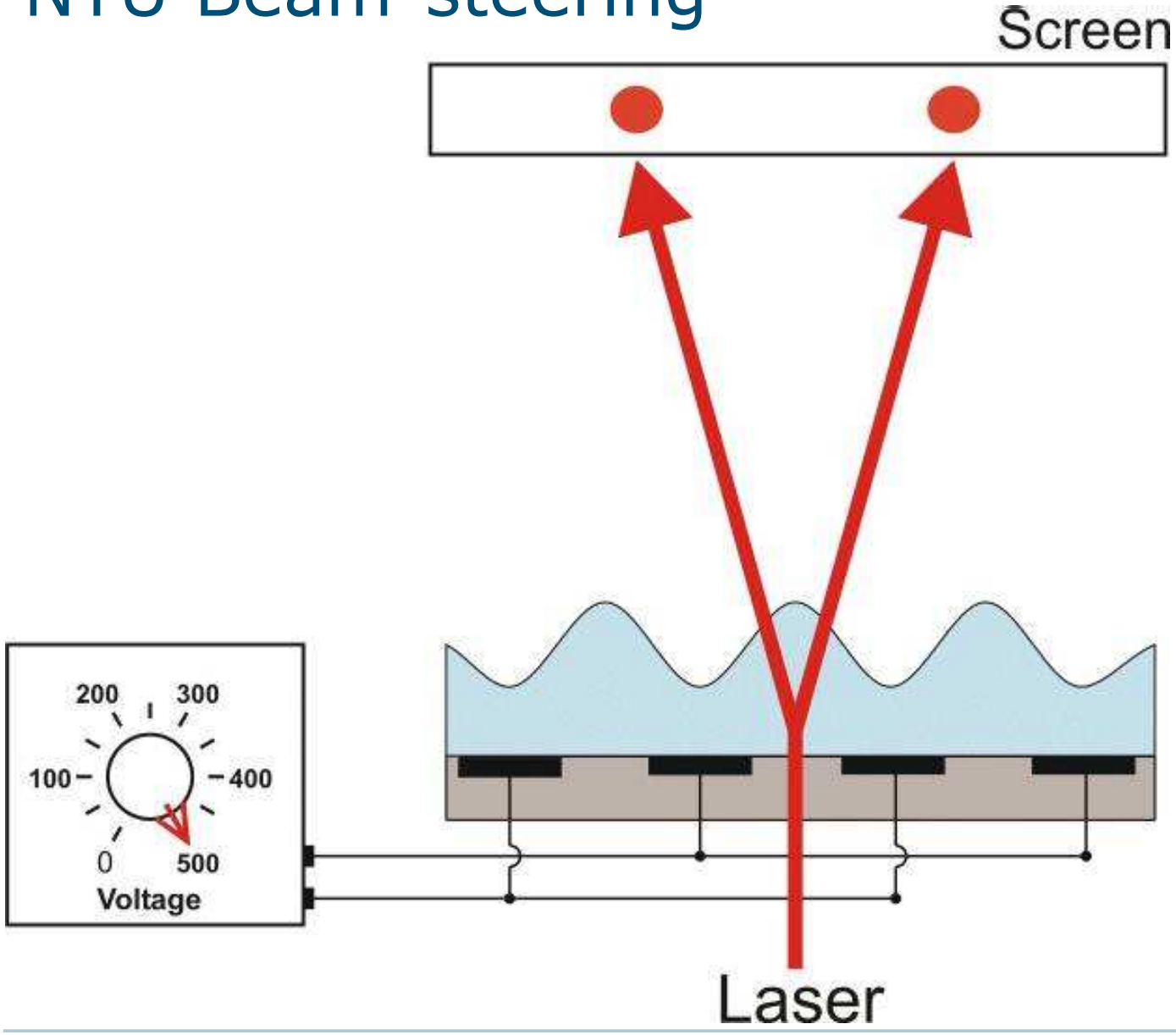
Edge of a CD under white light

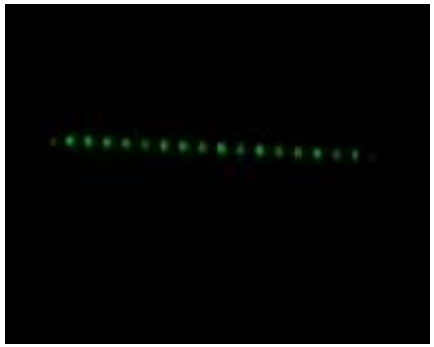
Diffraction using programmable electrical control of oil-air interface

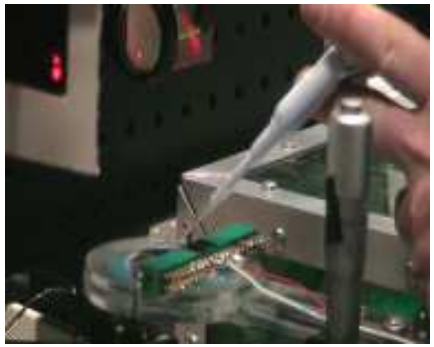


Acknowledgement: Dr Carl Brown, Dr Mike Newton with Gary Wells

NTU Beam-steering







Journey's End

What is Science for me?

A means to understand the world around us

A way to develop new tools

An application of imagination, but one that requires us to work within constraints …

In my Empires of solids and liquids with their surfaces

Known scientific principles are both guides and boundaries

And experiments provide paths and roads

But the unspoken Queen and Servant of Science is …… Mathematics

$$\cos\theta_e^W(x) = r(x)\cos\theta_e^s \qquad \cos\theta_e^{CB}(x) = f_1(x)\cos\theta_1^s + f_2(x)\cos\theta_2^s$$

$$Z_L = \sqrt{i\omega\rho_f\eta_f}\tanh\left[\frac{\sqrt{2i}\,d}{\delta}\right] \qquad \left(\frac{\Delta\omega}{\omega}\right) \approx -\frac{1}{\pi}\sqrt{\frac{\omega\rho_f\eta_f}{2\rho_s\mu_s}}$$

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Internal Collaborators

Academics	Dr Mike Newton, Dr Carl Brown, Dr Martin Bencsik, Dr Gareth Cave (Chemistry)
	Dr Carl Percival (Chemistry), Prof. Carole Perry (Chemistry),
	Prof. Brian Pyatt (Bio Sci.), Prof. Bob Rees (Bio. Sci.), Prof. Tony Dodi (ANRI/NTU)
PDRA's	Dr Neil Shirtcliffe, Dr Carl Evans, Dr Paul Roach, Dr Yong Zhang,
	Dr Dale Herbertson, Dr Simon Stanley, Mr Rob Morris, Dr Andrew Hall, ….
PhD's	Ms Sanaa Aqil, Mr Steve Elliott, Ms Nicola Doy, Mr Shaun Atherton, Mr Gary Wells,
+	Former colleagues, students and research fellows

External Collaborators

Dr Electra Gizeli & Dr Kathryn Melzak (Crete/Cambridge), Prof. Mike Thompson (Toronto), Prof. Yildirim Erbil (Istanbul), Dr Stefan Doerr (Swansea), Dr Stuart Brewer (Dstl), Dr Andrew Clarke & John Fyson (Kodak), Dr Ralf Lücklum (Magdeburg), Dr Neil Thomas (UoN), Ms Huey-Jen Fang, Prof. Chris Hardacre (QUB), Prof. Ray Allen & Dr Jordan MacInnes, …..

Demonstrations/Organization

Drs Newton, Shirtcliffe, Brown & Bencsik, Gary Wells, Dave Parker, Dr James Hind, Laurice Fretwell, Ian Rogers Dr Christian Thode + Kerri H, Kathryn P & Lesley A

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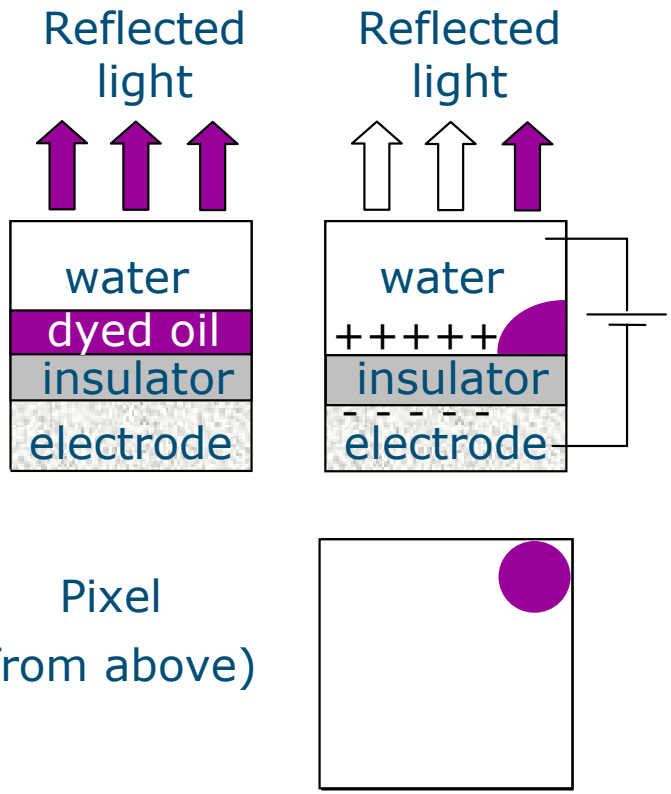
Appendices

Example: Liquid Paper

Oil layer-to-droplet transition



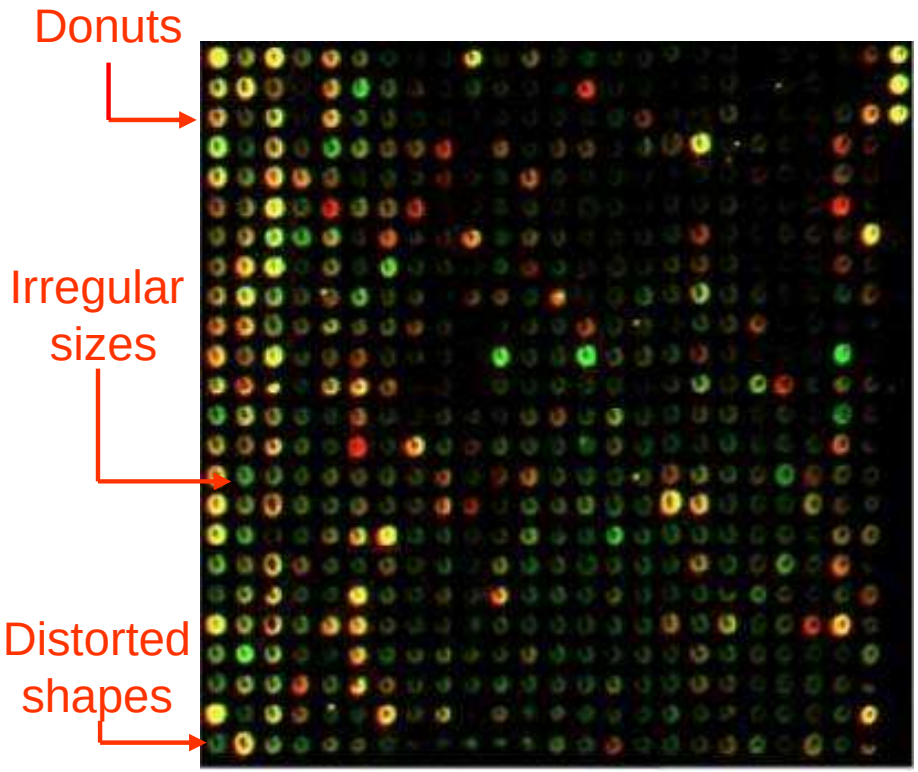
LiquaVista's Sunlight readable displays

Courtesy: Dr Romaric Massard (LiquaVista, USA)

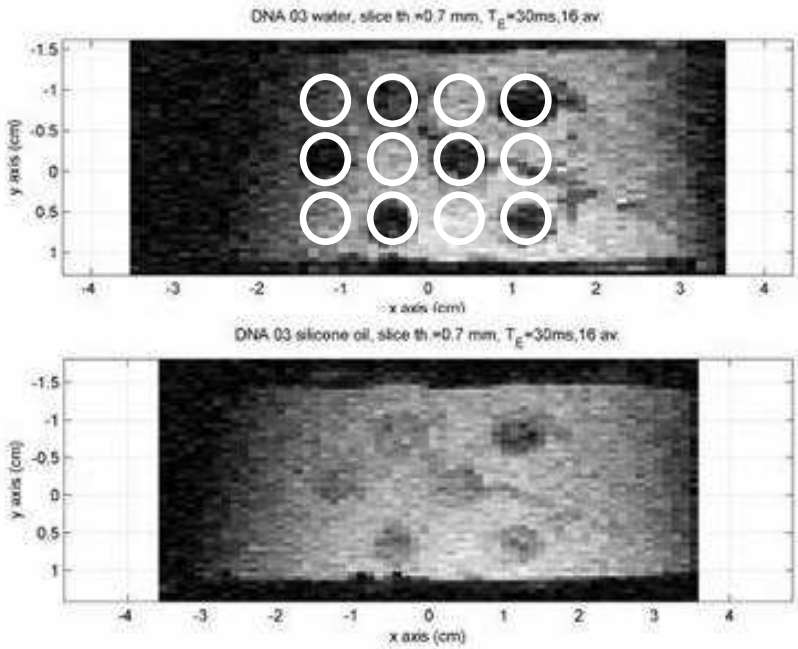
Application: DNA Microarrays by MRI

Thousands of tiny droplets/spots containing strands of DNA deposited onto a surface can be used to determine biomolecular interactions – a high-throughput technology in molecular biology/medicine. Usual detection method is fluorescence.

Spotted Fluorescent Array



Magnetic Nanoparticle-based Array



Imaged in water and silicone oil

Acknowledgement: Dr Martin Bencsik, Dr Gareth Cave and Dr Mike Newton