Wetting of Surfaces

Glen McHale

School of Biomedical & Natural Sciences
Nottingham Trent University

Email: glen.mchale@ntu.ac.uk

Overview

1. The Need to Understand Wetting

2. Wetting Issues in Spotted Microarrays

3. Principles of Wetting

The Need to Understand Wetting

An Overview - Three Examples

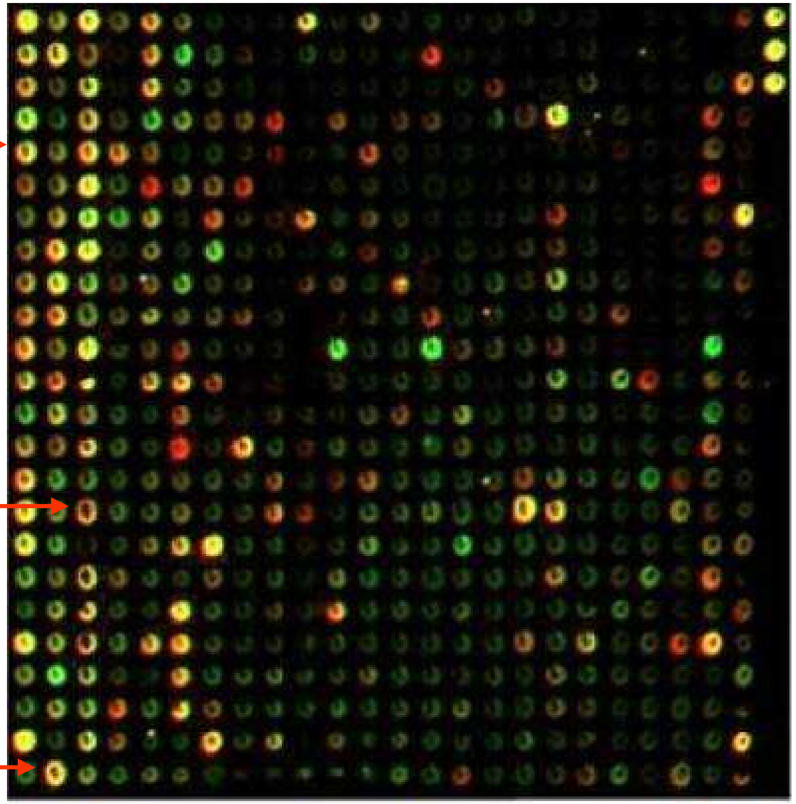
1. Spotted Microarrays
2. Liquid Confinement
3. Droplet Microfluidics

Spotted Fluorescent Microarrays

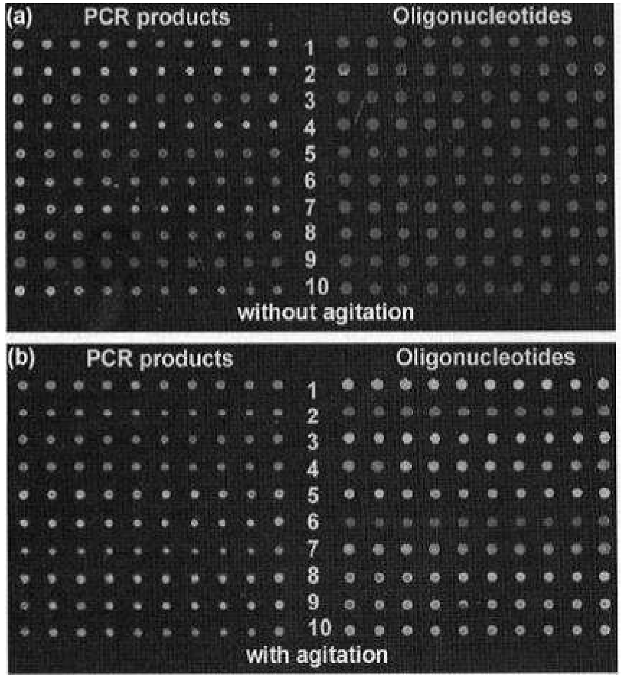
Donuts

Irregular sizes

Distorted shapes



Micro-mixing improves intensity, but doesn't stop donut's etc:



Wetting Dominated Effects

- Donut or "coffee/ring-stain" effect
- Size, shape, uniformity and reproducibility of deposition
- Drying effects (evaporative considerations)

Acknowledgement A. Wixforth, Superlattices & MicroStr. (2003), 33, 389; Anal. Bioanal. Chem (2004), 379, 982.

Liquid Confinement

Non-circular droplet

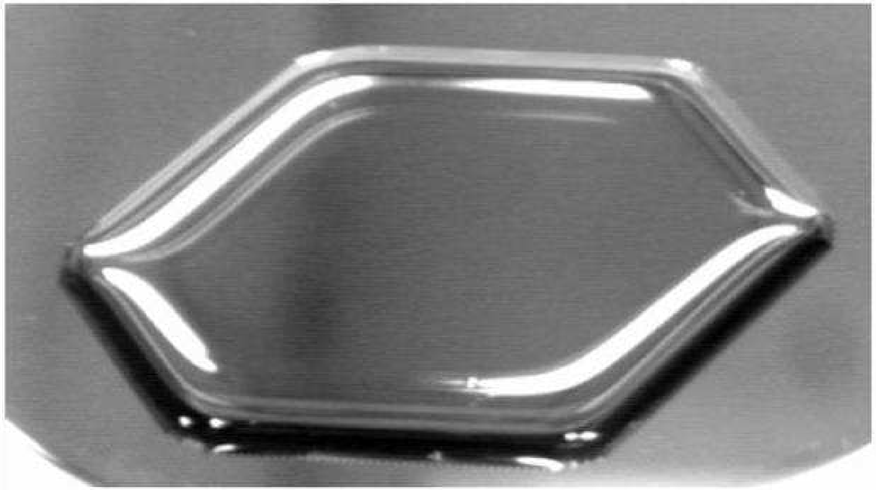
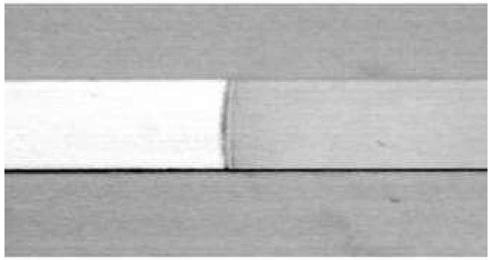


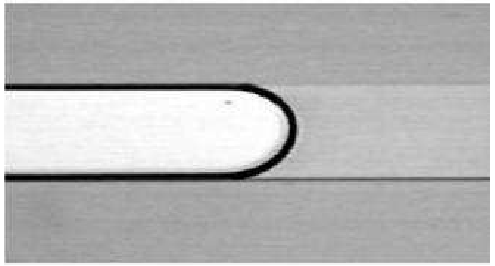
Figure 18

Large sessile drop setting on a hexagonal array of small non-wetting defects ($d = 0.4$ mm). The size of the drop is 3 cm.

Meniscus

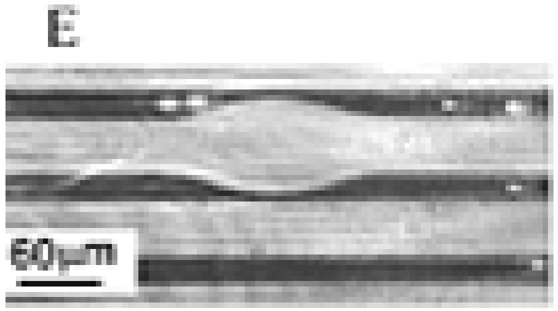


Water in hydrophobic channel



Water in hydrophilic channel

Virtual Channels



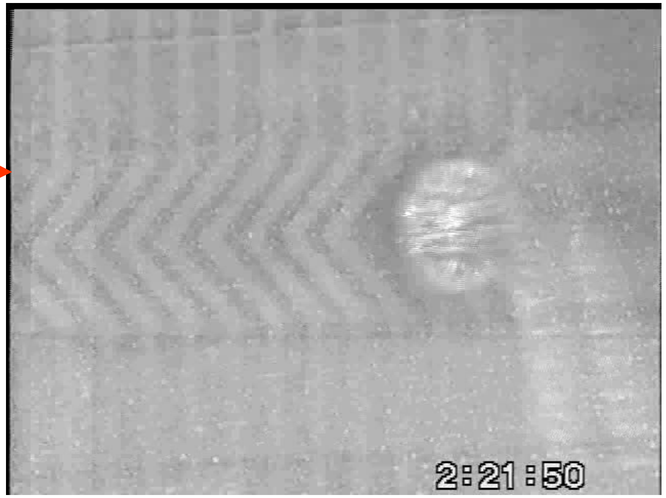
Hydrophobic/Hydrophilic & Surface Tension

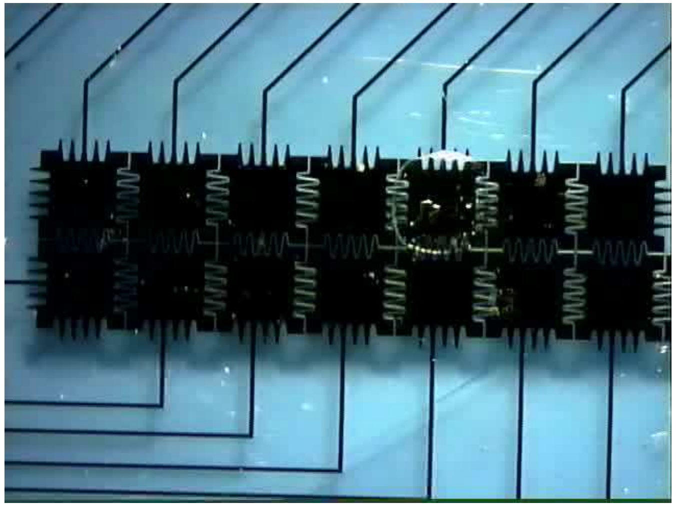
- Virtual tracks/confinement, micro-flow patterns, actuating forces, micro-contact printing, etc
- Self assembly and self organisation

Acknowledgement Max Planck Institute for Polymers & Colloids; Huang *et al*, Purdue Univ.; Fermigier *et al*, Oil & Gas Science and Technology – Rev. IFP, 56 (2001)

Droplet Microfluidics

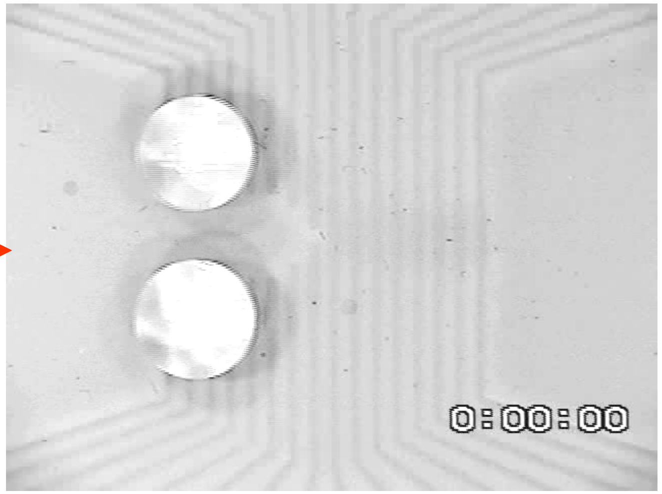
Contact Angle control

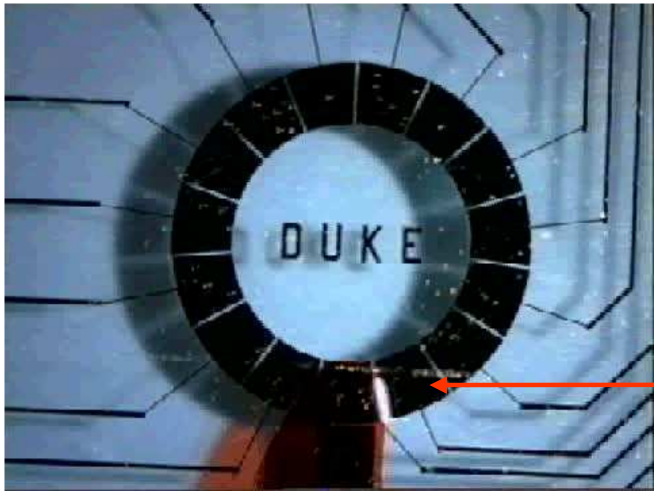




Reducing contact angle hysteresis

Droplet Coalescence





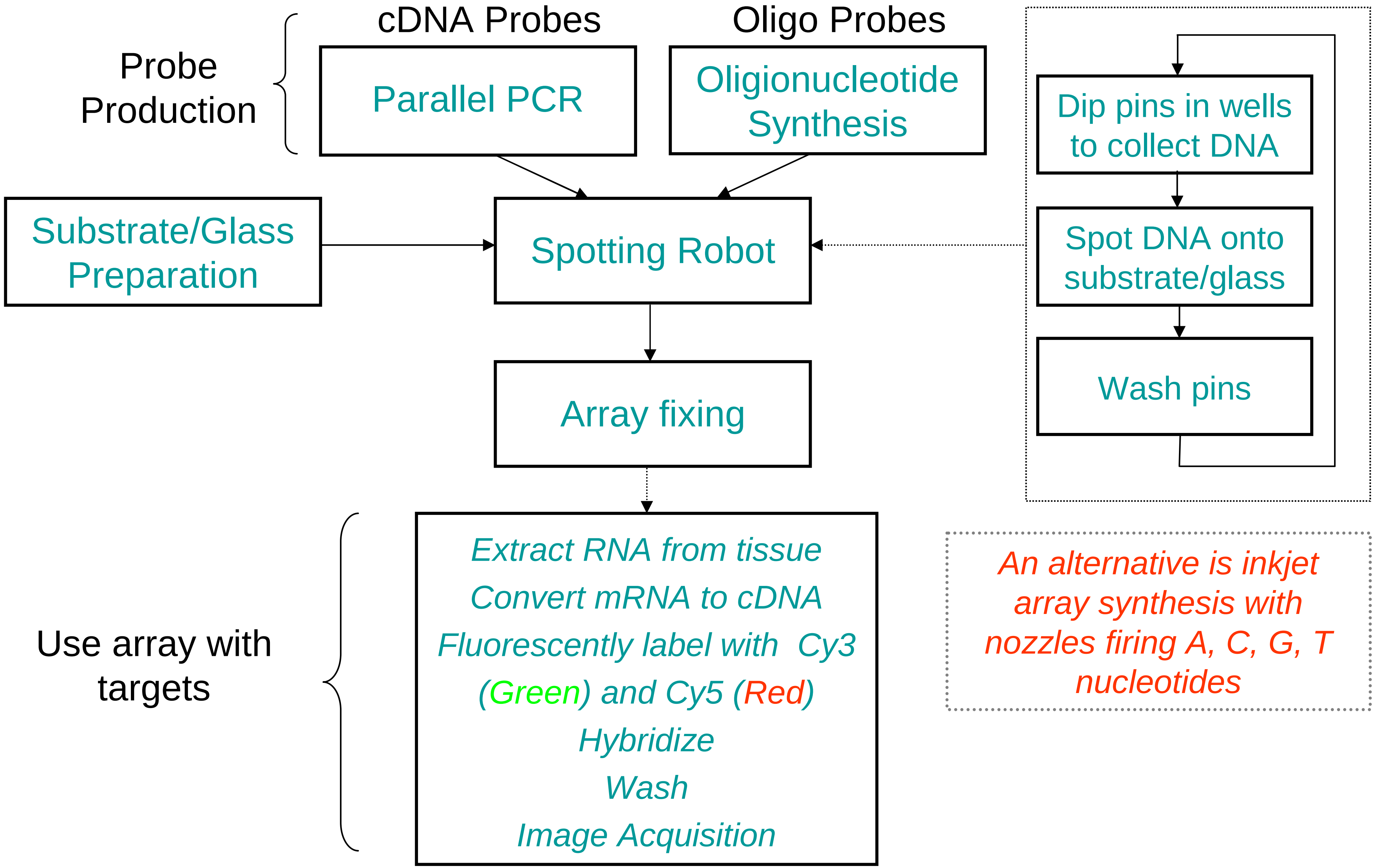
Breaking capillary bridges

Acknowledgement Duke Univ/Nanolytics – Pollack *et al*., APL (2000), 77, 1725; VTT – Torkkeli *et al*., Eurosensors XV (2001)

Spotted Microarrays

Wetting Issues

Spotted Microarray Principles



Acknowledgement Stekel, "Microarray Bioinformatics", ISBN 0-521-52587-X

Microarray Considerations

Critical Parameters

- Spot shape
- Spot size
- Concentration

Technologies

- Pins or Needles
- Pin & Ring
- Inkjet Printing

Quality Issues

- Print quality
- Substrate chemistry and hydrophobicity
- Spotting buffer viscosity, pH, evaporation, probe concentration
- Array hybridization quality

⇒ Spot quality

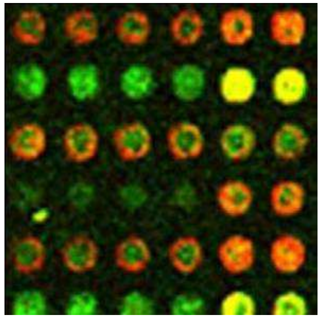
Halo's (High localized background/saturation)

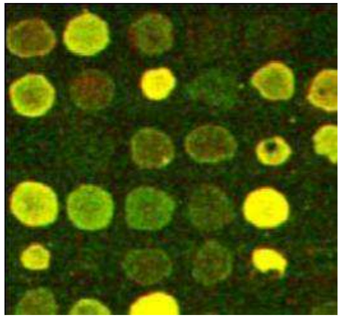
Donuts (Circles with holes in centre)

Irregular spot shape

Pin blockages

Particle/dust contamination, bubbles

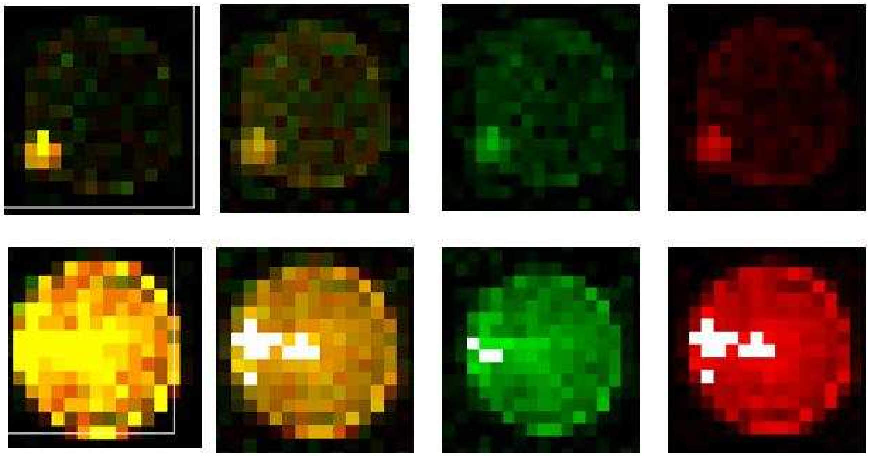




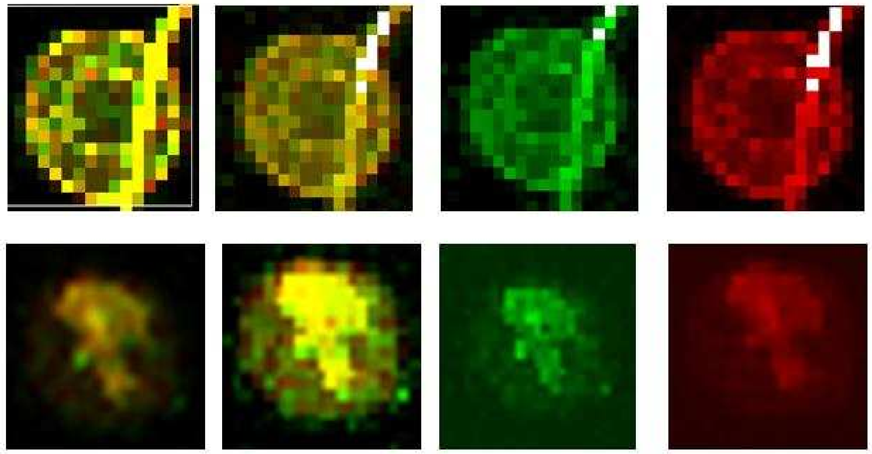
Example Effects

SMD, Genepix overlay, Cy3, Cy5

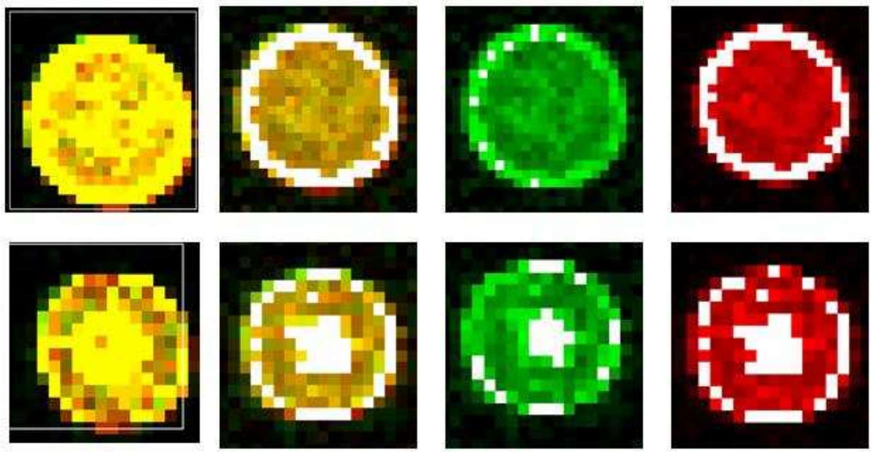
Dust Speck/Dust in Spot



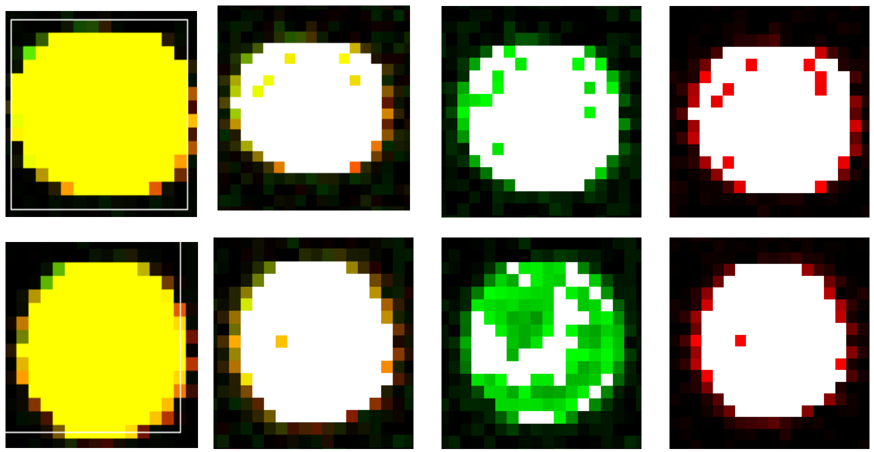
Streak/Heterogeneous



Donut/Saturation in Centre



Saturated in 1 or 2 Channels



Acknowledgement Shauna Somerville "*Flagged Spots Examples*" (2002), Carnegie Institution(Spotted cDNA microarrays)

Principles of Wetting

Capillarity

Size Matters

Liquid Surface & Surface Tension

- Behaves as if it is in a state of tension
- Surface tends to minimize its area in any situation
- For a free droplet, the smallest area is obtained with a sphere – otherwise all interfacial tensions matter
- Surface tension γ_{LV} is energy per unit surface area or force per unit length

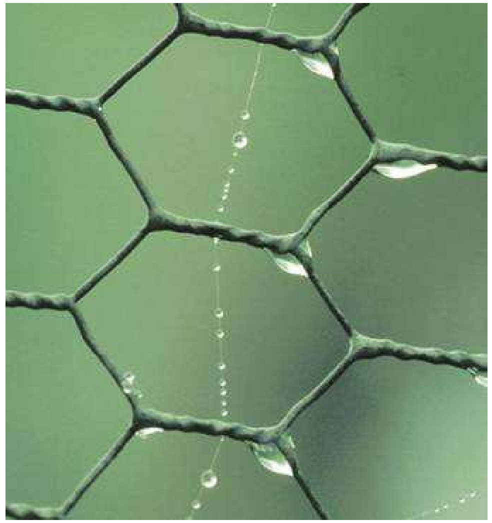
Capillary Length

- Surface tension forces scale with length
- Gravity force scales with length^3

Small sizes $\Rightarrow$ Surface tension wins over gravity

- Small means << 2.7 mm for water

- Characteristic speed = ratio of γ_{LV} to viscosity

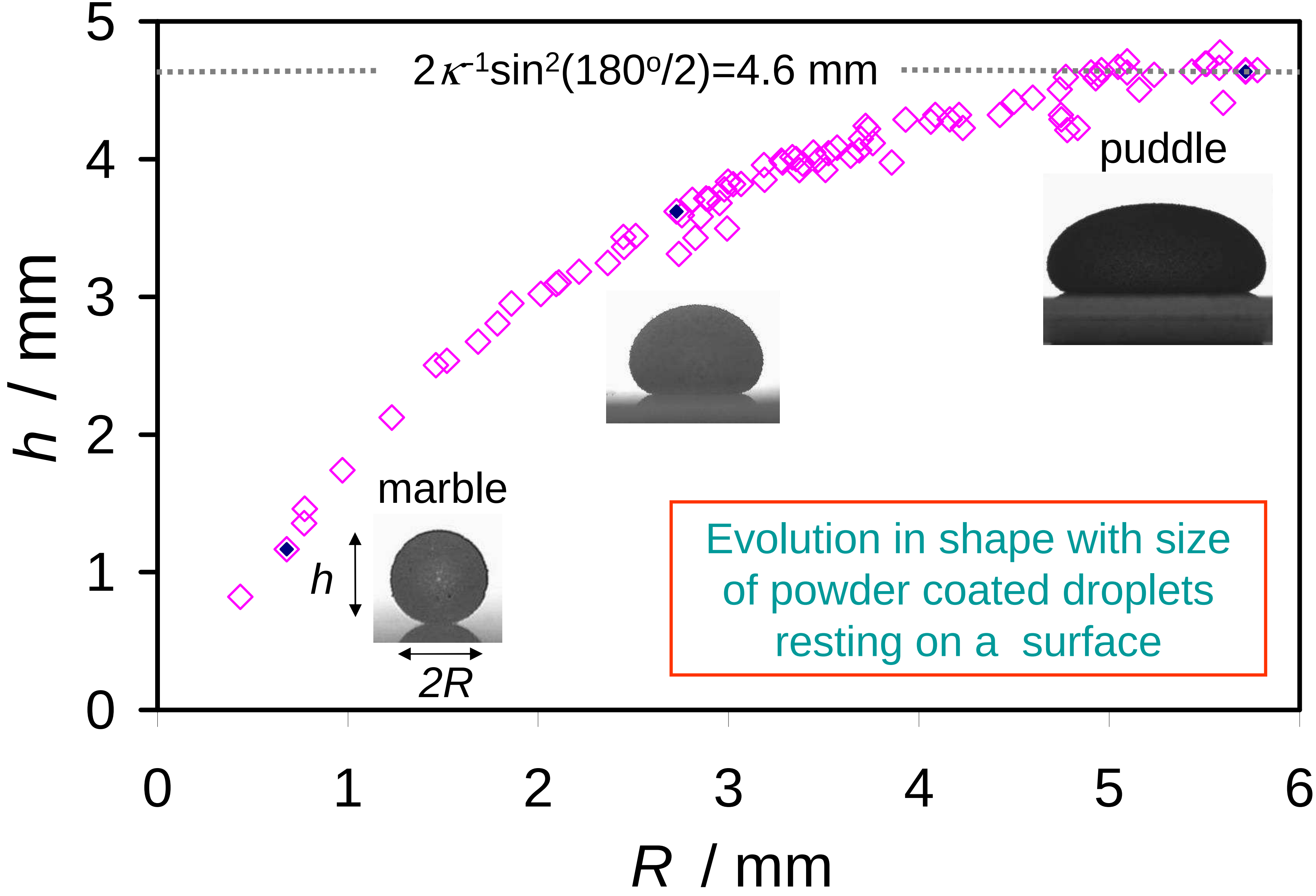


$$\kappa^{-1}=(\gamma_{LV}/\rho g)^{1/2}$$

$$V^{*}=\gamma_{LV}/\eta$$

Acknowledgement www.brantacan.co.uk

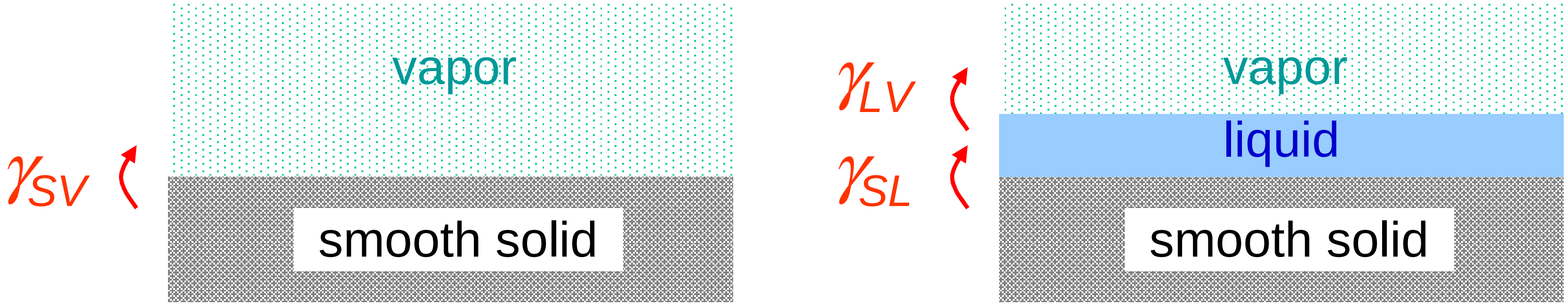
Size Data ("Liquid Marble")



Film Formation

Smooth and Flat Surface

Is it energetically favorable for a layer of liquid to form on a surface?



Film forms when: $\gamma_{SV} > (\gamma_{SL} + \gamma_{LV})$

Spreading Power

$$S = (\gamma_{SL} + \gamma_{LV}) - \gamma_{SV}$$

$S>0 \Rightarrow$ spreads into film (*complete wetting*)

$S<0 \Rightarrow$ remains as droplet (*partial wetting*)

Cautions

Not true on curved surfaces (i.e. capillaries, fibers)

Not true on patterned surfaces (topographically or chemically patterned)

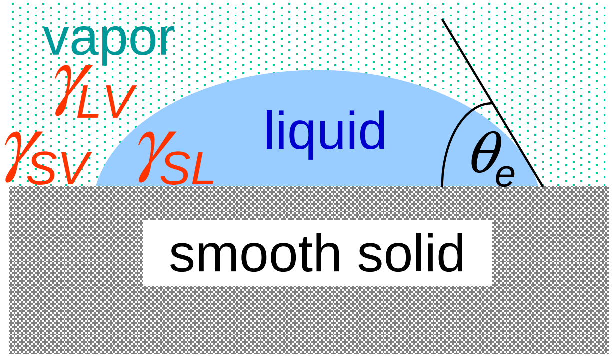
Droplet Formation & Contact Angle

Young's Law

Summarises surface chemistry

What is the equilibrium contact angle, θ_e>0?

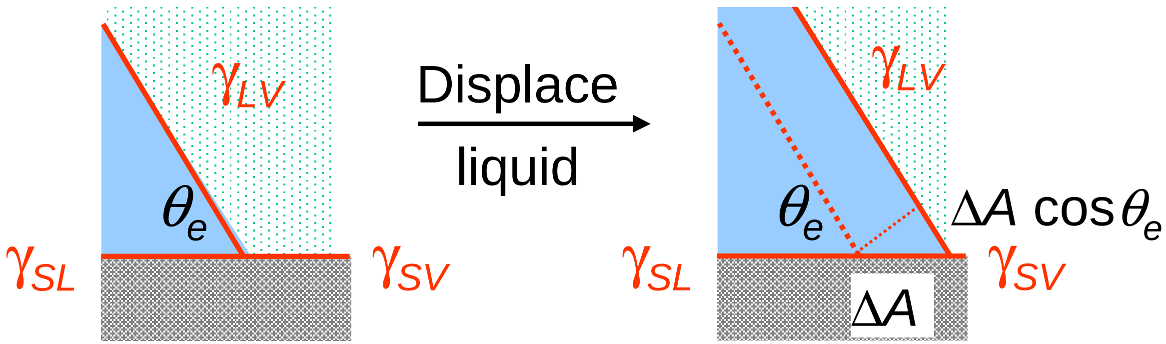
$$\cos\theta_e = (\gamma_{SV} - \gamma_{SL})/\gamma_{LV}$$



Link to spreading power: $S = \gamma_{LV}(1-\cos\theta_e)$

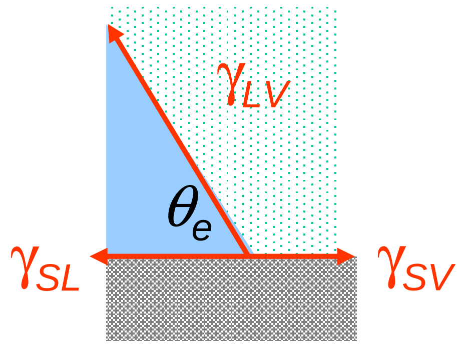
Contact angle is only meaningful when >0º

Minimum Energy



$$\Delta F = (\gamma_{SL} - \gamma_{SV})\,\Delta A + \gamma_{LV}\Delta A\cos\theta_e \rightarrow 0$$

Force Balance

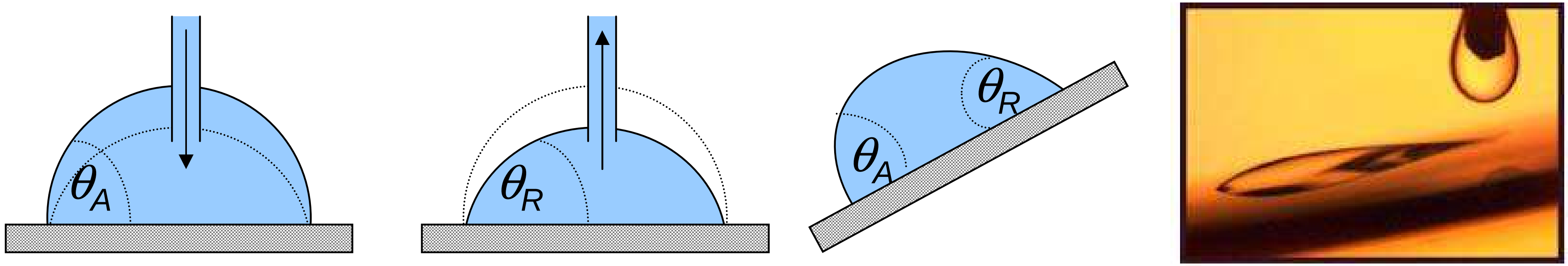


$$\gamma_{SL} + \gamma_{LV}\cos\theta_e = \gamma_{SV}$$

Contact Line Pinning

Advancing & Receding Contact Angles

- Increase/decrease volume until edge moves
- Tilt stage until droplet moves – Front and back edge angles



Withdrawing a needle/pin causes a receding contact angle

Droplet Motion

- Force to overcome contact line pinning scales as $\gamma_{LV}(\cos\theta_R - \cos\theta_A)$
- Freely spreading droplet has driving force due to difference between dynamic contact angle and Young's contact angle $\gamma_{LV}(\cos\theta_e - \cos\theta)$

Acknowledgement D. Ross, *et al*., Science (1997), 278, 664;

Droplet Size & Contact Angle

Spreading on Deposition

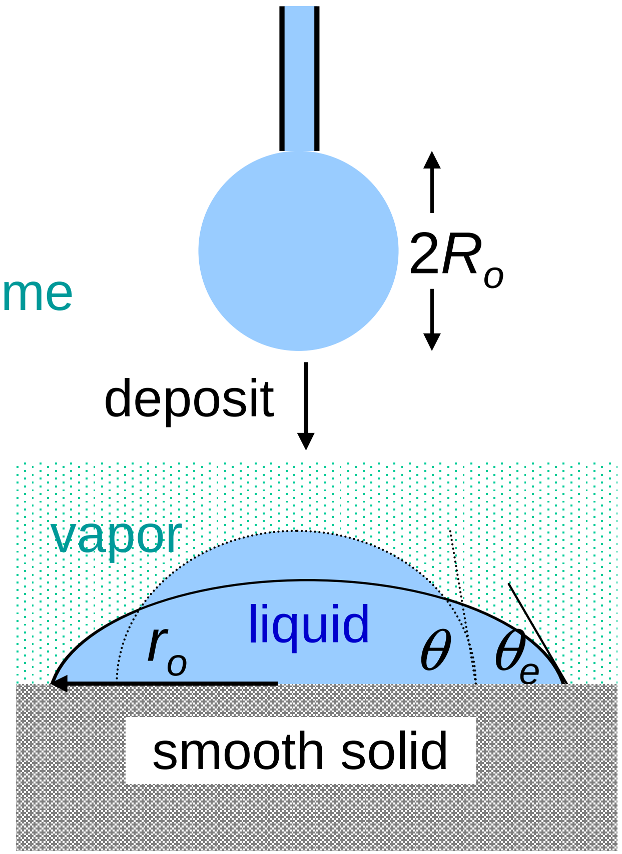
Initial volume $V_o = 4\pi R_o^3/3$

Driving force is $\gamma_{LV}[\cos\theta_e - \cos\theta] \rightarrow 0$

Droplet spreads down to equilibrium angle θ_e

Spot size determined by contact angle and initial volume

$r_o = (4/\beta)^{1/3} R_o \sin\theta_e \qquad \beta = (1-\cos\theta_e)^2(2+\cos\theta_e)$



Spot Size Errors

$r_o \approx 6.75\, R_o / \theta_e^{1/3} \qquad \theta_e$ in degrees and small

% error in r_o = % error in R_o

% error in r_o = One-third the % error in θ_e

% error in A_{SL} = Double the % error in R_o

Size Examples

Water-on-Glass

θ_e for glass is 15° -50°

θ_e for microscope slides is 27° -37°

Hydrophilic/clean glass $\theta_e \rightarrow 0°$

"Touch" detachment

Example Size Errors

R_o/µm	V_o/pL	θ_e°	r_o/µm	A_{SL}/mm²
30±3	113±35	8	101±10	0.032±0.007
30±3	113±35	15	82±8	0.021±0.004
30±3	113±35	27	67±7	0.014±0.003
30±3	113±35	37	59±6	0.011±0.002
30	113	8→15	101→82 18%	0.032→0.021 34%

Water-on-Aminopropylsilane Coated Glass

Data from Erie microarray

θ_e for water is 40° ±5°

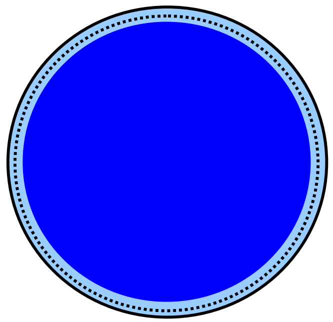
No receding angle given

R_o/µm	V_o/pL	θ_e°	r_o/µm	A_{SL}/mm²
30	113	35	60.5	0.0115
30	113	40	57.4	0.0104
30	113	45	54.8	0.0094

18%

40°±5° gives a ±5% error in spot radius

40°±5° gives a ±10% error in spot area



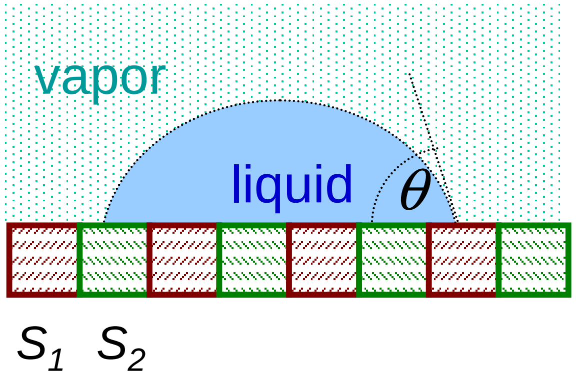
Reference http://www.eriemicroarray.com/custom/sized.aspx

Surface Heterogeneity

Chemical Heterogeneity

Average cosines using surface fraction *f*

$$\cos\theta_{CB} = f\cos\theta_1 + (1-f)\cos\theta_2 \quad \textit{Cassie-Baxter}$$



Example

Aminosilane coated glass (θ_1=40°) with patches of clean glass (θ_2=0°).

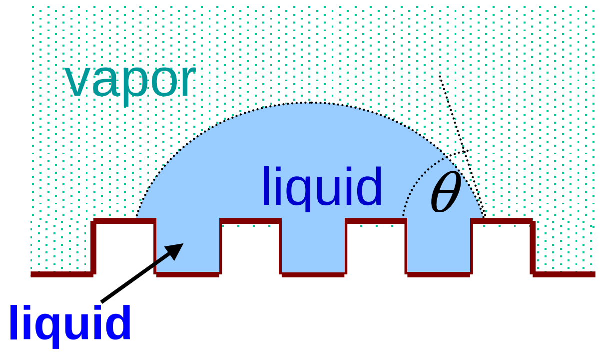
$$\cos\theta_{CB} = f\cos 40^o + (1-f)\cos 40^o = 0.766f + (1-f)$$

% Patch	θ_{CB}	Comment
10%	37.9°	4% incr. in spot area
25%	34.5°	12% incr. in spot area
50%	28.0°	31% incr. in spot area

Roughness/Topography

Amplify cosine using roughness factor, *r*

$$\cos\theta_W = r\cos\theta_e \quad \textit{Wenzel}$$



Example

Aminosilane coated glass (θ_e=40°)

r=1.07 (~ 1 nm ht every 30 nm) ⇒ 35° ⇒ 12% incr. in spot area

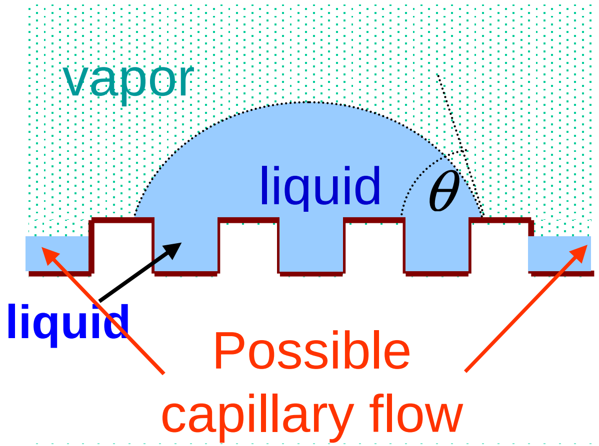
r=1.15 (~ 1 nm ht every 14 nm) ⇒ 28° ⇒ 31% incr. in spot area

Extreme Effects of Roughness

"Sticky" Surfaces

Increases hysteresis ("sticky") surface

May get capillary flow into surface features

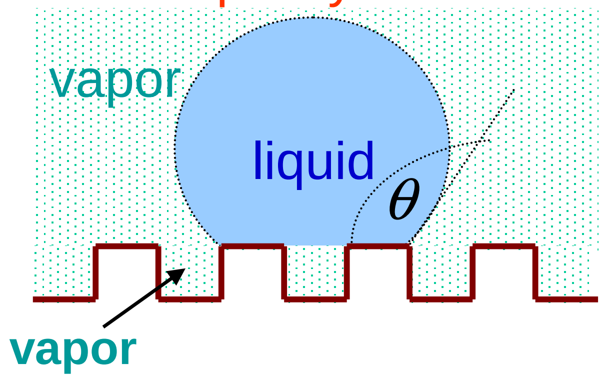


Super-Hydrophobicity & "Slippy" Surfaces

If surface protrusions thin and tall, and

hydrophobicity high enough may get "skating" droplet

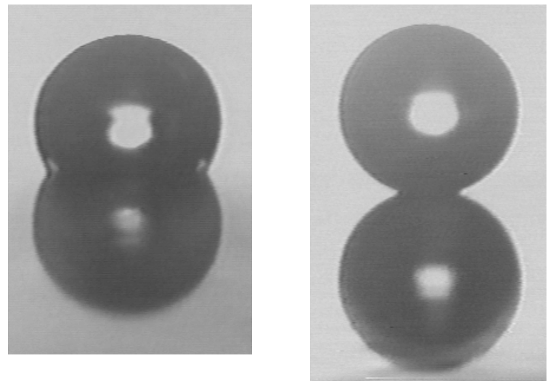
Decreases hysteresis ("slippy") surface – mobile droplet



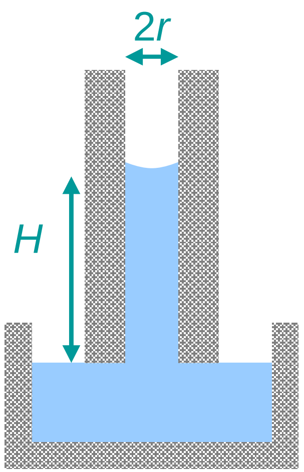
$$\cos\theta_{CB} = f\cos\theta_e + (1-f)\cos 180^o$$

$$\Rightarrow \cos\theta_{CB} = f\cos\theta_e - (1-f)$$

Cassie-Baxter on solid-air surface



Capillary Rise

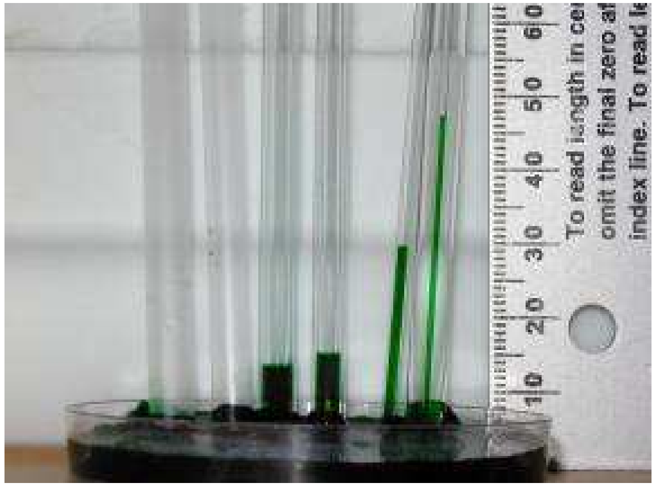


Rise Inside a Tube

If surface energy $\gamma_{LV} > \gamma_{SL}$, liquid rises in a tube until rise is balanced by extra weight of liquid column

$\theta_e < 90^o \Rightarrow$ Liquid rises in tube

$\theta_e > 90^o \Rightarrow$ Liquid depressed in tube



$$H/\kappa^{-1} = 2\,\kappa^{-1}\cos\theta_e/r$$

Strongest effect is for a thin tube

Water, r=10 μm, $\theta_e = 0^o$	$\Rightarrow$ H= 1.49 m
widen r to 50 μm	$\Rightarrow$ H= 0.299 m

Rise on Outside of a Solid Fiber

Complex, but for $\theta_e = 0^o$ $\Rightarrow$

$$H = r\cosh^{-1}(1/r\kappa) \sim r\log_e(2/r\kappa)$$

Water, r=10 μm, $\theta_e = 0^o \Rightarrow$ H= 63 μm

Acknowledgement Robinson, WTAM; Brochard-Wyart *et al*, J. Phys. France 51 (1990) 293; Clanet, J. Fluid Mech. 383 (1999) 307; Furbank & Morris, Phys. Fluid 16 (2004) 1777.

Spotting Pins & Capillary Rise

Spotting Process

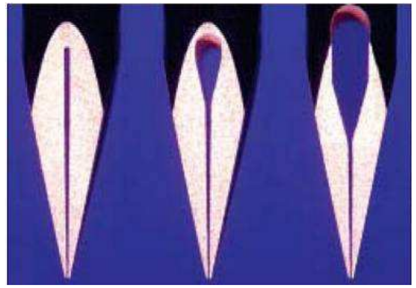
Pin types: Solid pin, split/quill/slotted pin, pin & ring

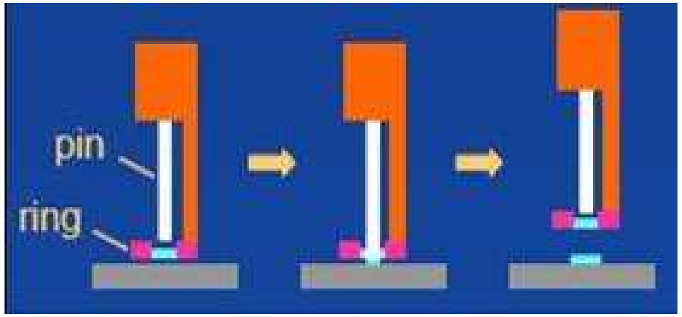
Liquid uptake by capillary rise

Spots printed via capillary bridge/adhesion

Spots of 50-500 μm diameter

Optional flat hydrophilic tips to allow *liquid film to form and "low/non-contact" spotting. Alternatives includes pin-and-ring.*





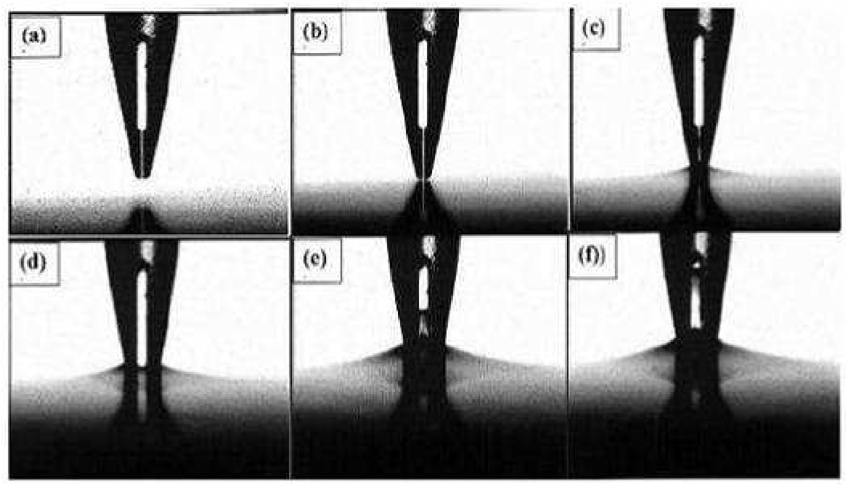
Example Pin Loading Process

100 μm slot, 20 μm exit

(a), (b) Pin approaches distilled water

(c) Rapid rise up outside of pin and partially up slot with speed determined by γ_{LV} and η, θs and widths (>12 mm/s)

(d)-(f) Slower capillary filling of larger reservoir



Acknowledgement www.FlyChip.com; TeleChem. Intl.; J.A. Love, Whitehead Institute Center for Microarray Technology; Stealth Micro Spotting pins; Anke Becker, Bielefeld University.

Dripping and Jetting Droplets

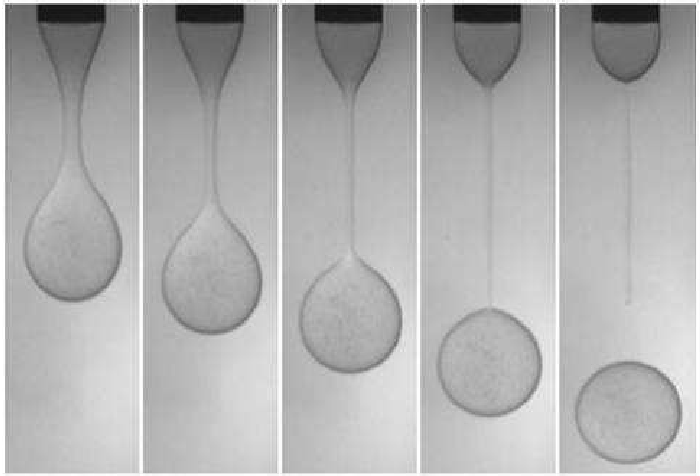
Size of a Dripping Drop

Inside radius, *r*, of tube determines size

$$R_{drop} \sim (3r\ \kappa^{-2}/2\alpha)^{1/3}$$

Factor $\alpha \sim 0.6$

r=10 μm, water ⇒ *R*= 571 μm (***very large***)



Size of a Jetting Drop

Area of tube to area of *n* droplets

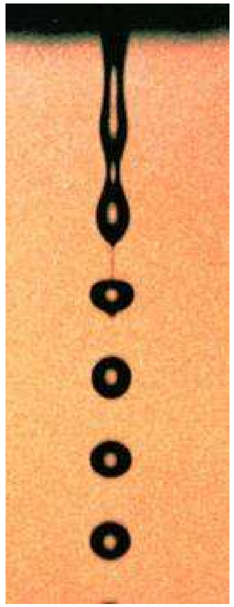
$$\frac{S_n}{S_o} = \frac{3R}{2r}$$

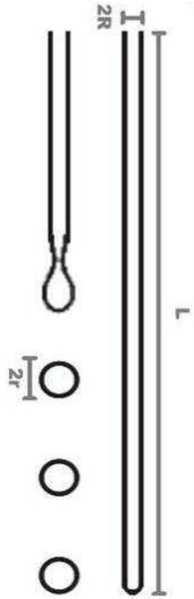
Energetically droplets can be more stable

Induced when disturbance wavelength $\lambda > 2\,\pi R$

Typically *r* ~1.9 x aperture radius

Much smaller droplets than in the dripping case





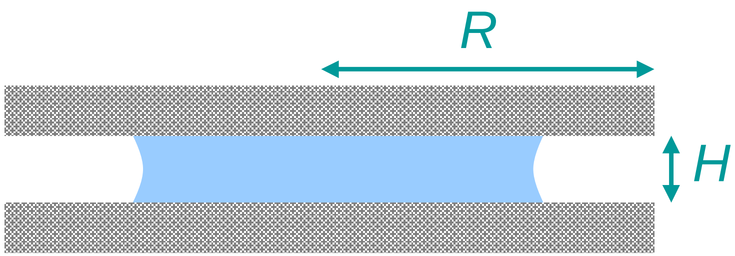
Acknowledgement Robinson, WTAM; Brochard-Wyart *et al*, J. Phys. France 51 (1990) 293;
Clanet, J. Fluid Mech. 383 (1999) 307; Furbank & Morris, Phys. Fluid 16 (2004) 1777.

Capillary Adhesion and Bridges

Capillary Adhesion

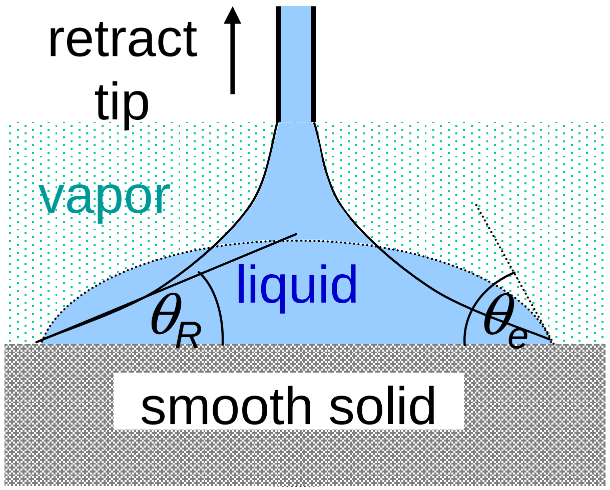
Contact angle $\theta_e < 90^o \Rightarrow$ Plates stick together

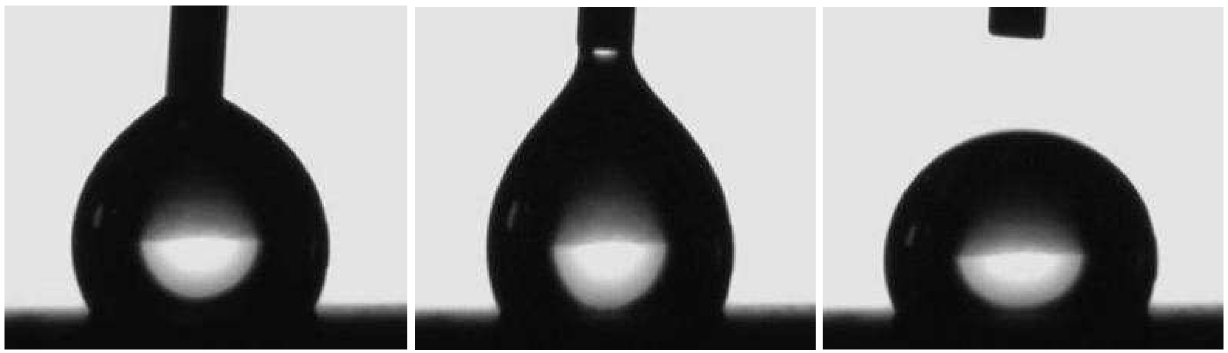
Force of attraction ~ $\pi R^2 \times 2\ \gamma_{LV} \cos\ \theta_e / H$



Example Water, R=1 cm, H= 5 µm, $\theta_e = 0^o \Rightarrow$ Force of attraction is 10 N

Deposition By Stretching of Capillary Bridge





Needle retraction with contact line pinning causes dependence on receding angle

Droplet attached to substrate depends on droplet volume and contact angles of needle/pin and substrate

Spotting Pins & Deposition

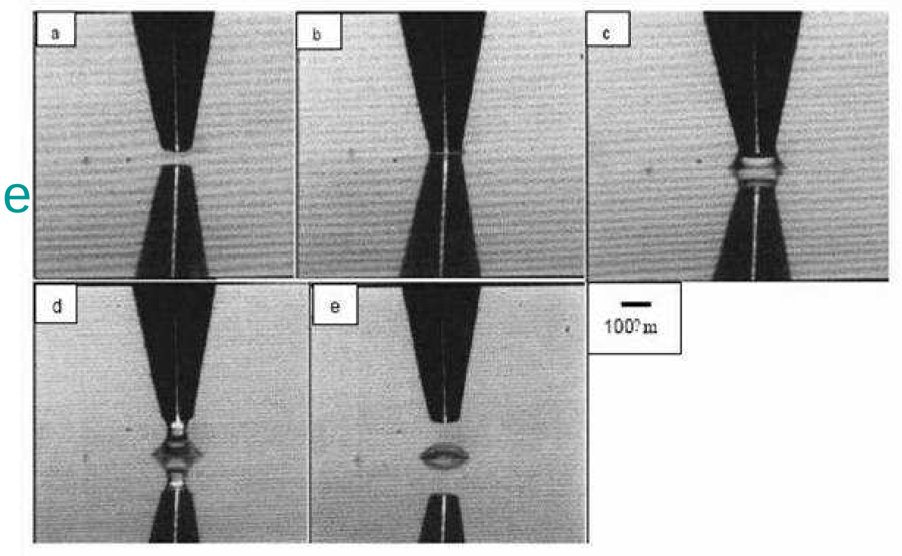
Example Pin Spotting Process

100 µm slot, 20 µm exit, distilled water loaded

(a)-(c) approach and spot forms – capillary bridge

determined by θ_{pin}, θ_{glass}, curvature in reservoir (i.e. width) and $\theta_{receding}$

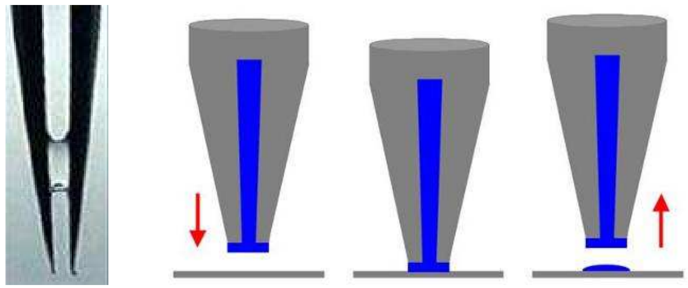
(d), (e) bridge stretches and breaks



Spot size depends on geometric parameters (tip and reservoir) and wetting properties (pin and substrate)

Mechanical Contact

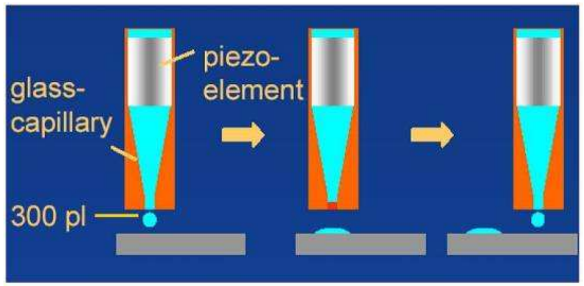
Tweezers need contact/tapping to eject, so formation of film on flat tip removes this need



Inkjet Printing

Induced capillary jet/tube break-up - 250-300 µm spot size

Non-contact/independent of substrate wetting properties



Acknowledgement www.FlyChip.com; TeleChem. Intl.; J.A. Love, Whitehead Institute Center for Microarray Technology; Stealth Micro Spotting pins

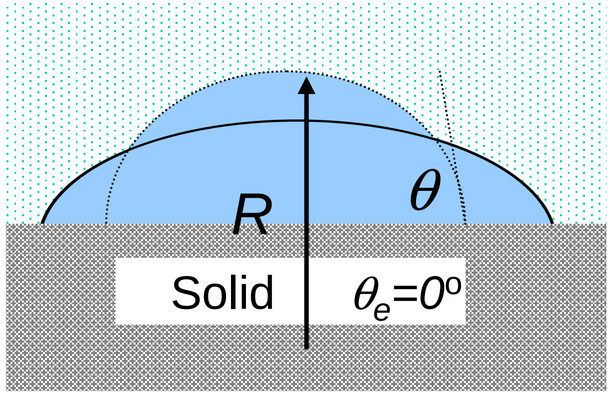
Laplace Excess Pressure

Pressure Across a Curved Surface

$$\Delta P = \gamma_{LV}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$$

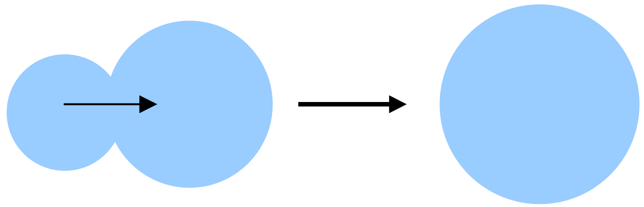
Two principal radii of curvature, R_1 and R_2

If principal radii of curvature are equal: $\Delta P = \frac{2\gamma_{LV}}{R}$



Reducing ΔP is an alternative way to explain why a droplet spreads into a film on surface with $\theta_e = 0^o$. *Droplet spreads until the spherical radius R is infinitely large*

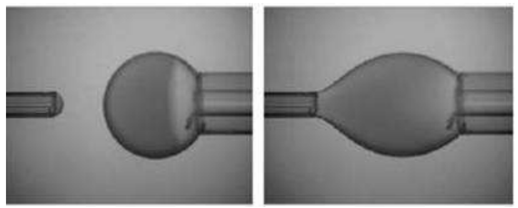
Coalescence and Drainage



Two droplets merging can reduce total surface energy - Smaller one drains into larger on.

Smaller droplet has higher curvature and so higher pressure

Can be used to form capillary bridges



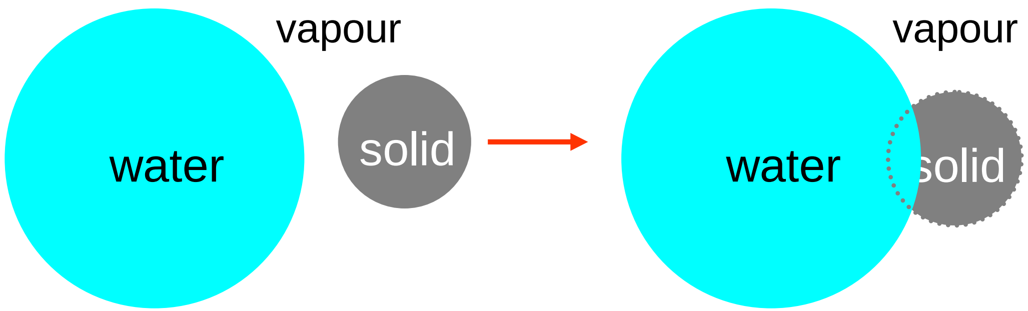
Acknowledgement K. Curran, *et al.* Microfluid Nanofluid (2005) 1, 336

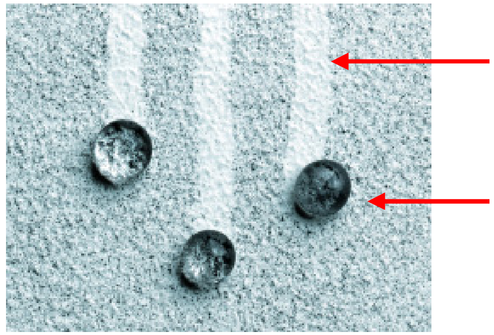
Adhesion of Dust

Particle Attachment

To minimise surface energy grains prefer to cling to water-air interface

More hydrophobic grains “stick out” further, but even highly hydrophobic grains attach themselves to a droplet of water

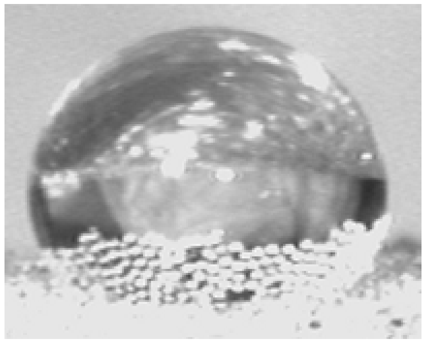


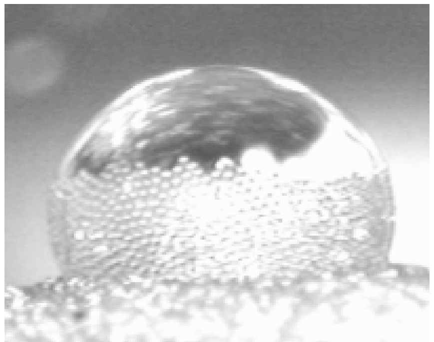


Dust cleaned away

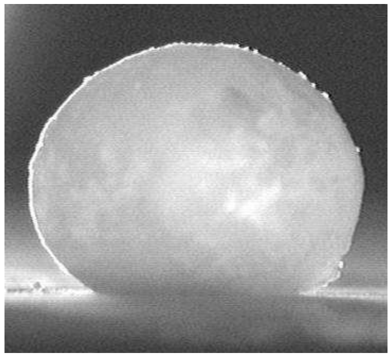
Dust coated droplet

Hydrophobic Silica Particles





Extreme Case – Liquid Marbles



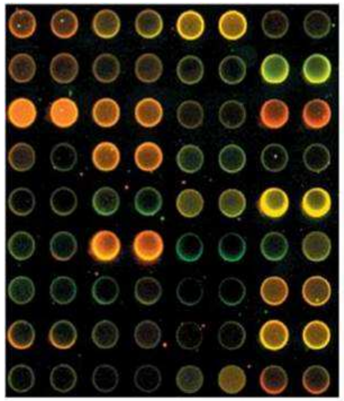
Reference McHale *et al*, Eur. J. Soil. Sci. 56 (2005) 445-452, and McHale *et al*, Submission to APL (2006)

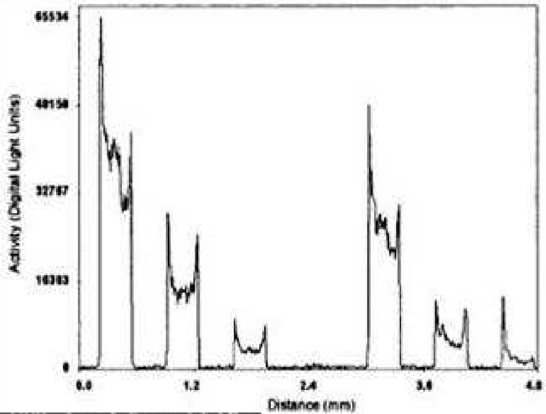
Donuts & Contact Line Pinning

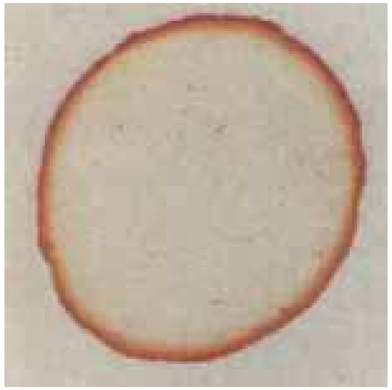
"Coffee" Ring Stains

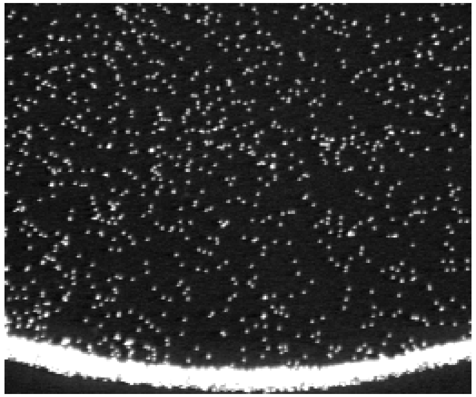
- Evaporation of droplet with solute
- Contact line is pinned
- Deposition often occurs at edge of droplet
- Relative humidity determines rate

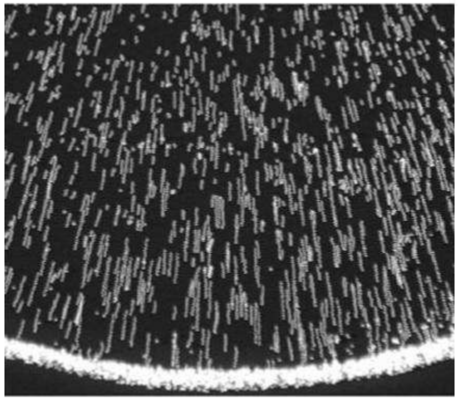
low humidity ⇒ fast ring formation





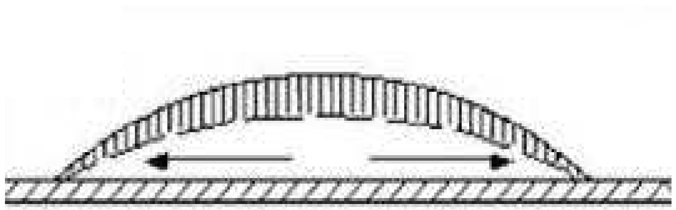






Suppression of Ring Stains (after Blossey)

- Initial solute concentration is high
- Contact angle is very small
- Reduce contact line pinning
- Initial deposition needs to be homogeneous - strong memory of initial distribution



Acknowledgement Deegan *et al*, Nature 389 (1997) 827; Wixforth *et al*. Superl. Microstr. 33 (2003) 389; Abal. Bioanal. Chem. 379 (2004) 982. Blossey & Bosio, Langmuir

Diffusion Limit & Mixing

Diffusion Limit

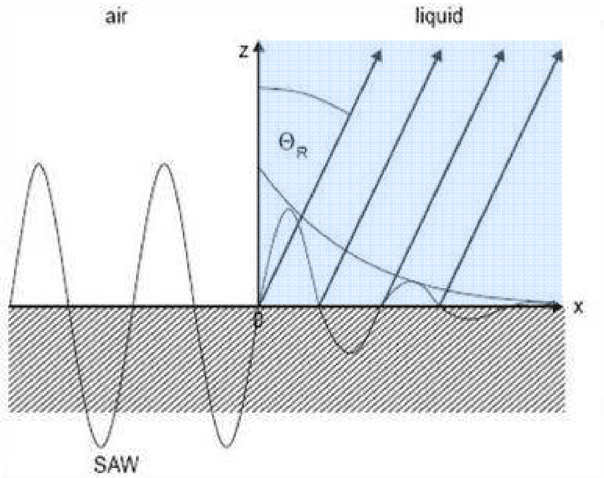
Diffusion time for 1 mm motion of 100 nm DNA is 30 hours. Implies slow hybridization in a fluid film of 50 μm

Table 1 Calculated diffusion times for different diffusion lengths and three different particle sizes. A DNA segment of only 100 nm lengths needs about 30 h to diffuse over a distance of only 1 mm

diffusion length (μm)	potassium ion (0.2 nm)	Oligonucleotide (6 nm)	PCR product (100 nm)
1	0.2 ms	6 ms	100 ms
10	20 ms	600 ms	10 s
100	2 s	60 s	20 min
1000	200 s	100 min	30 h

Wixforth/Advalytix Solution

Use Surface Acoustic Wave (SAW) streaming to induce micro-agitation mixing



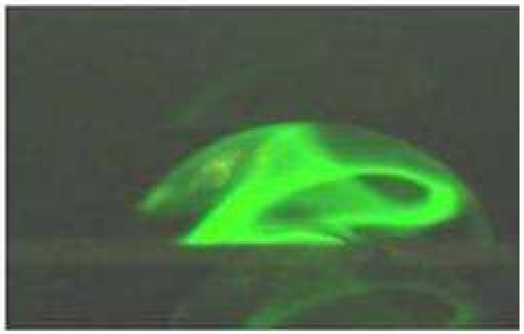
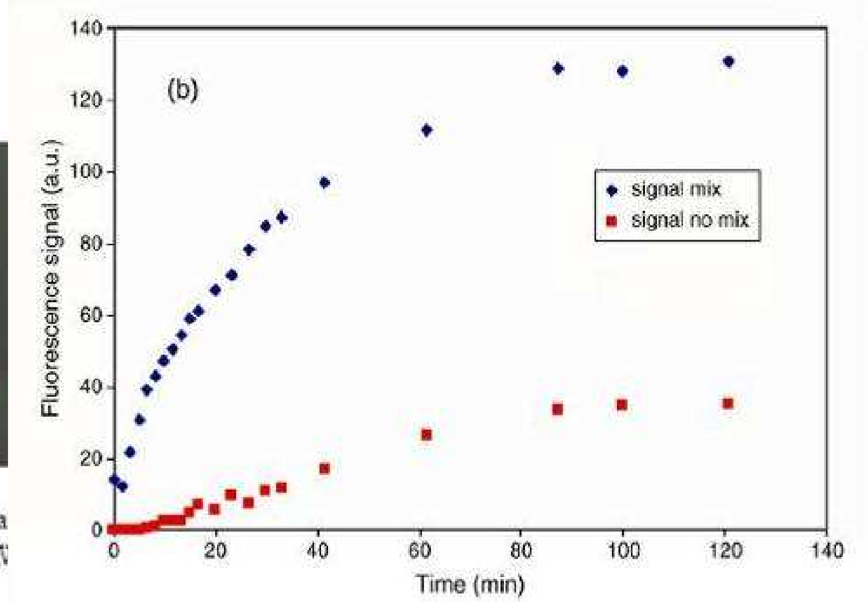


Fig. 3. SAW induced internal streaming in a sma
dye on the surface of the chip is dissolved by SA



Fluorescence labeled micro array experiment with and without SAW mixing.

Acknowledgement Wixforth *et al*., Anal. Bioanal. Chem. 379 (2004) 982. www.advalytix.com

Not Covered

1. Contact Angle Measurement Methods
2. Dewetting & Film Bursting
3. Electrowetting & Double layers
4. Marangoni Forces/Surface Tension Gradients
5. Surfactants

Take Home Messages

1. Capillarity dominates for sizes much less than the capillary length, i.e. for water this means the sub-300 micron range
2. Patterns of hydrophobicity/hydrophilicity can confine water to spots and "virtual" channels. They also distort spot shapes
3. Substrate with θ_e=40°±5° $\Rightarrow$ ±10% error in spot area
4. If θ_e=40°, then 7% roughness $\Rightarrow$ 10% increase in spot area
5. Dust/particulates attach to water-air interfaces
6. Evaporation <u>and</u> contact line pinning $\Rightarrow$ ring-stains/donuts

The End

Acknowledgements

Collaborators

Prof. Mike Thompson (Toronto), Prof. Yildirim Erbil (Istanbul)

Dr Stefan Doerr (Swansea), Dr Andrew Clarke (Kodak)

Dr Mike Newton, Dr Neil Shirtcliffe, et al. at NTU

Funding Bodies (EPSRC/Dstl & EU)

GR/R02184/01 – Super-hydrophobic & super-hydrophilic surfaces

GR/S34168/01 – Electrowetting

EP/C509161/1 – Extreme soil water repellence

Dstl via EPSRC/MOD JGS

EU COST Action D19 - Chemistry at the nanoscale

Illustrative Images

See reference/acknowledgement footnotes on individual slides