2.674
Introduction to Microfluidics II
- Droplets and Surface

Sang-Gook Kim

Understanding diffusion

- Macroscopic diffusion ‘results’ from random motion of individual molecules

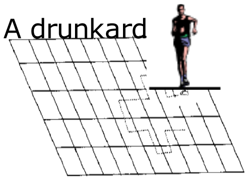
$$\overline{x^2} = 2 \cdot D \cdot t$$

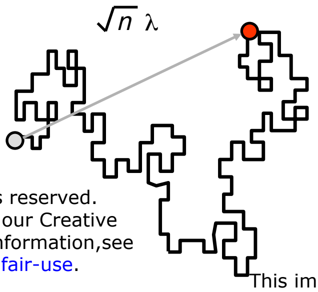
- When a large number of molecules is observed, diffusion seems to be a smooth, continuous process with no indication of underlying randomness

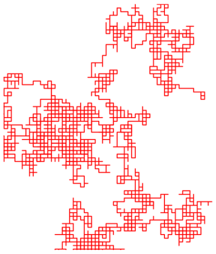
Observe random motion of microspheres in the lab!

Random walk -2D, 3D

A drunkard



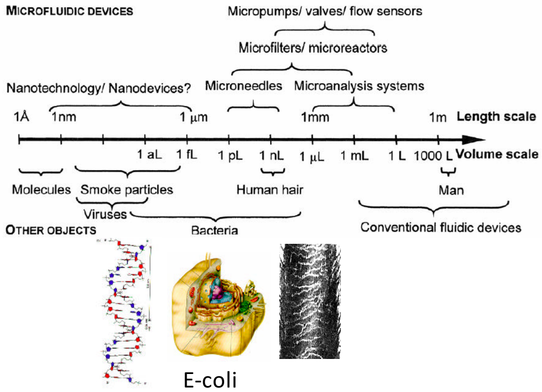




Sullivan.t.j at English Wikipedia.

Scales of Fluidics

Microfluidic devices - dimensions



E-coli

1 molecule in 1 mL = 1.6×10^{-18} M
1 molecule in 1 nL = 1.6×10^{-15} M
1 molecule in 1 pL = 1.6×10^{-12} M

Credit: Dr. Karen Cheung, UBC ECE

Droplets

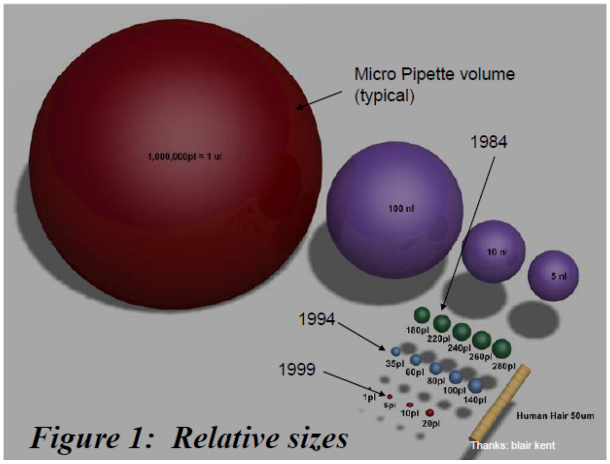
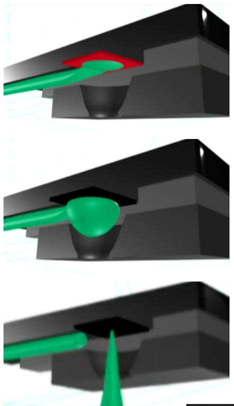
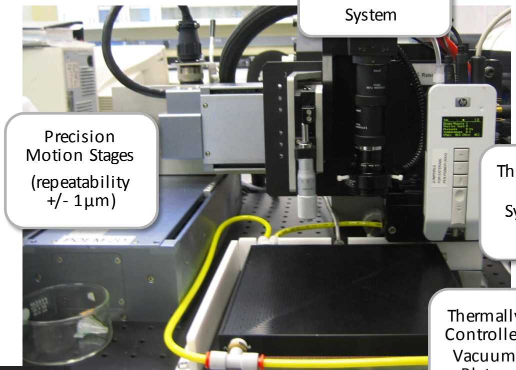


Figure 1: Relative sizes

HP POEM Thermal Ink Jet System



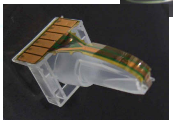


Alignment Machine Vision System

Precision Motion Stages (repeatability +/- 1µm)

Thermal Ink Jet Pico-liter System (TIPS) Controller

Thermally Controlled Vacuum Platen



- Droplet sizes: 200 - 0.5pl
- Disposable nozzles with 0.5ml reservoir

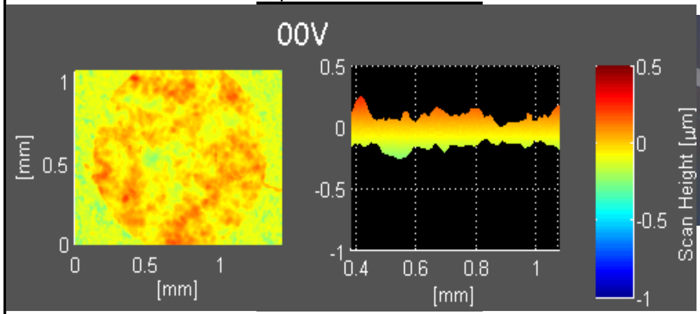
Bathurst, MIT, 2012

Printed PZT Devices

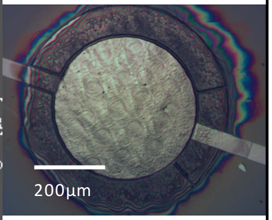
- To confirm the quality of printed PZT capacitors and MEMS devices were fabricated and tested
- A Standard PZT device structure was used:

  Si Substrate / 200nm SiO_2 / 20nm Ti / 200nm Pt / PZT 300-700nm

Ferroelectric Test Capacitors



Released MEMS Structures



Bathurst, MIT, 2012

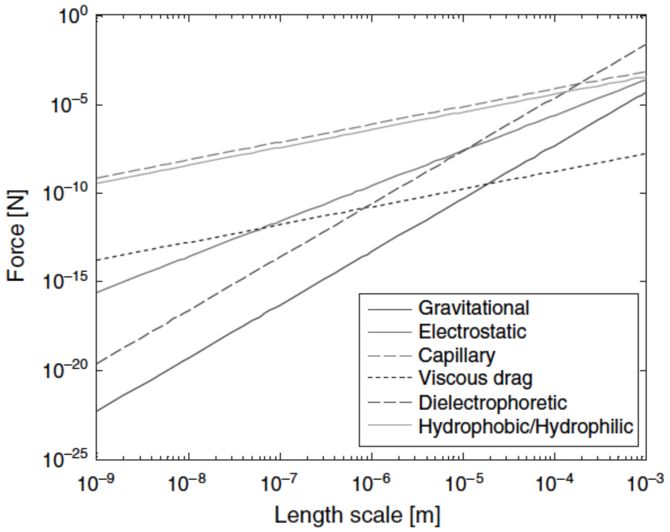
Scaling of Forces

Types of forces	Equation
Capillary force	$F_C = 4\pi R\gamma\cos\theta$
Hydrophobic/hydrophilic	$F_H \approx \dfrac{2\gamma(1-\cos\theta)(\pi R^2)}{d}$
Viscous drag force	$F_d = 6\pi\eta(R)v$
Electrostatic force	$F_{ES} = \dfrac{1}{4\pi\varepsilon_0\varepsilon_m}\dfrac{\{q_1(2\pi R_1^2)\}\{q_2(2\pi R_2^2)\}}{r^2}$
Dielectrophoretic	$F_{DEP} = \dfrac{3}{2}\left(\dfrac{4}{3}\pi R^3\right)\varepsilon_m\left(\dfrac{\varepsilon_o-\varepsilon_m}{\varepsilon_o+2\varepsilon_m}\right)\nabla\lvert\bar{E}\rvert^2 \approx \dfrac{3}{2}\left(\dfrac{4}{3}\pi R^3\right)\varepsilon_m\left(\dfrac{\varepsilon_o-\varepsilon_m}{\varepsilon_o+2\varepsilon_m}\right)\dfrac{r^2V^2}{d^5}$
Gravitational force	$F_G = g\rho\left(\dfrac{4}{3}\pi R^3\right)$
Electrophoretic	$F_{EP} = q(4\pi R^2)\lvert\bar{E}\rvert$
Magnetic	$F_M = \dfrac{\mu_0\mu_m}{4\pi}\dfrac{q_{M1}q_{M2}}{r^2} = \dfrac{\mu_0\mu_m}{2}(\pi R^2)M^2$

Sang-Gook Kim, Multi-scale Assembly: Design, Processes and Complexity, In; Nanomanufacturing, S. Chen, Ed., American Scientific Publishers, 2009

Scaling of Forces

on a sphere



Sang-Gook Kim, Multi-scale Assembly: Design, Processes and Complexity, In; Nanomanufacturing, S. Chen, Ed., American Scientific Publishers, 2009

Surface Tension

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γ - Force per unit length of interface

Denotes the energy required to create an interface

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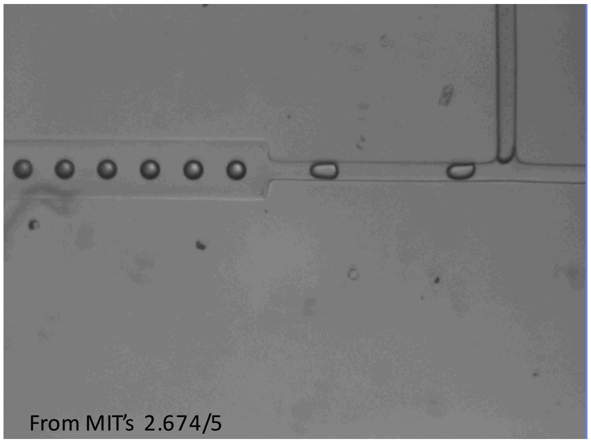
Droplet formation - A balance of surface tension forces and viscous forces



From MIT's 2.674/5

Emulsion and Surfactant

- Mixture of Immiscible liquids
- Amphiphilic Surfactant
- Water soluble or oil soluble

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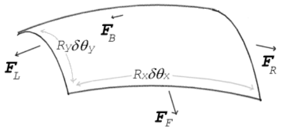
Droplet formation

- Dynamic instability between surface tension and shear stress causes plug formation
- Laplace pressure

$$\Delta P = \gamma\left(\frac{1}{R_x} + \frac{1}{R_y}\right)$$



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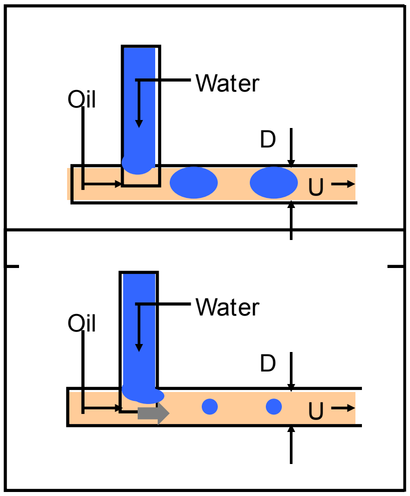


Two phase flow

- Surface tension favors large droplet

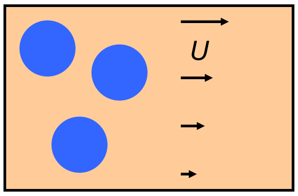
  Laplace pressure: $P_L = \dfrac{2\gamma}{r}$

- Shear stress tends to break up droplet

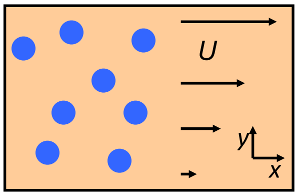
  Shear stress: $\tau = \mu \dfrac{dU}{dy}$

- Droplet size:

$$P_L \approx \tau \Rightarrow r \sim \frac{2\gamma}{\mu\left(dU/dy\right)}$$



Small shear stress



Large shear stress

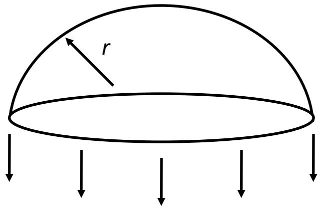
Capillary number

- Viscous shear stress (N/m²)

$$\tau_{viscous} \sim \mu \frac{U}{D}$$

- Laplace pressure (N/m²)

$$P_{Laplace} \sim \frac{2\gamma}{r}$$



- Ratio of viscous force to surface tension force:

$$Ca \sim \frac{\tau_{viscous}}{P_{Laplace}} \sim \frac{\mu U/D}{2\gamma/D} \sim \frac{\mu U}{\gamma}$$

Droplet formation

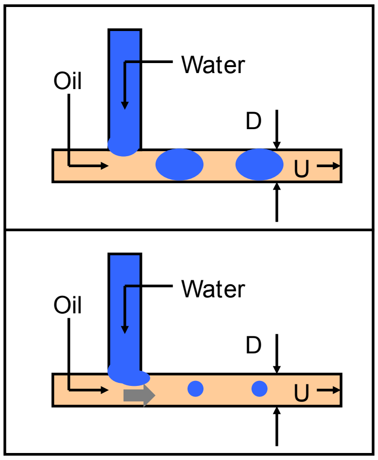
- Dynamic instability between surface tension and shear stress causes plug formation

$$Ca = \frac{U\mu}{\gamma}$$

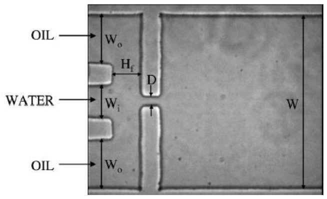
$$\frac{dU}{dy} \sim \frac{U}{D} \Rightarrow r \sim \frac{2\gamma}{\mu\left(dU/dy\right)} = \frac{2\gamma D}{\mu U}$$

$$r \sim \frac{2D}{Ca}$$

  - Small *Ca*: Droplet size governed by channel geometry
  - Large *Ca*: Droplets break up

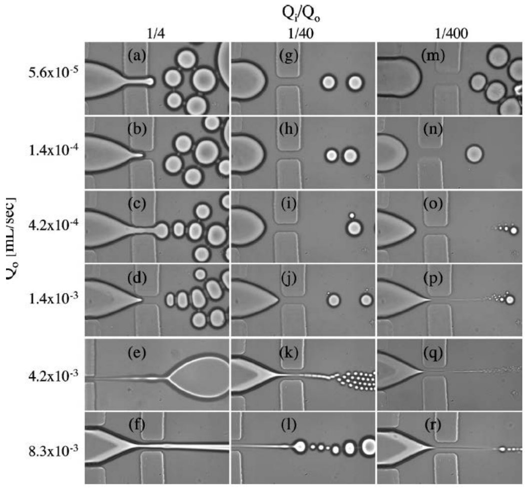


Droplet formation by flow focusing



$$Ca = \frac{U\mu}{\gamma}$$

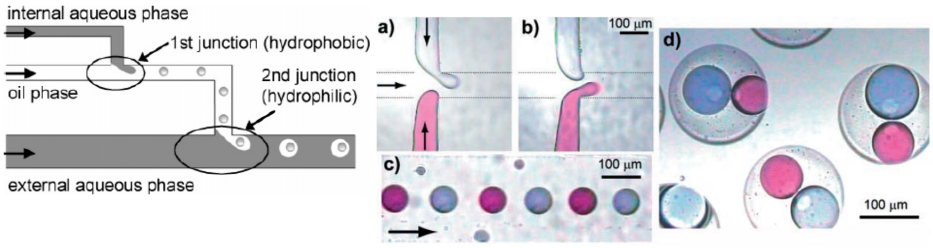
Phase diagram of droplet formation



Anna et al, Applied Physics Letters, 82, 364 (2003)

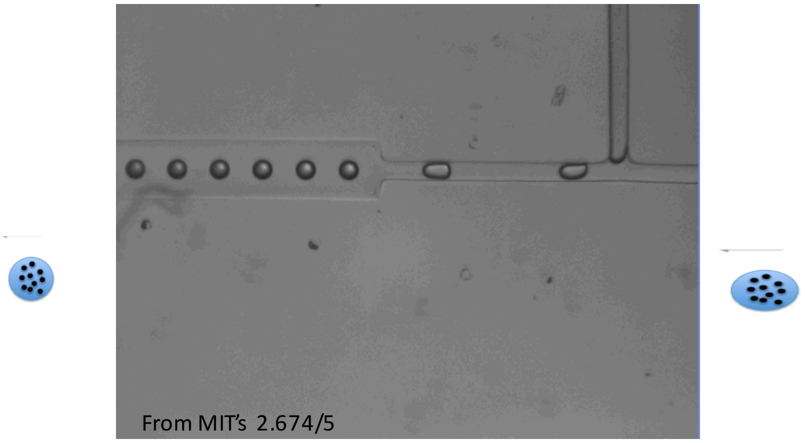
Droplet microfluidics

- Why use droplets?
  - Droplets can act as micro-reactors
  - Useful for emulsion and particle synthesis
  - Useful for large-scale screening of cells and molecules

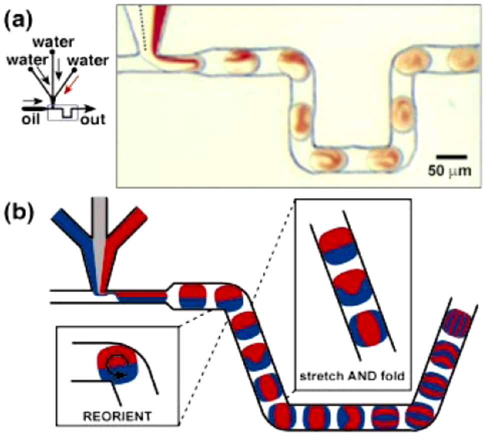


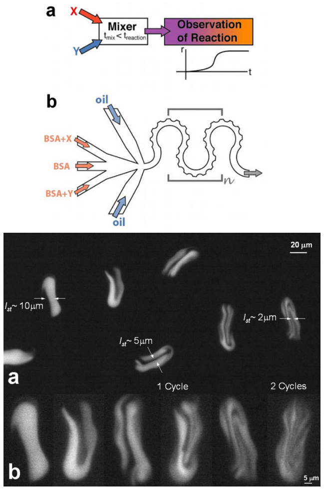
Okushima et al, Langmuir 20, 9905 (2004)

Droplet-Wall Interaction


From MIT's 2.674/5

Mixers employing baker's transform: Droplets

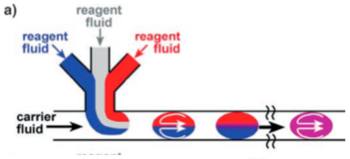


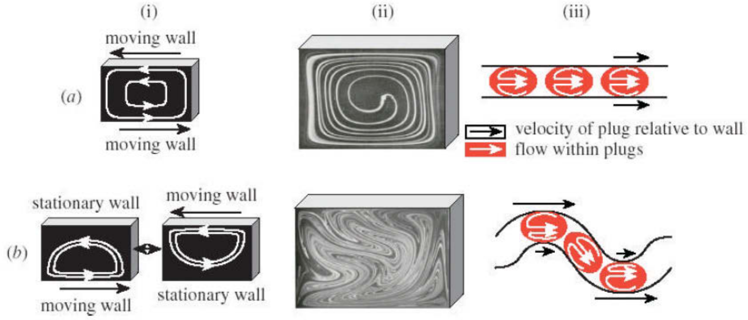


Song et al., Applied Phys. Lett. (2003)

Liau et al., Analytical Chem. (2005)

Mixers employing blinking flow





Bringer et al., Philos Transact A (2004)
Ottino, The kinematics of mixing: stretching, chaos, and transport

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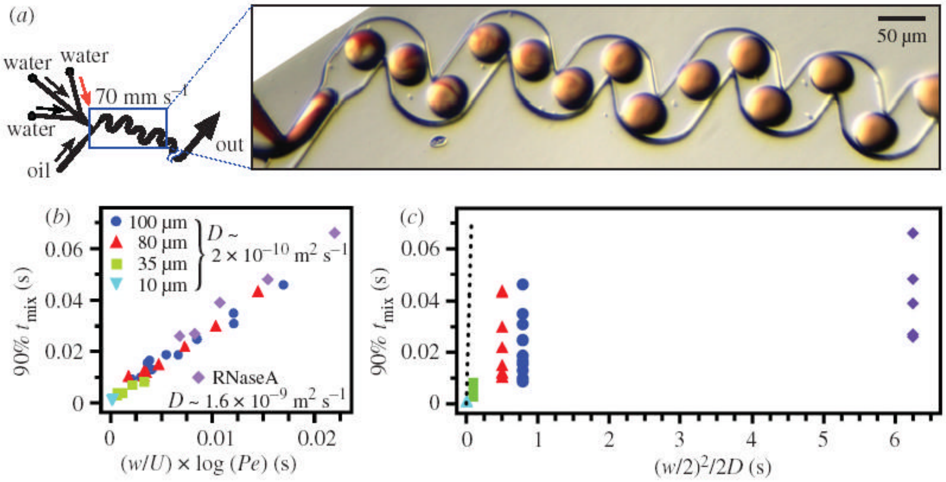
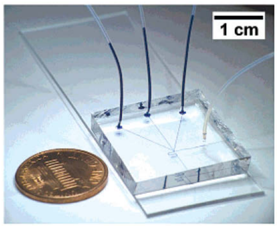
Mixers employing blinking flow

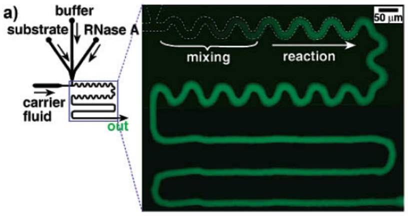


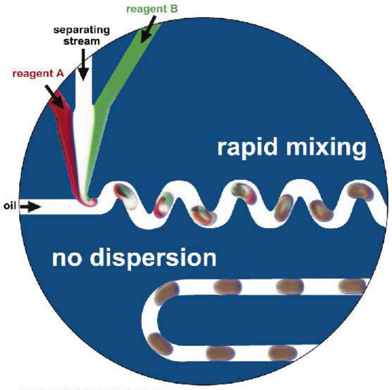
Bringer et al., Philos Transact A (2004)
Ottino, The kinematics of mixing: stretching, chaos, and transport

Droplets as reactors

Measurement of fast reaction kinetics







Aqueous droplets of 250 pL formed in a microfluidic channel in a continuous flow of a water-immiscible fluid act as microreactors that

Song & Ismagilov, JACS (2003)

Synthesis of particles

- Rapid mixing provides homogeneous reaction environment
- Addition of reactants within millisecond intervals- Control of reaction in time
- More homogeneous particle production

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Shestopalov et. al *Lab Chip* 2004

Synthesis of particles

Polymerization of droplet contents results in nanoparticles
Use in medicine, agriculture, cosmetics

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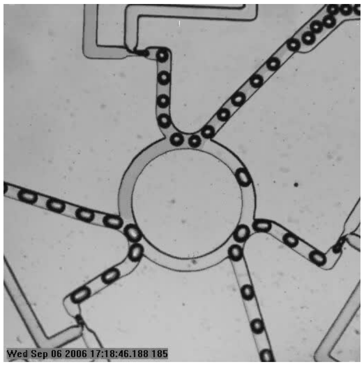
Microfluidic logic



Ring Oscillator, Prakash and Gershenfeld, Science (2007)

Wetting

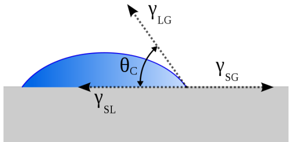
- Surface energy (J/m^2) = Surface tension (N/m)
- Wetting occurs when work of wetting is positive.

$$W_s = \gamma_{SG} - \gamma_{SL} - \gamma_{LG} \geq 0$$

- Hydrophobic when work of wetting is negative.

$$W_s = \gamma_{SG} - \gamma_{SL} - \gamma_{LG} \leq 0$$

- Young's Equation



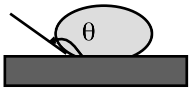
$$\gamma_{SG} = \gamma_{LG}\cos\theta + \gamma_{LS}$$

Young's Equation, Phil. Trans. Roy. Soc, 1805

Super Hydrophobicity

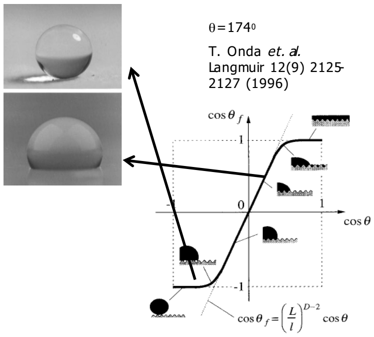
Hydrophobic, θ>90^0

Hydropilic, θ<90^0



Super hydrophobic, θ>150^0

- Chemical modification, coating
- Nanostructured surface

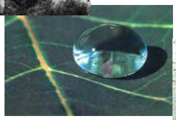


θ=174^0

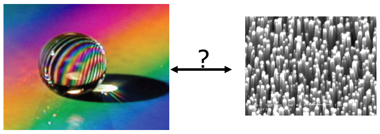
T. Onda *et. al.* Langmuir 12(9) 2125-2127 (1996)

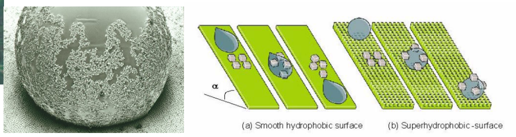
Lotus Effect

- Some plant leaves have near 170^0 contact angle, and show no accumulation of dirt. (Lotus Effect)
- Superhydrophobicity by nano patterned surface
- Self-cleaning surface (no car wash?)



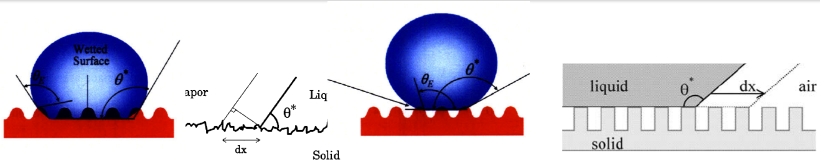
W. Barthlott and C. Neinhuis, Planta 202, 1 (1997)





Nanotech Lecture: 'Self-Cleaning Surfaces' by Dr. Vesselin Paunov

Effect of surface roughness



Wenzel's model

- If the surface has a high free energy, roughness promotes wetting.
- If it has low free energy, roughness promotes hydrophobicity.

$$\cos\theta^* = r\cos\theta$$

$$r = \frac{actual\_area}{projected\_area}$$

$$\theta^* = apparent\_contact\_angle$$

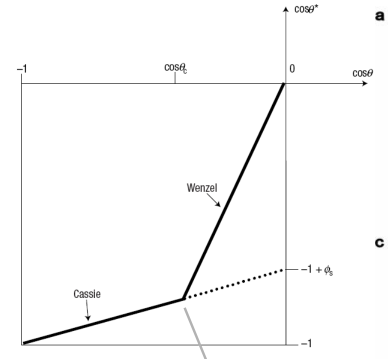
Cassie's model

- Wettability of heterogeneous (solid+air) surfaces
- Contact angle on air fraction is 180^0.

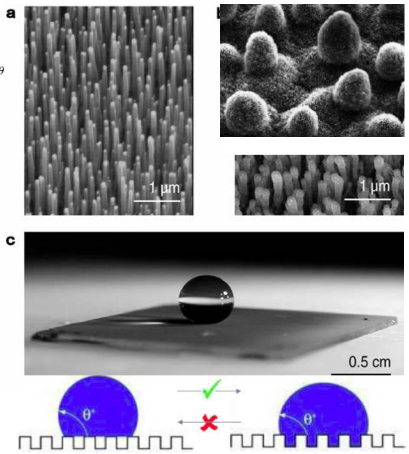
$$\cos\theta^* = -1 + \phi_s(\cos\theta + 1)$$

$$\phi_s = solid\_fraction\_surface$$

Cassie to Wenzel transition



A. Lafuma Nature Materials 2 457-460 (2003)



$$\cos\theta_c = \frac{\phi_s - 1}{r - \phi_s}$$

Electrowetting

Digital microfluidics

Electrowetting on Dielectrics (EWOD)

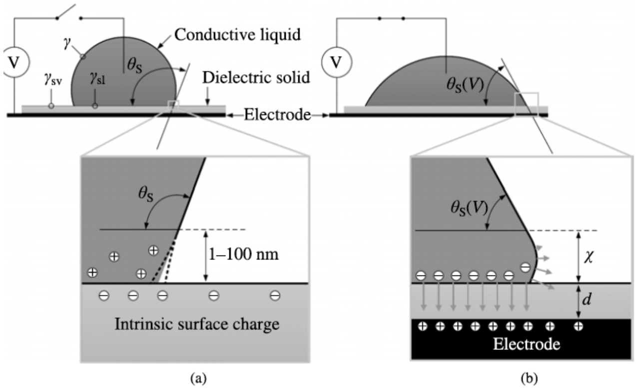
Droplets can be manipulated by electrowetting

Application of voltage bias between electrodes used to manipulate droplets

Complex operations can be performed

Electrowetting

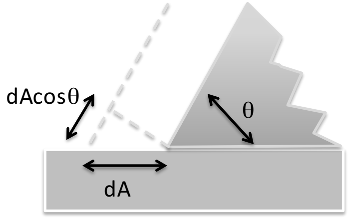
W. C. Nelson, C.-J. 'CJ' Kim / J. Adhesion Sci. Technol. 26 (2012) 1747–1771 1751



$$\frac{Interfacial\_Force}{Length} = C\frac{V^2}{2}$$

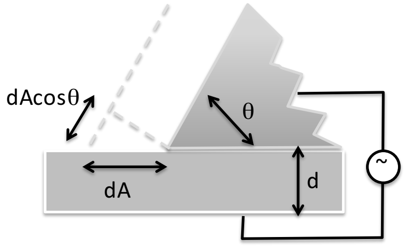
Energy Balance

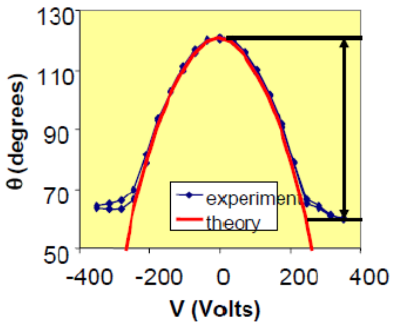
$$W_s = \gamma_{SG} - \gamma_{SL} - \gamma_{LG} \geq 0$$



$$dW = \gamma_{LG} \cos\theta dA + \gamma_{SL} dA - \gamma_{SG} dA = 0$$

Contact Angle vs. V



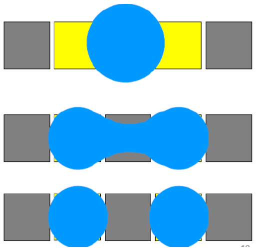


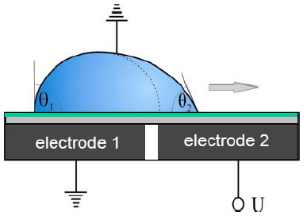
$$cos\theta = cos\theta_o + \frac{1}{2}\frac{\varepsilon_o\varepsilon_r}{\gamma d}V^2$$

Lippmann Young Equation

Drop Manipulation

- Merge
- Split
- Move





Digital microfluidics

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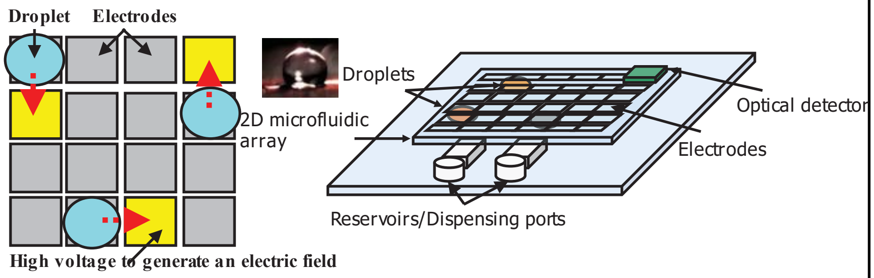
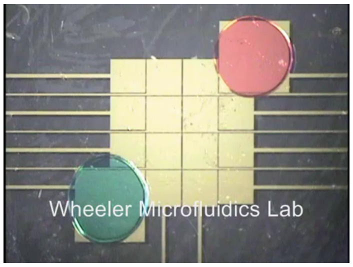
Chip for estrogen assay

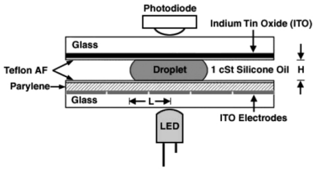
Mousa et al, Science Trans. Med. 1,1 (2009)



Digital microfluidics



Wheeler group, U Washington



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