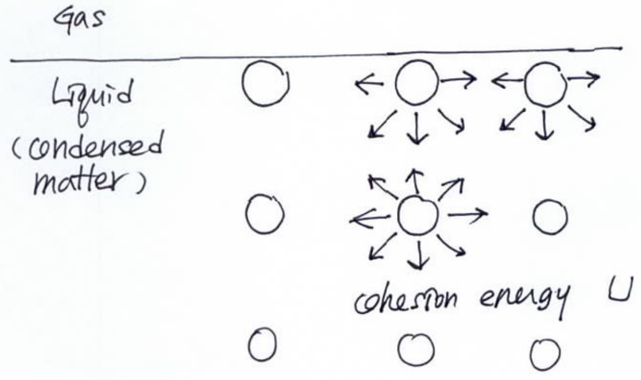
Surface Tension

- Physical origin



: unhappy (energetically unfavorable state)
→ minimizes surface area

: happy

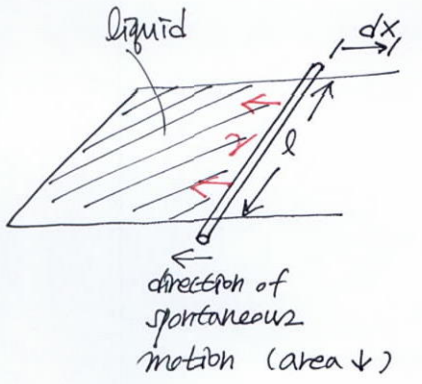
(surface molecule : short of $\sim U/2$
(molecular size a, exposed area $\sim a^2$

surface tension γ ~ energy shortfall / unit area

$\sim \frac{U}{2a^2}$ [J/m^2] or [N/m]

material	interaction	U	γ [mJ/m^2]
oils	van der Waals	$\sim kT$ $\sim \frac{1}{40} eV$ ($T = 25°C$)	20
water	hydrogen bonding		72
mercury	strongly cohesive metallic	1eV	500

- Mechanical Definition



Exerting force F on the rod to move it by dx :

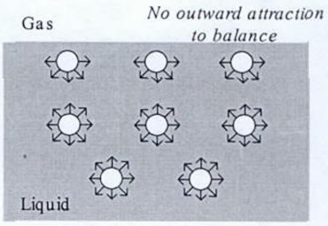
work done

$\delta W = F dx$

$= \underset{\text{2 interfaces.}}{2}\gamma \cdot \underbrace{l \cdot dx}_{\text{area increase}}$

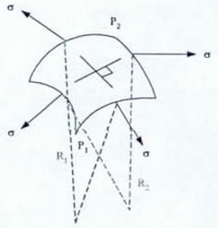
What is the surface tension?

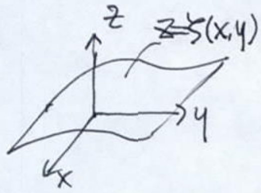
- Surface of the liquid ~ stretched membrane in tension
  - minimize the surface area



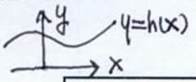
- Force balance for a curved surface (static): Young-Laplace eq.

$$P_1 - P_2 = \sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)$$





curvature : mathworld.~~com~~wolfram.com/Curvature.html



$$\kappa = \frac{\partial^2 h/\partial x^2}{[1+(\partial h/\partial x)^2]^{3/2}} \rightarrow \frac{\partial^2 h}{\partial x^2} \quad \text{for } \left(\frac{\partial h}{\partial x}\right)^2 \ll 1.$$

$$\frac{1}{R_1}+\frac{1}{R_2} = +\left(\frac{\partial^2 \zeta}{\partial x^2}+\frac{\partial^2 \zeta}{\partial y^2}\right)$$

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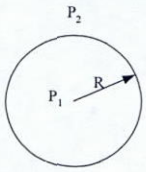
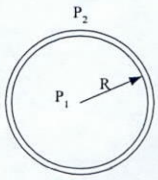
Drops and bubbles

$$P_1 - P_2 = \frac{2\sigma}{R}$$



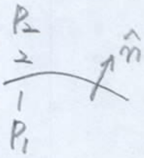
Soap bubbles and foams

$$P_1 - P_2 = \frac{4\sigma}{R}$$



Dynamic boundary conditions

- Normal $$P_2 - P_1 + \sigma\left(\frac{1}{R_1}+\frac{1}{R_2}\right) = 2\mu_2\frac{\partial v_{n,2}}{\partial n} - 2\mu_1\frac{\partial v_{n,1}}{\partial n}$$



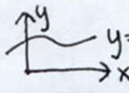
- Tangential $$\mu_2\left(\frac{\partial v_{n,2}}{\partial \tau}+\frac{\partial v_{\tau,2}}{\partial n}\right) - \mu_1\left(\frac{\partial v_{n,1}}{\partial \tau}+\frac{\partial v_{\tau,1}}{\partial n}\right) = \frac{\partial \sigma}{\partial \tau}$$

Kinematic B.C at the interface.

Let $F(x,y,z,t) = \text{const} = 0$: eq. of the bounding surface

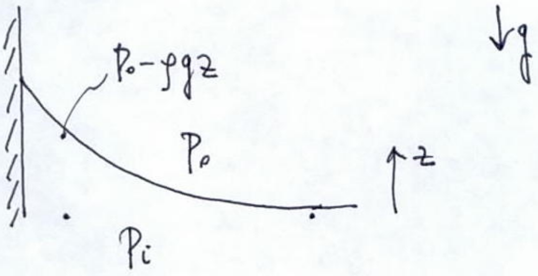
KBC: $\frac{DF}{Dt} = \frac{\partial F}{\partial t} + (\bar{u}\cdot\nabla)F = 0.$

ex) $F(x,y,t) = y - \eta(x,t)$: $\frac{\partial F}{\partial t} = -\frac{\partial \eta}{\partial t}$, $u\frac{\partial F}{\partial x} = -u\frac{\partial \eta}{\partial x}$, $v\frac{\partial F}{\partial y} = v$



$\therefore v = \frac{\partial \eta}{\partial t} + u\frac{\partial \eta}{\partial x}$ on $y = \eta(x,t)$

Equilibrium condition on the surface in a gravitational field



$$p_i - p_0 = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

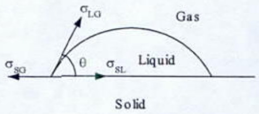
$$-\rho g z = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

$$\rho g z + \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = 0.$$

Contact angle: static

- Young's equation

$$\sigma \cos\theta_{eq} = \sigma_{SG} - \sigma_{SL}$$



- Wetting regimes
  - θ=0: complete wetting
  - 0< θ<90º: wetting (hydrophilic)
  - 90º< θ<180º: nonwetting (hydrophobic)
  - θ=180º: complete nonwetting

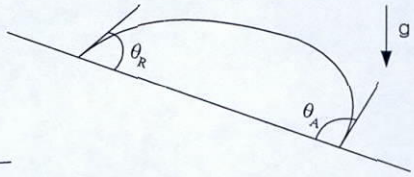
Partial wetting (0<< θ <<180º)

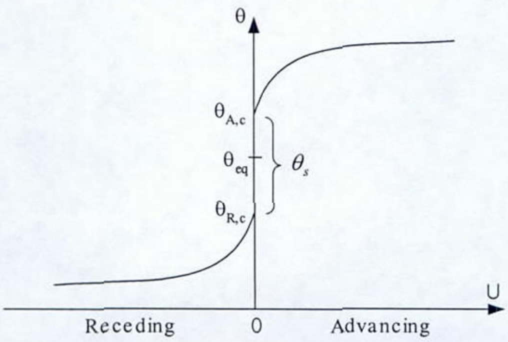
- Selected data
  - water/paraffin: 110º, w/Pt: 40º, mercury/glass: ~130º

Dynamic contact angle

- Contact angle hysteresis

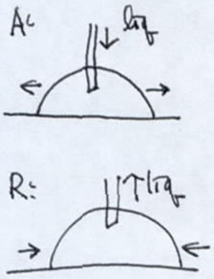
$$\theta_R < \theta_s < \theta_A$$





Hoffman's law

$$Ca \equiv \frac{\mu U}{\sigma} = 0.013\left(\theta_A^3 - \theta_{eq}^3\right)$$

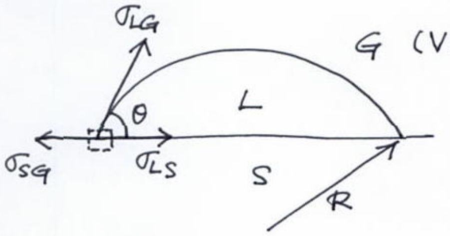


* Ultrahydrophobic surface

* Chemical treatment of surfaces

- previous papers
- next papers

* Young's equation



· force balance : $\sigma_{SG} = \sigma_{LS} + \sigma_{LG}\cos\theta$

$$\sigma_{LG}\cos\theta = \sigma_{SG} - \sigma_{LS}.$$

· thermodynamic approach

volume $V = \frac{\pi R^3}{3}(1-\cos\theta)^2(2+\cos\theta) = \text{const.}$

surface area $S = 2\pi R^2(1-\cos\theta)$

Gibbs free energy $G = \gamma S + \pi(R\sin\theta)^2(\gamma_{SL} - \gamma_{SV})$

$$= \left[\frac{9\pi V^2}{(1-\cos\theta)(2+\cos\theta)^2}\right]^{1/3}\left[2\gamma - a(1+\cos\theta)\right]$$

$$a = \gamma_{SV} - \gamma_{SL}$$

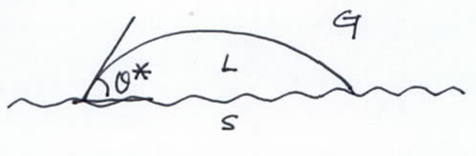
$$\frac{dG}{d\theta} = \left[\frac{9V^2\pi}{(1-\cos\theta)^4(2+\cos\theta)^5}\right]^{1/3} 2\,(a - \gamma\cos\theta)\sin\theta.$$

$\frac{dG}{d\theta} = 0$ when $\theta = \theta_{eq}$.

$$a - \gamma\cos\theta_{eq} = 0.$$

$$\gamma\cos\theta_{eq} = \gamma_{SV} - \gamma_{SL}$$

* The Wenzel equation (regime, state)



roughness $f = \dfrac{\text{real surface area in contact with liquid}}{\text{projected area onto the horizontal plane}}$

· area of liquid-solid interface $= \pi (R\sin\theta)^2 f$

$$G = \gamma S + \pi (R\sin\theta)^2 f\,(\gamma_{SL} - \gamma_{SV})$$

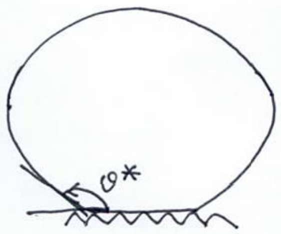
$$= \gamma S \cancel{+} - \pi (R\sin\theta)^2 a \quad . \qquad a = f\,(\gamma_{SV} - \gamma_{SL})$$

$\frac{dG}{d\theta} = 0$ when $\theta = \theta^*$

$$a - \gamma \cos\theta^* = 0 .$$

$$\cos\theta^* = \frac{a}{\gamma} = f\,\frac{\gamma_{SV} - \gamma_{SL}}{\gamma} = f \cos\theta_{eq} .$$

* The Cassie-Baxter equation (regime, state)



$\frac{L}{S}$

$\frac{L}{V}$

area fraction ϕ : contact area of S & L / total projection

$1-\phi$: contact area of L & V / total proj.

$$G = \gamma S + \pi (R\sin\theta)^2 \left[\phi\,(\gamma_{SL} - \gamma_{SV}) + (1-\phi)\,\gamma \right]$$

$$= \gamma S - \pi (R\sin\theta)^2 a$$

$$a = \phi\,(\gamma_{SV} - \gamma_{SL}) - (1-\phi)\,\gamma$$

$\frac{dG}{d\theta} = 0$ when $\theta = \theta^*$

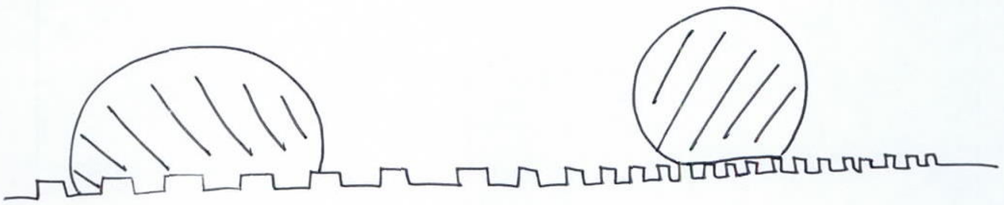
$$a - \gamma \cos\theta^* = 0 .$$

$$\gamma \cos\theta^* = \phi\,(\gamma_{SV} - \gamma_{SL}) - (1-\phi)\,\gamma$$

$$\cos\theta^* = \phi \cos\theta_{eq} - (1-\phi)$$

$$= \phi\,(\cos\theta_{eq} + 1) - 1$$

* Roughness and superhydrophobicity



θ : thermodynamic contact angle on a smooth solid surface

r : roughness factor $\equiv \dfrac{\text{actual area of rough surf.}}{\text{geometric projected area}} > 1$.

θ' : contact angle at rough surface.

Wenzel model

$$\cos\theta' = r\cos\theta$$

$0° < \theta < 90°$: $\theta' < \theta$

$90° < \theta < 180°$: $\theta' > \theta$

Cassie / Baxter model

$$\cos\theta' = f_1\cos\theta - f_2 \quad = -1 + \phi_s(1+\cos\theta)$$

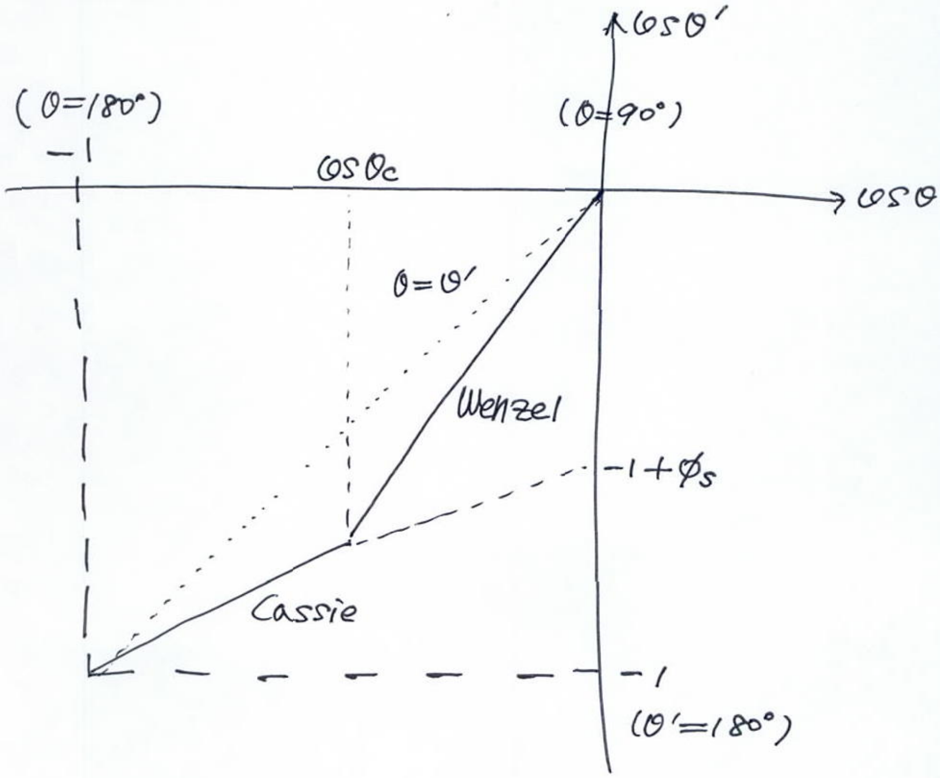
f_1 : fraction of liquid area in contact with solid (ϕ_s)

f_2 : " " " air ($-1 + \phi_s$)

if $f_1 = 0$, $f_2 = 1$ (supported by air layer)

$\rightarrow \theta' = 180°$

as $f_1 \downarrow$, $f_2 \uparrow$ — $\theta' \uparrow$



cos θ'
(θ=180°)
(θ=90°)
−1
cos θc
cos θ
θ=θ'
Wenzel
−1+φs
Cassie
−1
(θ'=180°)

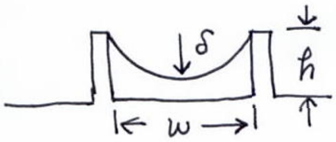
Quality of superhydrophobic surfaces

(1) contact angle hysteresis

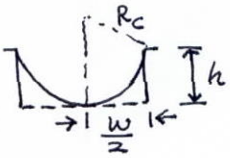
$$\Delta\theta = \theta_{A,c} - \theta_{R,c}$$

usually small $\Delta\theta$ desired

(2) Cassie – Wenzel transition



(i) failure by

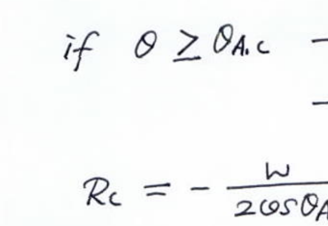


$h < \frac{w}{2}$

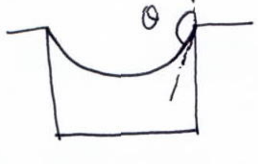
$$R_c = \frac{h}{2} + \frac{w^2}{8h}$$

$$\Delta P_c \sim \frac{\sigma}{R_c} \sim \frac{\sigma}{h\left(\frac{1}{2} + \frac{w^2}{8h^2}\right)}$$

given w,



(ii) critical contact angle condition



if $\theta \geq \theta_{A,c}$ → imbibition into gap
→ failure of Cassie

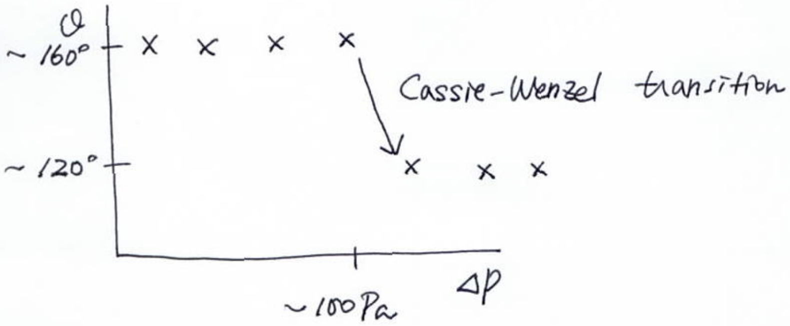
$$R_c = -\frac{w}{2\cos\theta_{A,c}}$$

$$\Delta P_c \sim \frac{\sigma}{R_c} \sim \frac{-2\sigma\cos\theta_{A,c}}{w}$$

experiments

①

$$\Delta p = \sigma \left(\frac{1}{R_1} + \frac{1}{R_2} \right)$$



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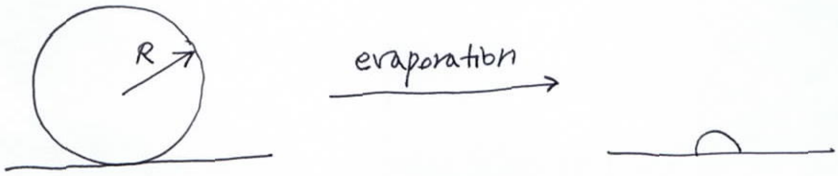

$$\Delta p = \frac{2\sigma}{R}$$