Ceramic and Colloidal Processing

Surface Tension, Wettability and Hydrophobic Surfaces: Exercises

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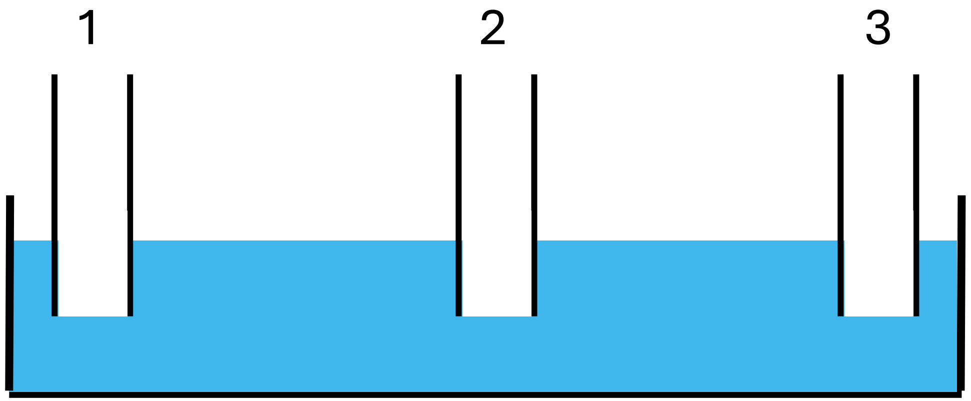
Lausanne, 07 October 2025

Exercise 1: Capillary Rise in Capillaries with Different Wettabilities

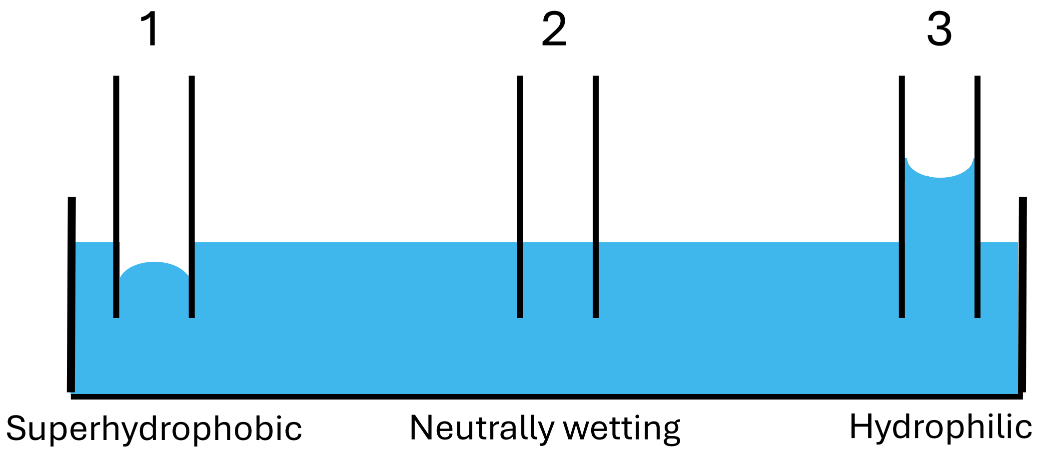
Three identical capillaries with different wettabilities are dip in a water bath as shown in the schematic below. The contact angle of water θ_w on the inner capillaries surfaces are given as:

- Capillary 1: $\theta_{w1} = 164°$
- Capillary 2: $\theta_{w2} = 90°$
- Capillary 3: $\theta_{w3} = 27°$



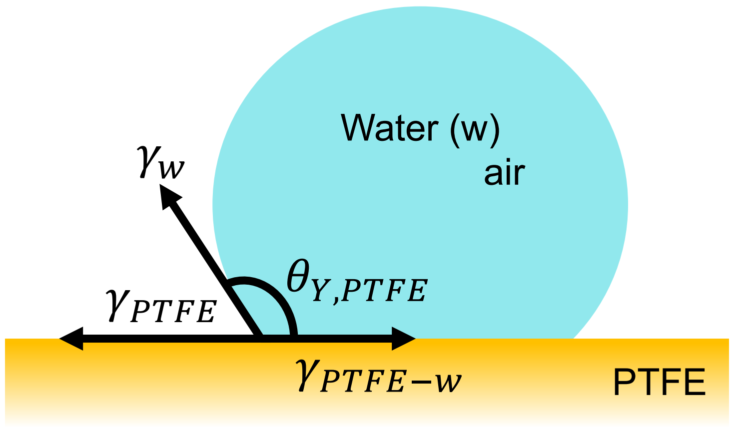
Question a) Qualitatively draw the water meniscus inside the three capillaries

Solution:



Exercise 2: Young‘s Equation

A water droplet is placed on a smooth surface consisting of polytetrafluoroethylene (PTFE). With a goniometer we measure the contact angle $\theta_{Y,PTFE}$.



- Given:
  - Water surface tension: $\gamma_w = 0.072\,\frac{N}{m}$
  - Surface tension of PTFE: $\gamma_{PTFE} = 0.020\,\frac{N}{m}$
  - Young’s contact angle of water on PTFE: $\theta_{Y,PTFE} = 115°$

Question a) Calculate the interfacial tension between water and PTFE (γ_{PTFE-w})

Solution

Young’s equation:

$$\cos(\theta_{Y,PTFE}) = \frac{\gamma_{PTFE} - \gamma_{PTFE-w}}{\gamma_w}$$

$$\Leftrightarrow \gamma_{PTFE-w} = \gamma_{PTFE} - \gamma_w \cdot \cos(\theta_{Y,PTFE}) = 0.020\,\frac{N}{m} - 0.072\,\frac{N}{m} \cdot \cos 115° \approx 0.0504\,\frac{N}{m}$$

Exercise 3: Surface Tension Extimation by Capillary Rise

Using the capillary rise method, we want to experimentally estimate the surface tension of water. This is done in ambient conditions.

Given:

- Outer capillary diameter $d_{out} = 3\ mm = 0.003\ m$
- Wall thickness of capillary t $= 0.5\ mm = 0.0005\ m$

} Inner capillary diameter $r = \frac{d_{out} - 2t}{2} = 0.001\ m$

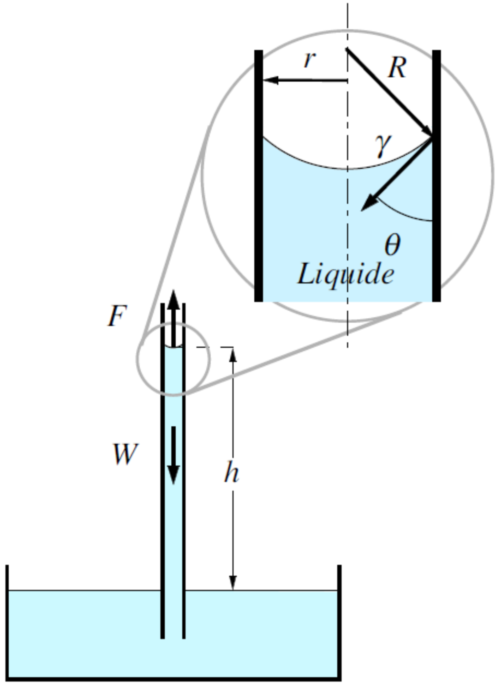
- Water density $\varrho_w = 1 \frac{g}{cm^3} = 1000 \frac{Kg}{m^3}$
- Gravitational acceleration $g = 9.81 \frac{N}{Kg}$
- Capillary rise $h = 14\ mm = 0.014\ m$
- Water contact angle with the inner capillary surface $\theta = 17°$

Question a) Calculate the water surface tension based on the aforementioned parameters

Solution: $\gamma = \frac{rhg\varrho_w}{2\cos\theta} = \frac{0.001m \cdot 0.014m \cdot 9.81\frac{N}{Kg} \cdot 1000\frac{Kg}{m^3}}{2 \cdot \cos 17°} \approx \frac{0.13734}{2 \cdot 0.9563} \frac{N}{m} \approx 0.0718 \frac{N}{m}$

Question b) We repeat the same measurement using a capillary whose material on the inner surface has a different wettability. In this case the contact angle of water is $\theta = 40°$. The geometry doesn't change. Does h indcrease, become smaller or remain unchanged? And why? (qualitative explanation).

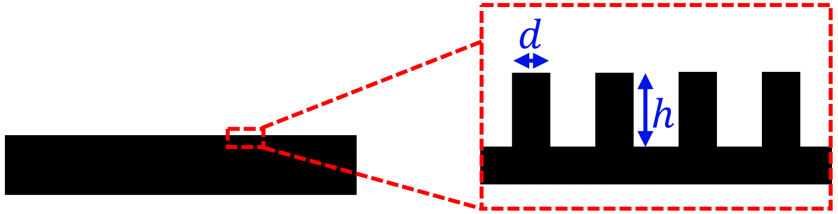
Solution: Surface is more hydrophobic⇒capillary forces reduce (they can sustain less water mass in the capillary)⟹ h reduces



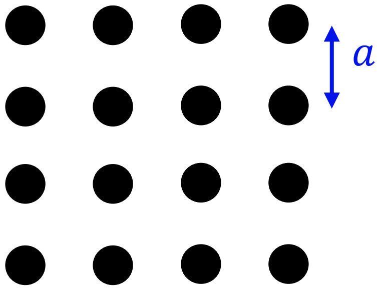
References
1. Picture: Andrea Testino, Ceramic and Colloidal Processing, Lecture slides, EPFL, 2024

Exercise 4: Wenzel and Cassie-Baxter States

Consider a rough PTFE surface consisting of circular micropillars arranged like in the schematic below:



Side view



Top view

$$f_R = \frac{\text{actual area}}{\text{projected (apparent) area}}$$

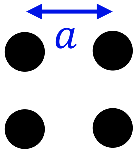
Given:

- Pillar height $h = 20\ \mu m$
- Pillar diameter $d = 10\ \mu m$
- Interpillar distance $a = 30\ \mu m$

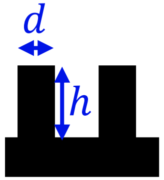
Question a) Calculate the roughness factor f_R of the surface (hint: simplify the problem by considering a single unit cell consisting of 4 pillars)

Solution:

Simplification: consider a unit cell consisting of 4 pillars that repeats in all directions (assume surface consists of n unit cells)



Top view



Side view

$\text{projected (apparent) area} = a^2 \cdot \text{n}$

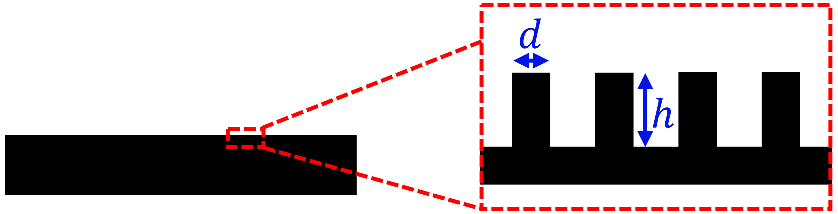
$\text{actual area} = (a^2 + d \cdot h \cdot \pi) \cdot n$

$$f_R = \frac{\text{actual area}}{\text{projected (apparent) area}} = \frac{(a^2 + d \cdot h \cdot \pi) \cdot n}{a^2 \cdot \text{n}} = \frac{a^2 + d \cdot h \cdot \pi}{a^2}$$

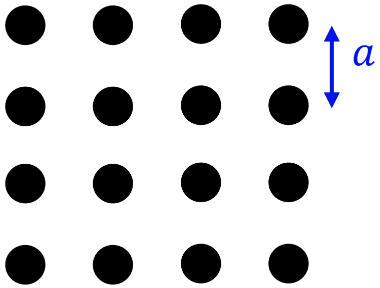
$$= \frac{30^2 + 10 \cdot 20 \cdot \pi}{30^2} \approx 1.698$$

Exercise 4: Wenzel and Cassie-Baxter States

Consider the same surface made of PTFE from the previous slide. Consider its top surface as a smooth surface consisting of PTFE and air (dashed line).

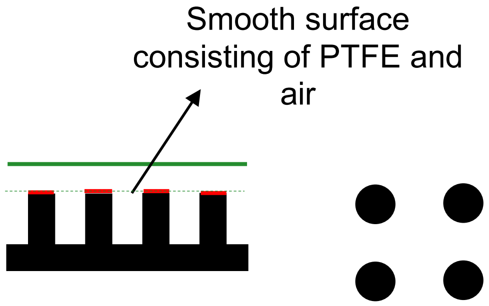


Side view



Top view

$$\varphi_{PTFE} = \frac{A_{PTFE}}{A_{tot}}$$



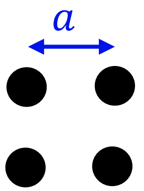
Given:

- Pillar height $h = 20\ \mu m$
- Pillar diameter $d = 10\ \mu m$
- Interpillar distance $a = 30\ \mu m$

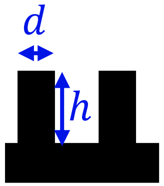
Question b) Calculate the fractional surface area occupied by PTFE φ_{PTFE} (hint: reduce problem to a single unit cell consisting of 4 pillars)

Solution:

Simplification: consider a unit cell consisting of 4 pillars that repeats in all directions (assume surface consists of n unit cells)



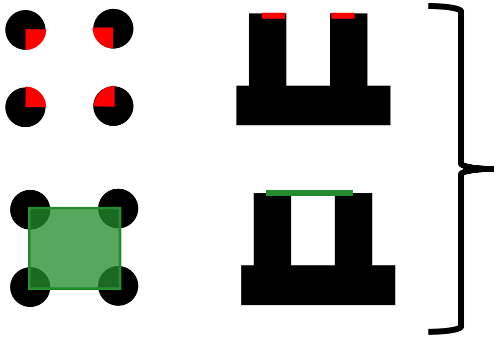
Top view



Side view

$$A_{PTFE} = \left(\frac{d}{2}\right)^2 \cdot \pi \cdot \mathrm{n}$$

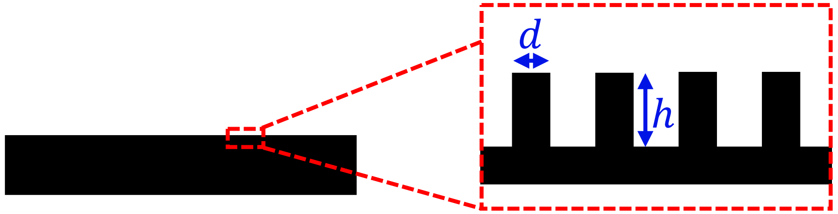
$$A_{tot} = a^2 \cdot \mathrm{n}$$



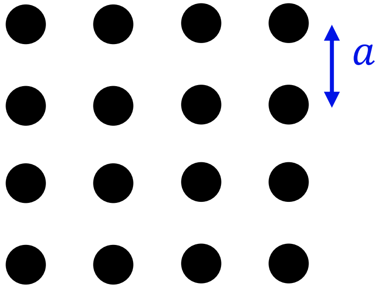
$$\varphi_{PTFE} = \frac{A_{PTFE}}{A_{tot}} = \frac{\left(\frac{d}{2}\right)^2 \cdot \pi \cdot \mathrm{n}}{a^2 \cdot \mathrm{n}} = \frac{\left(\frac{d}{2}\right)^2 \cdot \pi}{a^2} = \frac{\left(\frac{10}{2}\right)^2 \cdot \pi}{30^2} \approx 0.0873$$

Exercise 4: Wenzel and Cassie-Baxter States

Consider the same surface made of PTFE from the previous slide.



Side view



Top view

$$\cos\theta_{Y,c} = \frac{\varphi_{PTFE} - 1}{f_R - \varphi_{PTFE}}$$

Given:

- Pillar height $h = 20\ \mu m$
- Pillar diameter $d = 10\ \mu m$
- Interpillar distance $a = 30\ \mu m$

Question c) Using the results obtained in a) and b), calculate the critical Young's contact angle of the surface.

Solution:

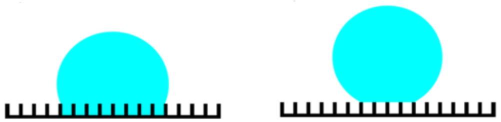
$$\cos\theta_{Y,c} = \frac{\varphi_{PTFE} - 1}{f_R - \varphi_{PTFE}} \Leftrightarrow \theta_{Y,c} = \cos^{-1}\left(\frac{\varphi_{PTFE} - 1}{f_R - \varphi_{PTFE}}\right) = \cos^{-1}\left(\frac{0.0873 - 1}{1.698 - 0.0873}\right) \approx \cos^{-1}(-0.5666) \approx 124.52°$$

Question d) Assuming that the Young's contact angle of water on PTFE is $\theta_{Y,PTFE} = 115°$, determine whether a water droplet placed on this surface will be in Wenzel or Cassie Baxter state.

Solution:

- If $\theta_{Y,PTFE} < \theta_{Y,c} \Rightarrow$ Wenzel state
- If $\theta_{Y,PTFE} > \theta_{Y,c} \Rightarrow$ Cassie-Baxter state

In our case we have $\theta_{Y,PTFE} = 115° < \theta_{Y,c} = 124.52° \Rightarrow$ Wenzel state



Wenzel state   Cassie-Baxter state