Lecture 6: Focus on some (non) wetting situations

Introduction

This chapter – inspired by the work of Quéré [1] - is dedicated to wetting under non classical conditions and its applications. It can thus be seen as an extension of the first chapter about capillarity. The review of "exotic" situations is non exhaustive but focuses on the mostly used cases: Leidenfrost effect, lotus effect and liquid marbles.

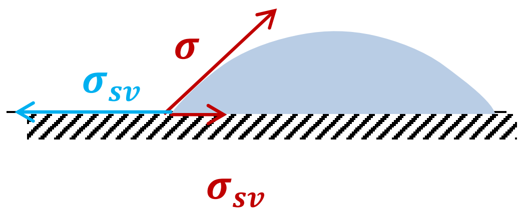
All these situations and their consequences on wetting have been intensively studied in the last decade due to their excellent potential for applications such as superwetting to prevent dewetting, superhydrophobicity, self cleaning,… Yet, many questions remain open.

1) Smooth surfaces

We first quickly recall the governing equations of wetting for the ideal case i.e for a smooth surface colder than the boiling point of the liquid of interest.

Spreading parameter

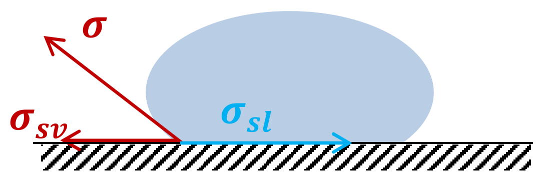
The spreading parameter S is defined as: $\boldsymbol{S = \sigma_{sv} - \sigma_{sl} - \sigma}$ where σ is the surface tension of the liquid, σ_{sv} the surface energy of the solid facing vapor and σ_{sl} the surface energy of the solid covered by liquid. If S>0, a drop spreads fully - the film formed has a thickness of a few molecules - while if S<0 it forms a small lens.



Drying parameter

Conversely, a drying parameter D can be defined as: $\boldsymbol{D = \sigma_{sl} - \sigma_{sv} - \sigma}$

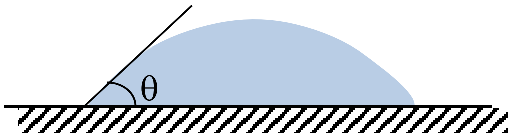
If D>0, the contact line will be withdrawn by surface forces until a film of vapor comes between the solid and the liquid leaving a fully dry solid. This only happens under particular circumstances as the Leidenfrost effect but is never observed for smooth surfaces of hydrophobic materials. To approach D>0, it is possible to take advantage of roughness effects.



Contact angle and Young-Dupré relation

For S<0 ($\boldsymbol{\sigma_{sv}} - \boldsymbol{\sigma_{sl}} < \boldsymbol{\sigma}$) and D<0 ($-(\boldsymbol{\sigma_{sv}} - \boldsymbol{\sigma_{sl}}) < \boldsymbol{\sigma}$), at equilibrium, it is possible to define a unique contact angle θ between the liquid and the substrate. The contact angle θ is given by the Young Dupré relation:

$$-1 < \cos\theta = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma} < 1$$



2) "Hot" surfaces: vapor layer

Definition of "hot"

In this section, the term hot refers to a temperature much larger than the boiling temperature of the liquid of interest.

When a vapor layer isolates the liquid from the substrate

If the "substrate" is hot, the liquid evaporates while entering in contact with it building up a thin layer of vapor. The "low" thermal conductivity of the vapor and the permanent feeding of this layer by the liquid of interest allow a drop to stay in non wetting conditions. This is the Leidenfrost effect [2].

The life time of such drops has been studied and it has been found that the shrinkage in volume is "slow" with typically 10^{-4}m/s. [3]

The volume of liquid in contact with the solid can also be much more important than the volume of a drop (maximal volume is in the order of a drop of diameter the capillary length). In this case, the liquid layer floats above the substrate. As the vapor layer grows, chimneys appear regularly to allow some release. This aspect has been investigated in [3].

To conclude, we can say that even if the life time of the liquid is reduced under the Leidenfrost effect, it is the only non wetting configuration which can be achieved without "coating the liquid" (see last section of this lecture). All other superhydrophobic stages reached by making use of the lotus effect only allow approaching this situation, the contact angle of 180° being never reached.

Leidenfrost water drop levitating on a silicon wafer at 200°C

From [3]

3) Rough and microtextured surfaces: toward superhydrophobicity

3)1) Roughness

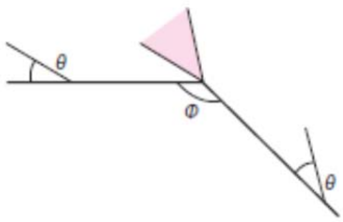
Definition: Surface roughness measures the texture of a surface and is quantified by the vertical deviations of the surface from its ideal form. In practice it is often necessary to know both the amplitude and frequency of these deviations to fully characterize the roughness of a surface.

Daily life: it is important to note that most solids are naturally rough at a micrometric scale. Microgrooves are generated by lamination or molding, compaction leads to typical roughness at the scale of the compacted powder,…

3)2) Effect of roughness on wetting

Contact angle hysteresis:

The Young Dupré relation stipulates that the liquid meets the solid with a contact angle θ. Hence at a local defect (rugosity) as represented in the figure below, the contact angle can take a wide range of values. More precisely if the reference direction is the horizontal one, the contact angle can be found between θ and $\pi - \phi + \theta$.



Possible positions of the contact line at the edge with some defects, from [1]

This is practically observed when the contact line is pinned. In such cases the contact angle is not unique anymore. Indeed, the contact angle can vary till the contact line suddenly depins and move toward the next series of pinning defects. The maximum effective contact angle observed is referred to as the advancing contact angle θ_a while the minimum one is the so-called receding angle θ_r. Classically the advancing contact angle is measured while injecting more liquid on a sessile drop and the receding angle is obtained when sucking some of the drop liquid away.

The contact angle hysteresis is defined as the difference between the maximum (advancing) contact angle and the minimum (receding) contact angle i.e $\Delta\theta = \theta_a - \theta_r$

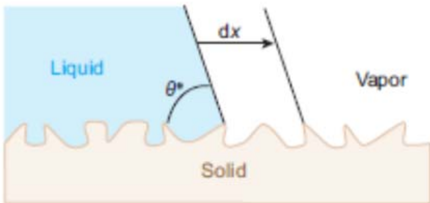
Order of magnitude: on a rough substrate, $\Delta\theta$ varies dramatically from nearly zero to a value in the order of θ_a itself (receding angle → 0).

The pinning observed due to the edges of the topologic defects considered above can also be found in presence of chemical defects (heterogeneity).

Wenzel state

Roughness not only impacts the contact angle hysteresis but also modifies the typical or apparent angle which is often very different form the one predicted by Young-Dupré. Wenzel (1996) used a geometrical argument to explain this phenomenon. We now introduce the roughness factor r defined as the ratio between the real surface area when observed at the micro/nano-scale and the apparent surface area (naked eyes observation). By definition r > 1.

A drop placed on such a rough surface will exhibit an apparent contact angle θ^*, see figure below.



Drawing of the Wenzel state: the Wenzel law can be found via an energy balance while displacing the contact line of a distance dx, From [1]

By performing an energy analysis considering the contact line is moved of dx, we obtain the Wenzel relation – where θ the contact angle given by the Young-Dupré relation (ideally smooth surface) :

$$\cos \boldsymbol{\theta}^* = \mathbf{r} \cos \boldsymbol{\theta}$$

Wenzel equation predicts that roughness enhances wettability: if the solid is hydrophilic (θ<90°) it becomes even more hydrophilic with $\theta^* < \theta$. On the contrary, an hydrophobic surface will be even more hydrophobic if rough: $\theta^* > \theta > 90°$.

We also see that as r can be made arbitrarily large, roughness should allow complete wetting and complete drying ($\cos \theta^*$>1 or $\cos \theta^*$<-1 respectively). Indeed, such behaviors are never observed because Wenzel assumptions are not often satisfied.

Even when the Wenzel state is achieved, it is difficult to check whether the Wenzel relation is satisfied or not. Indeed as the liquid conforms to the roughness, pinning of the contact line is particularly strong in this stage. Thus, the contact angle hysteresis is huge and it is barely impossible to extract a single apparent contact angle θ^*. Recent work on the validity of the Wenzel law shows that such an average model can be used only if the drop is much larger than the defects.

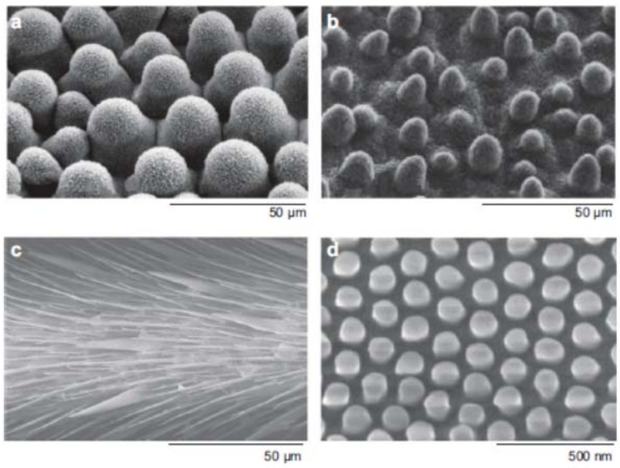
To remember: the roughness modifies wetting at two levels: (i) the ideal character of the Young Dupré relation is lost so that there is not a single contact angle anymore; (ii) the value of the *apparent angle is changed due to the fact that the real contact area (liquid solid) is larger than the apparent one.*

3)3) Microstrutured surfaces

Brief history

The burst of activity in this domain can be related to the following three factors: (i) the experiments of the researchers from the Kao Corporation in Japan which showed extremely large contact angles on fluorinated rough surfaces (~1990 similar results were obtained in the 40´s but had been forgotten); (ii) the investigation of the structures found on the leaves of certain – hydrophobic - plants by Neinhuis and Barthlott (~1990 Germany, this kind of research has been extended to animals); and (iii) the recent development of microfabrication technology opening the path to new and controlled designs.

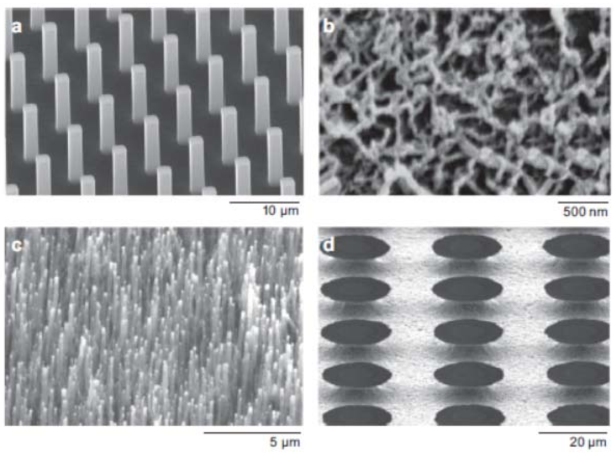
Some examples of natural superhydrophobic materials



(a) leaf of the so-called elephant´s ear (Wagner and Neinhuis);

(b) lotus leaf (Barthlott and Neinhuis); (c) leg of a water strider (Lei Jiang) and (d) surface of a mosquito eye. From [1]

Some examples of synthetic superhydrophobic materials



Pictures from [1].

(a) micropilars from Reyssat;

(b) surface decorated by nanofibers (Gao and McCarthy);

(c) carbon nanotube grafted on a surface (Bico) and

(d) mushroom pattern from McKinley

3)4) Effect of microstructure on wetting

Results of Kao

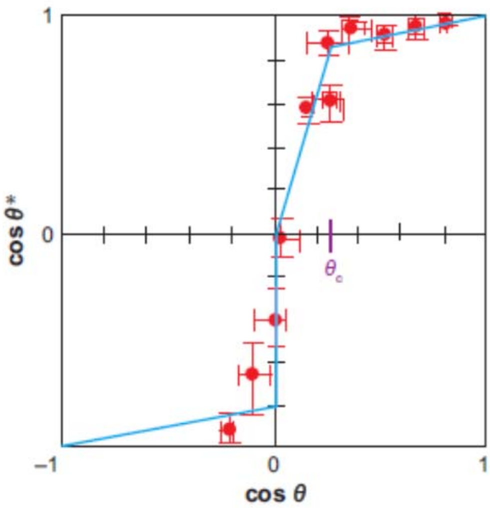


Figure from [1]. Kao results

Various liquids are used on microtextured surfaces. Classical contact angles (θ) obtained on flat substrate are compared to the apparent contact angles (θ^*) obtained for the same material in the presence of microtexture.

- cos θ not smaller than -0,3 (110°) limit of contact angle for flat substrates
- as soon as $\cos\theta < 0$ --> jump of $\cos\theta^*$ $(170°)$ superhydrophobicity - lotus effect
- $\cos\theta > 0$: first linear increase of $\cos\theta^*$ probably Wenzel (slope 3)
- cos $\theta > 0$: second linear with trivial behavior θ —> 0 ==> θ^*—> 0 (penetration of the liquid in the structure)

Interpretation of superhydrophobicity

The superhydrophobicity is caused by the entrapment of air in the microtextures surface. For a given drop size, the liquid has less contact with the substrate than if the substrate was flat. It is the so-called Cassie regime also known as Fakir regime.

Cassie regime

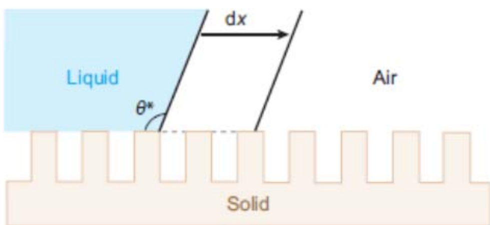


Figure from [1]. Drop on the microtextures surface in the Cassie Regime. Air is entrapped in the structure and should be accounted in the energy balance

There is a critical angle, above which the Cassie regime is more favorable than the Wenzel one (air is entrapped). This threshold can be found vis an energy balance approach leading to:

$$\cos\theta_c = -1(1-\varphi_s)/(r-\varphi_s)$$

Here $\boldsymbol{\varphi_s}$ if the pilar density and r is the roughness. Yet for smaller roughness factor, the criterion for air trapping is not obeyed and Cassie regime can be observed while the Wenzel one would be more favorable. The Cassie state is thus metastable.

When the Cassie regime establishes, the apparent contact angle is given by:

$$\cos \boldsymbol{\theta}^* = -\mathbf{1} + (\mathbf{1} + \cos \boldsymbol{\theta})\boldsymbol{\varphi_s}$$

For more details about Cassie and transition to Wenzel, see coming exercise.

Some applications:

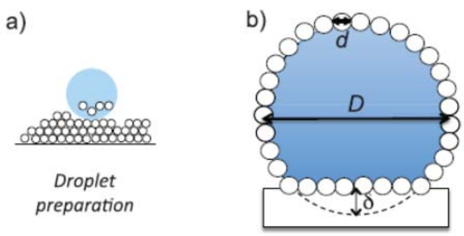
Huge slip length at canals wall, anisotropy, non sticky water,…

4) Coating the liquid: another way to non wetting state

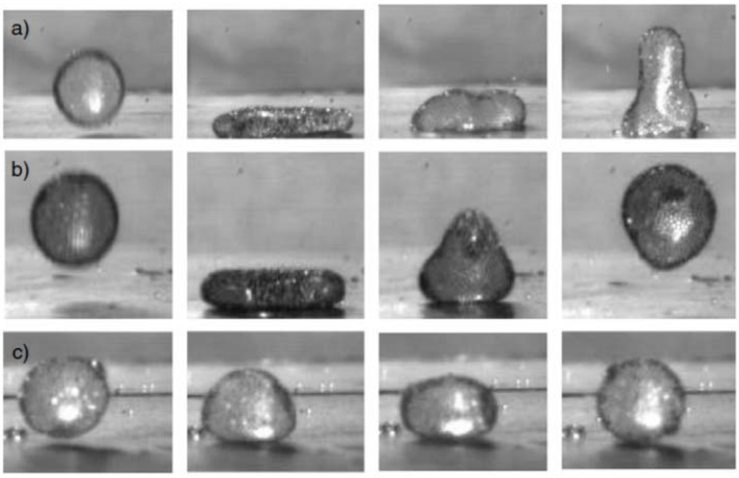
Refered as liquid marbles [4]

Hydrophobic micro/nano particles at air/liquid interface → liquid is isolated from its environment.

Liquid marble preparation is depicted in the next figure, taken from [5]



When these objects are falling onto a substrate, depending on velocity and size, 3 regimes are observed. These three regimes: impalement, bouncing, non-bouncing are represented in the figure below, taken from[3]. For more information, see coming exercise.



References:

[1] Quéré (2008)
[2] Leidenfrost
[3] Biance (2005)
[4] Aussillous (2001)
[5] Planchette (2012)