Exercise 6: Liquid pearls

Introduction

In this exercise session, we focus on liquid pearls i.e drops in a non wetting or quasi non-wetting state.

The exercise comprises two independent parts focusing respectively on microtextured surfaces mimicking the lotus effect [1-4] and hydrophobic particles which adsorb at air/liquid interface to form so-called liquid marbles.

The basic principles of these two phenomena are presented here together with their limitations.

Superhydrophobic surfaces

In this first section, we are interested in microtextured hydrophobic surfaces which give rise to super hydrophobic properties. In this exercise, we consider a surface made of regular pillars array. The micro-pillars have a height h, a radius r and are separated by a distance (wall to wall) l. Their surface density is noted ϕ as represented on figure 1.

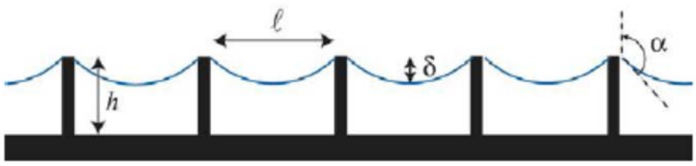


Figure 1 : microtextured surface, adapted from [2]

1) Which configurations can a liquid drop adopt when placed on top of such a substrate? For each of these two states, give the energetic cost and deduce the apparent contact angle θ^* assuming a smooth substrate made of the same material has a contact angle of θ.
2) Under which conditions is the Cassie state favorable when compared to the Wenzel one? Note that the Cassie state is actually observed even if these conditions are not fulfilled; in this case it is a metastable state.

In the following we try to establish the threshold (in term of pressure) leading to the transition between these two regimes. We note A the surface area of a cell comprised between four neighboring pillars and P the pressure in the drop. This pressure can originate from interface curvature (Laplace) or from an impact of the drop (kinetic pressure).

3) What is the pressure force to which the air/liquid interface is subjected to for a cell of area A?

4) What is the expression of the capillary force allowing for balancing this pressure? We write σ the surface tension of the liquid and consider that N_p is the number of pillars present in one cell of the microtextured surface. Express N_p as a function of A, ϕ, and r. Deduce the expression of the pressure at equilibrium as a function of ϕ, σ, r and θ.

We now consider that the pillar radius is small compared to the lattice size p. It can be shown that under this assumption: $\frac{2\phi}{1-\phi} \approx 2\frac{r^2}{p^2}$

5) Considering the position of the interface in the microstructure, which kind of configurations could lead to the impalement of the drop in the surface?

In this exercise, we will actually consider two possible origins of impalement. The first one was described by Reyssat and Bartolo [1,4] and the second one was shown by Bartolo [3,4]. In the first mechanism considered, the impalement of the liquid within the structure corresponds to the contact of the interface with the bottom of the surface. The figure 2 below illustrates this condition.

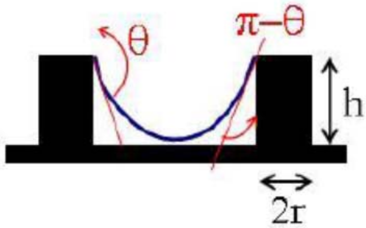


Figure 2: impalement of the liquid in the substrate occurs if the curved interface reaches the bottom of the substrate. Adapted from [3]

6) How can you express this condition? Deduce the impalement pressure for such a surface as a function of σ, h and p.

We now consider the second mechanism at play. This mechanism corresponds to the situation where the angle α defined in the figure 1 reaches the advancing contact angle θ_a of the material. Under this condition, the contact line slides down along the pillar till the curved part of the interface enters into contact with the bottom of the substrate as presented before.

7) How can this be expressed using θ_a?

The experimental results obtained by Bartolo et al. are represented in the Figure 3. Drops are in contact with a superhydrophobic surface (evaporation: circles; compression: squares; and impact: triangles) having pillars of height h. The threshold between bouncing and impalement is plotted as a function of the pillars height. Two regimes are observed: first the transition varies linearly with the pillar height. After a certain critical height, the transition is not function of the pillar height anymore.

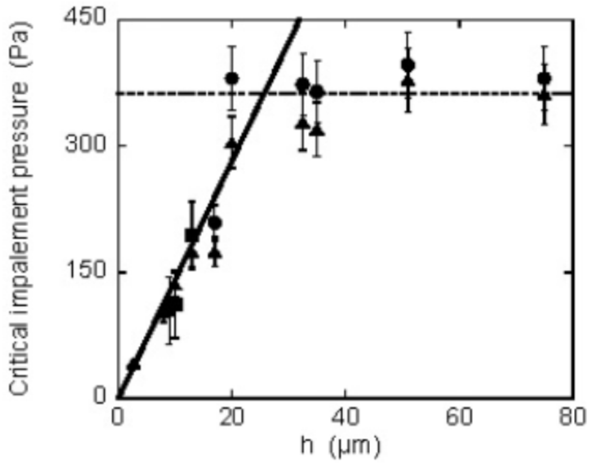


Figure 3: impalement threshold measured by Bartolo, figure taken from [3].

8) Can you comment on these results? The second regime observed for high pillars was not seen in the work of Reyssat, see figure 4. Could you give some possible reasons?

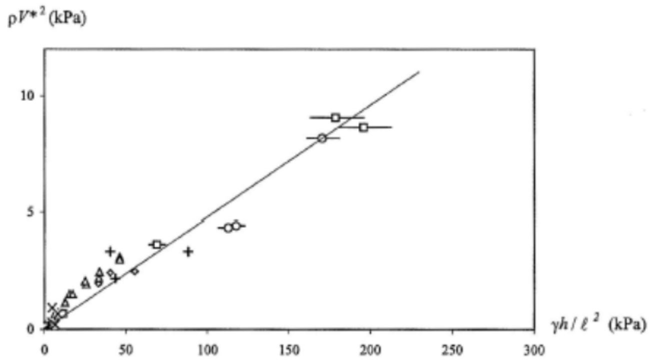


Figure 4: impalement threshold measured by Reyssat. Impacts only, figure taken from [2].

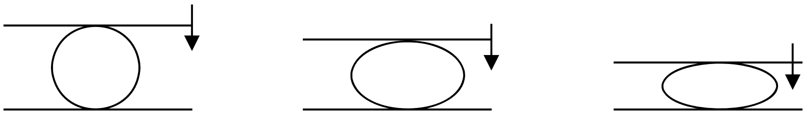
Liquid marbles

It is also possible to reach non-wetting situations by coating the liquid with hydrophobic microparticles. These coated drops are thus called liquid marbles. In this section we are interested in the mechanical robustness of such armors when subjected to deformations. The deformations can have different origins and happen in a quasi static regime when a liquid marble is slowly compressed into a press or with a dynamic component when impacts are considered. We will treat both situations.

Robustness versus contact with a solid

i) Quasi static results

Principle of the experiment [6]: a liquid marble is placed between two plates and slowly compressed leading to an increase of its interfacial area. Above a critical increase in interfacial area, the drop wets the surfaces confining it, see scheme below.



9) Can you give a qualitative interpretation of this observation?

ii) Dynamic threshold

Liquid marbles are now impacting a dry smooth substrate. By varying the falling height it is possible to adjust the velocity of the liquid marbles reaching the surface. Three regimes are observed [7,8]: bouncing, impalement and non bouncing. In this exercise we are interested only in the threshold between bouncing and impalement.

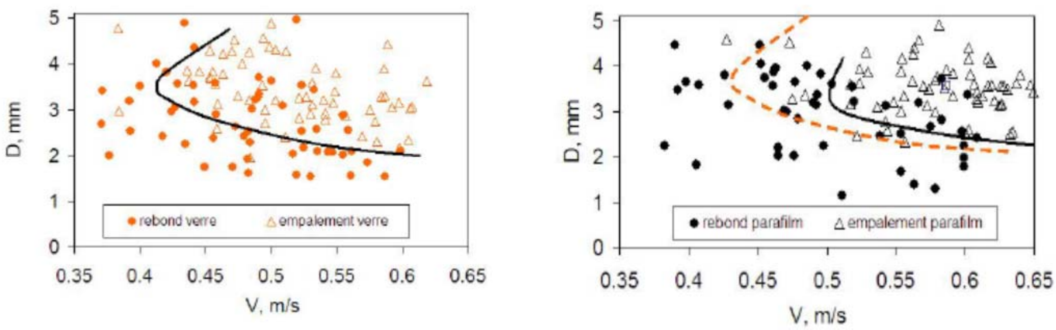


Figure 5: Typical outcomes of liquid marbles impacts onto glass (left) and paraffin (right), from [7].

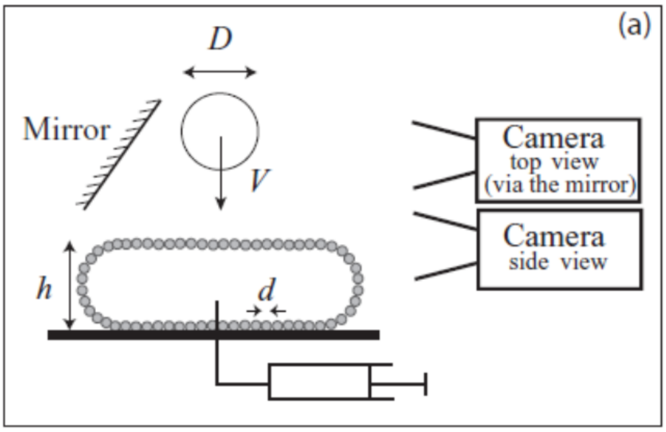
10) Can you qualitatively comment on the dependence of the transition with the drop diameter? Could you explain the differences observed between the two kinds of surfaces (glass and paraffin)?

The results of the figure 4 can be plotted against D_{max}/D where D_{max} is the maximum extension reached by the drop. It is found that the transition between bouncing and impalement corresponds to a critical value of this ratio.

11) Can you comment on this observation?

Coalescence threshold with a liquid drop

We now consider the experiment illustrated in the figure below from [9] and we would like to predict the threshold velocity between coalescence and non coalescence for a drop of diameter D impacting an armored puddle.



Experimental observations show that the hole opening in the armor has the shape of a crown located at the periphery of the impacting drop, see figure 6.

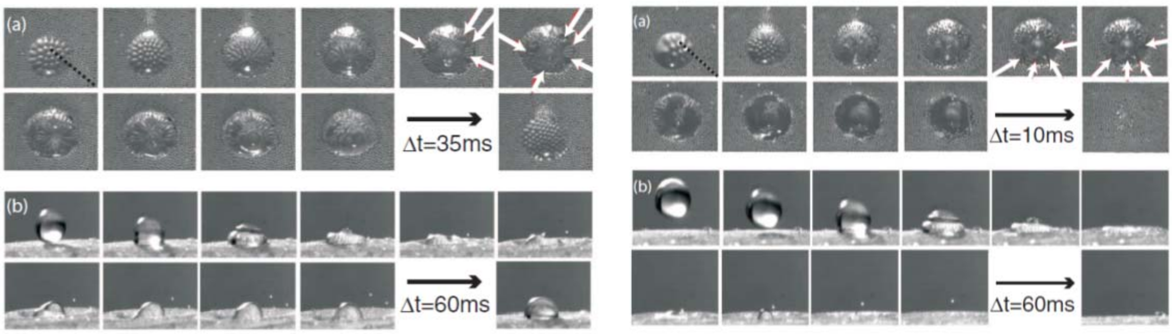


Figure 6: pictures of impacting drop, left from top to bottom: top and side views of the non coalescence regime and right from top to bottom: top and side views of the coalescence regime.

12) Write an energy balance to express the velocity threshold of the transition? Which condition on e the broadness of the crown allows coalescence if we assume that the interface has a curvature of κ under impact (κ^{-1} being the capillary length).

The experimental threshold is plotted with the theoretical threshold $V_{1,theo} = 2\sqrt{\frac{3.75\,\sigma}{\rho}}\kappa^{-1/4} d_{part}{}^{1/4} D$ in the diagram of the figure 7.

13) Can you comment on it? What do you expect if both drop and puddle are now covered? Is this in agreement with the results presented in figure 8?

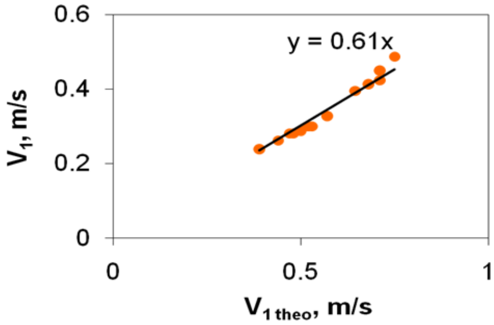


Figure 7: theoretical and experimental threshold obtained by Planchette when a drop impacts onto a coated puddle.

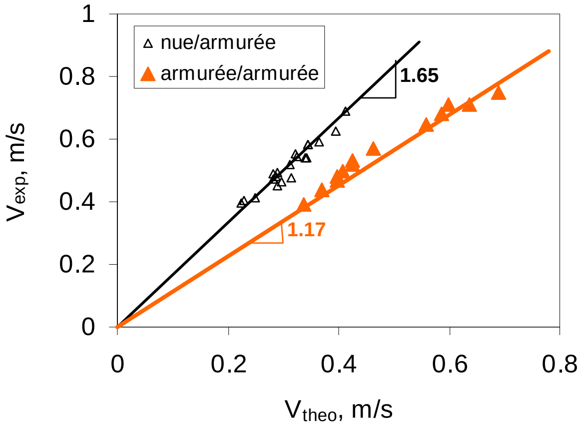


Figure 8: theoretical and experimental threshold obtained for simple and double armors configuration. The slope ratio is 1.41.

References

[1] Callies-Reyssat, PhD thesis, 2007
[2] Reyssat et al. 2008
[3] Bartolo at al., 2006
[4] Moulinet & Bartolo, 2007
[5] Aussillous, PhD thesis, 2002
[6] Aussillous, Nature, 2001
[7] Planchette, PhD thesis, 2011
[8] Planchette, EPL, 2012
[9] Planchette, PoF, 2013