Nanostructured Surfaces & Nanotribology

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Micro and nanoscale friction – Lotus effect

In any material surface properties are strictly connected to both chemistry and micro/nano scale topography. While traditionally manufactured surfaces show a random roughness which actually contrasts friction and wear, it has been recently discovered that many functional bio surfaces exhibit roughness structured in complex hierarchies determining their properties. For instance some plant leaves, like lotus, owe to such structures their exceptional super hydrophobic properties. Inspired by nature, the practice of creating micro- and nano-metric asperities is more and more specifically used to modify in a controlled way surface properties.

This technique can improve efficiency in tribological[1] systems also contributing to their environmental friendliness ('green tribology'). An example is represented by microorganisms and plants accumulation on boat hulls, with a consequent increase in fuel consumption up to 40%, or within industrial plants pipes, causing a huge decrease in efficiency. Chemicals have been traditionally used against it, but either their impact may be detrimental to the environment or their efficiency may be quite limited. A similar treatment has been applied in the deicing process of wind turbine blades, airplane wings and electrical cables. All this can be now efficiently replaced by micro structured manufacturing of surfaces which hinders the sticking of ice and filth thanks to the thin film of air forming at the interface.

Surface classification according to wettability

Among surface properties, **wettability** is very important for tribology issues, i.e. the adhesion level of liquids dropped on the examined surface. This property is mainly dependent on the terminal groups of molecules at the solid interface as they can be either hydrophobic or hydrophilic (**chemistry**). Nano-scale structuring, as it has already been shown, influences surfaces interaction too (**physics**).

[1] Tribology is the science of friction, lubrication and wear. From the greek 'tribos', which means 'rubbing' .

We will now discuss two fundamental parameters for a quantitative classification of surfaces according to their wettability: **static contact angle** and **rolling angle.** This will help us in understanding the physical mechanism at the base of wettability.

1. Static contact angle

This is the angle between the two tangents at the Liquid-Gas interface and at the Solid-Liquid interface, in correspondence to the contact line between the three phases (Fig. 1). The angle measure is taken as soon as the drop has been deposited on the sample substrate and the thermodynamic equilibrium among solid, liquid and gas has been reached.

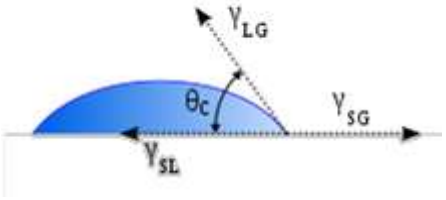
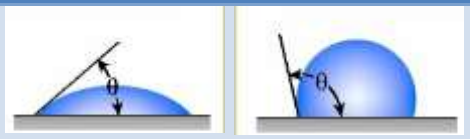


Fig.1 Static contact angle

Hydrophobic surfaces naturally minimize the contact interface between liquid and solid surface. Therefore contact angle is a very effective parameter to evaluate hydrophobicity: the larger the contact angle, the more spherical the drop shape and the more hydrophobic the surface or, if you prefer, the smaller the contact angle and the more flattened the drop shape plus the more hydrophilic the material. Glass with no special additional treatment for instance is hydrophilic: water drops totally spread out on the surface with a contact angle of just a few degrees. On the other hand Teflon is super hydrophobic and drops exhibit a rounded shape.

Contact angle (°C)	Surface type
0°	Superhydrophilic
> 30°	hydrophilic
30°-90°	intermediate
90°-140°	hydrophobic
>140°	Superhydrophobic



Hydrophilic **Hydrophobic**

Fig.2 Surface classification based on contact angle

To better understand how the drop shape depends on hydrophobic/hydrophilic properties of the surface, let's first of all consider a drop in space without any force, gravity included, acting on it except for intermolecular forces within the liquid itself. The drop will be perfectly spherical. The liquid molecules, in fact, actively interact with other molecules. Therefore the most advantageous energy configuration corresponds to the highest density of molecules. In other words, creating a surface has an energy cost, called capillary energy, which is proportional to the area, with the proportionality constant depending on surface tension ϒ. Without any external forces acting, a liquid minimizes surface while the volume is kept constant; this ultimately brings to the spherical shape.

Fig.3 At zero gravity, such as in outer space, drops are perfectly spherical.

However there are forces acting against this ideal trend. In a gravitational environment for instance, as drops are falling down in air, they still have a spherical shape provided that they are small enough to feel strongly the gravitational attraction. This 'ideal' condition is regulated by the following equation

$$\lambda_c = \sqrt{\gamma / \rho g}$$

where λ_c is called **capillary length**, γ is the surface tension of the drop at the liquid/air interface and ρ is the liquid density for a specific liquid. For distilled water at standard temperature and pressure it is $\lambda_c \sim 2$ mm, while for a soap bubble the value can reach up to 4 m! If the drop dimension exceeds λ_c, then gravity can't be overlooked any longer and the spherical shape reached thanks to forces balancing gets deformed.

Similarly, on being deposited on an hydrophilic surface, water droplets sticks to it. This is due to the attractive forces acting between the molecules of both liquid and solid and results in a spherical "cap shape" with the smallest contact angle possible. Once again the drop drifts towards a minimum energy state.

From what has been previously said, it's clear that surface phenomena are instrumental in determining the drop shape and the contact angle as well. Both factors in fact depend on the balancing of

- Interacting forces between solid and liquid, called **adhesion forces.** Born out of the attraction between the molecules of the two mediums, they make the interface area stretch thus causing the flattening of drops.
- **cohesion forces** which try to minimize surface thus inducing the drop typically spherical shape .

The profile of a small amount of liquid on a solid surface will form an angle θ (Fig. 4) either larger or smaller than 90°, according to whether the prevailing force is the total cohesion force, Fc (normal to the tangent to the drop profile in P and pointing inward) or the total adhesion force, Fa, (orthogonal to the solid surface and pointing towards it).

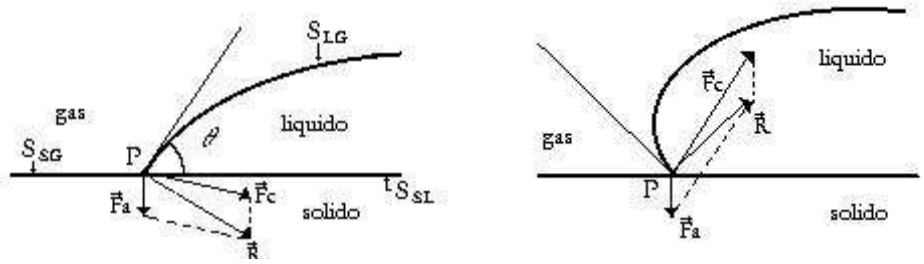


Fig.4 The contact angle amplitude depends on the balancing of adhesion and cohesion forces. SLG, SSL and SSG respectively are the surfaces separating liquid/gas, solid/liquid and solid/gas. Imagine Wikipedia http://it.wikipedia.org/wiki/Surface

In a word the liquid will shape itself in order to minimize surface free energy

As a rule hydrophobic solids, such as wax, exhibit quite a large contact angle, however they hardly reach more than 140°. To obtain even larger angles it is necessary to add to the chemical driven hydrophobic effect a physically induced one, obtained by nano structuring the solid surfaces with nanometer sized asperities. This allows for a **superhydrophobic** regime. Surfaces are structured into alternating pillars and voids at different hierarchical levels (micrometric pillars with nanometric asperities manufactured on their top), therefore the drop will appear almost suspended in air. In such conditions the drop will once again be an almost perfect sphere, exactly as it was in air, with contact angles typically between 160° and 175°, rolling easily even on a slight inclination. The reason for this is quite intuitive: when the contact surface between drop and solid is reduced to asperity tips only, then the adhesion forces, which make the drop stick to the surface, decrease

Contact angle of water θ [deg]	114	138	155	151	153
Roughness factor r	1.0	1.1	1.2	2.0	3.1
Pillar height c [µm]	0	10	36	148	282

Fig.5 http://www.scienzainrete.it/contenuto/articolo/Bolle-gocce-e-biglie.

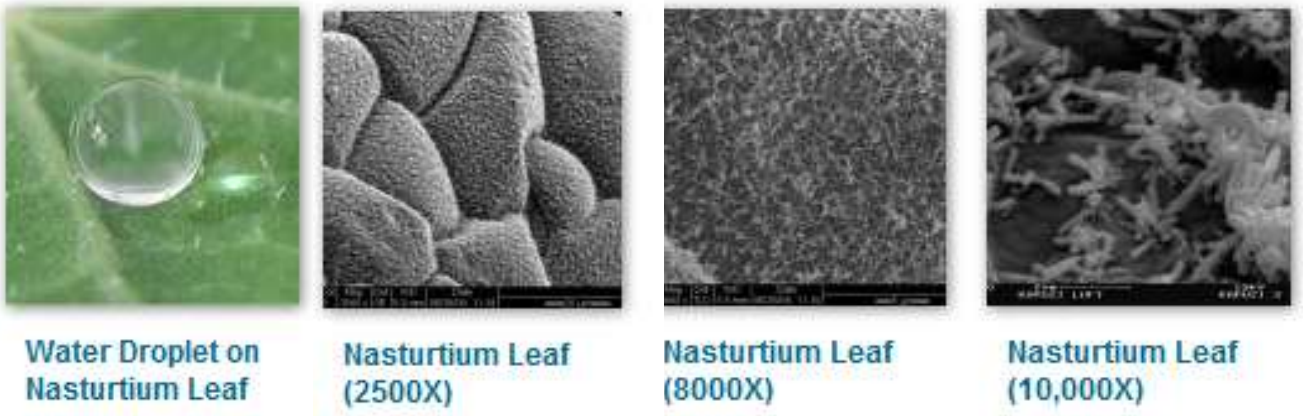


Fig.6 SEM (Scanning Electron Microscope) images from the surface of a nasturtium leaf. Blow ups. http://www.nisenet.org/image-collection

dramatically.

This particular and artificial structuring of surfaces is quite similar to what is found in Nature. On the surface of either lotus or nasturtium leaves (Fig.6) wax nanocrystals of a few tens of nanometers can be found. This is clearly visible from scanning electron microscopes pictures. The resulting effect is so spectacular that nowadays when you want to point out an extreme hydro repellency you speak of “Lotus effect”.

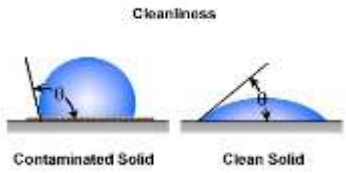


Fig.7 Contact angle for surface contamination measurement.

Static contact angle is often exploited as an indirect parameter of **surface cleanliness**. Wettability is in fact strongly influenced by surface smoothness and by the presence of impurities. Organic contaminants actually contrast wettability and on already hydrophilic surfaces they result in greater than average contact angles. In semiconductors manufacturing for instance, contact angles are exploited in quality controls such as wettability characterization of the silicon wafer, testing surface modifications produced through etching, passivation, ultrasound or cleaning processes and even to quantify the impact of resins, varnishes, oxidation, polishing, etc.

2. Roll off angle or tilt angle

The contact angle supplies info about the static equilibrium of the surface, however in many cases the surface most important feature is whether it allows the liquid to flow away quickly enough. To this aim, talking of superhydrophobicity, it is actually more useful to take into consideration a new parameter: the *tilt angle* (also called *roll off angle).* This is the minimum angle you have to tilt the surface before the drop starts moving down the incline. This parameter too is quite useful for surface classification, but the result doesn't necessarily correspond to the classification obtained through contact angle. Nowadays surfaces are said to be superhydrophobic when both the static contact angle is around 150° and the tilt angle is <10°.

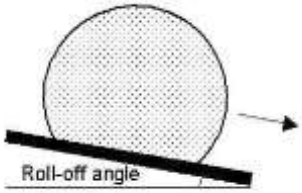


Fig.8 Tilt angle

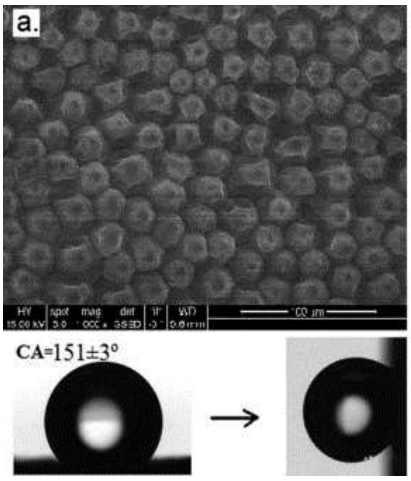


Fig. 9 Drops on rose petals show an incredibly high contact angle and at the same time an extremely strong adhesion. Image courtesy M Karaman Department of Chemical Engineering, Selcuk University, Konya, Turkey.

Lotus effect is widely known, but few people have ever heard of *petal effect*. It may be useful to compare the two of them. In some types of roses the petals, however exhibiting high contact angles, as clearly shown by the perfectly rounded drops forming, develop an extremely high adhesion impairing the rolling of droplets. This is quite different from what happens, for instance, on lotus or nasturtium leaves. In our case the drops stick tightly to the petal surface even when turned upside down. Of course this is true only if the drops actually are droplets on which, owing to the small dimensions, gravity action is not so strong.

Curiously enough the two above mentioned effects have similar origin. On the rose petals you may find micro and nanostructures, exactly as it happens on the surfaces whose superhydrophobicity originates from air pockets trapped between solid and liquid surface due to roughness. However in rose petals these structures are larger and allow water to seep in more easily: rows and rows of ordered and very close micro papillas, similar to extremely small pimples, cover the whole surface. Water soaking gives rise to rather strong interactions with the petal surface. However each microp

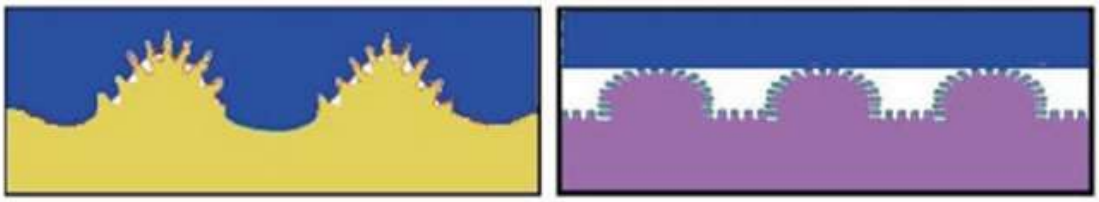


Fig.10 *a) Le gocce deposte su petali di rosa si "infilzano" aderendo sulle protuberanze. B) Diversa appare invece la microstrutturazione della superficie della foglia di loto che favorisce una minima adesione. Per gentile concessione M.Karaman Department of Chemical Engineering, Selcuk University, Konya, Turkey*

apilla is covered by nanogrooves, approx.. 760nm large, too small for water to seep in! Therefore the superhydrophobic effect is ensured.

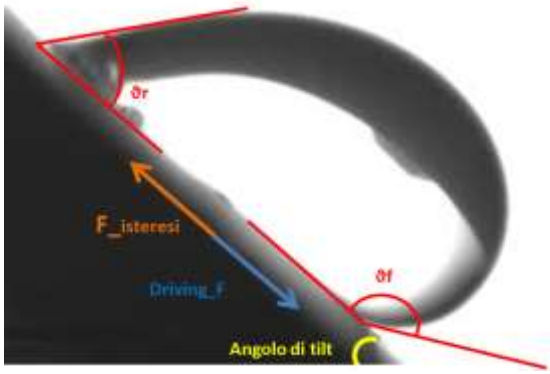


Fig.11 Contact angle hystheresis is a dynamic parameter offering information on drop mobility on the sample surface.

Tilt angle is related to the so called **contact angle hystheresis,** Δϑ. This is defined as the difference between the rear contact angle (ϑr), and the front contact angle (ϑf), of the drop deposited on an incline. Δϑ normally reaches up to 50°. The difference between the two angles is due to substrate dishomogeneity, namely small etherogeneities, alternating wettable/non wettable areas, asperities, etc. All these factors strongly impair the movement of the drop at the front therefore producing a curvature gradient which induces a pressure gradient at the interface[2]which ultimately leads to the insurgence of capillary force (*F_hysteresis*) opposed to the surface parallel component of

[2] The increase in curvature corresponds to an increase in pressure at the liquid-air contact line. Such a pressure will be lower on the drop rear end and higher at the advancing front end. At the back end adhesion forces at the solid-liquid interface will become increasingly more and more important than cohesion forces thus generating a reaction (capillary force) opposing weight.

gravity force (*driving_F*) (Fig.11).

In case of superhydrophobic surfaces the contact angle is extremely high (150°÷180°), while the hystheresis contact angle drastically decreases (<10°) since the air trapped under the liquid smooths out homogeneously the solid surface. Thanks to this double effect $\vartheta \rightarrow 180°$ $\Delta\vartheta \rightarrow 0°$ and even the adhesion of tiny droplets is much smaller than usual.

To reach maximum mobility it is necessary to maximize the contact angle and to minimize the hystheresis one. From a practical point of view it is possible to reduce progressively the solid surface by alternating it with micrometric void creeks so that the drop contact line will actually touch the surface only at the tips of the solid pillars. However a physical limit is posed by the maximum static pressure which can possibly be sustained by the air pillars (fig.12b -Cassie-Baxter state). In case of higher pressure water penetrates the internal cavities and closely adheres to the solid surface asperities, so that any mobility is impaired (fig. 12 a- Wenzel State).

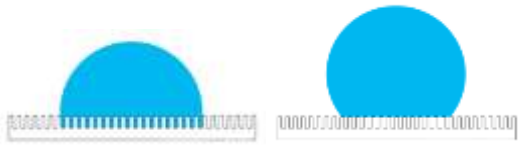


Fig.12 a) Wenzel Model e b) Cassie Baxter Model

With regard to the applicative field, the above described surface treatment will be useful for deicing in airplane wings, electrical cables, wind turbines blades, etc... Moreover improved mobility of liquids on surfaces may prove extremely important in the following areas:

a) Power plants and industrial plants whose functioning is based on heat transport through pipes: the condensed steam may form a thin water film and reduce efficiency.
b) Selfcleaning surfaces, where rolling droplets are meant to incorporate and sweep away contaminant particles which, being of larger dimensions compared to the surface structure, do not penetrate into the wrinkles and creeks.
c) Control and manipulation of single drops motion in microfluidics systems.
d) Car windshields, where the rain drops adhesion may impair visibility.
e) Goggles and masks, to avoid internal condensation[3].
f) Aerostatic balloons equipped with sensors sent out into the atmosphere for weather monitoring.

[3] In some cases however the opposite effect is desirable. Anti-fog coatings turn the windshields internal surface hydrophilic: condensed vapor is thus forced into an extremely thin and uniform water layer instead of many tiny droplets. In this way light scattering can be avoided and the glass total transparency is ensured.

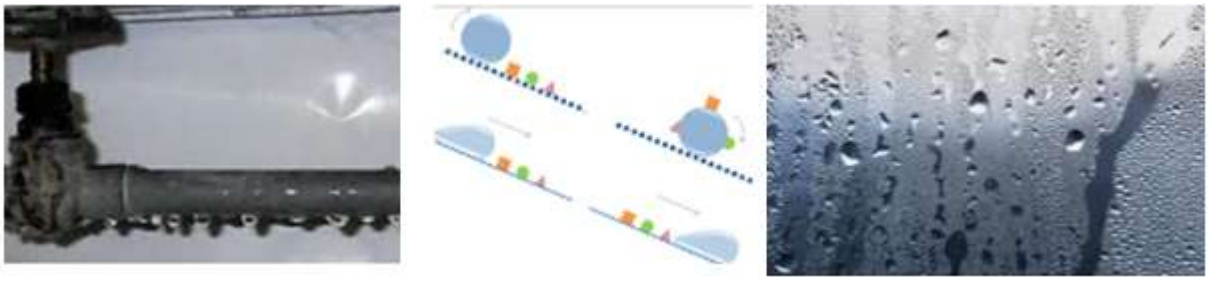


Fig.13 Fighting condensate on pipes, self-cleaning surfaces and windshields treatment against rain are just some of the many possible applications of superhydrophobic coatings.

Superhydrophobic coatings to reduce friction of a solid moving within a liquid ?

Once the motion of liquids on superhydrophobic surfaces has been studied, the following question naturally arises: what happens instead when a solid with superhydrophobic surface is moving within a liquid? It is not a purely scientific issue: such devices may bring to an incredibly high energy gain in case friction proved to be strongly reduced. However such an hypothesis doesn't find any experimental proof yet: nowadays applying superhydrophobic coatings seem to increase the friction of solid objects moving within a liquid rather than reducing it. Simple hydrophobic coatings are much more efficient, further proving that the key to the problem is the air layer which tipically forms at the solid-liquid interface in superhydrophobic conditions.

Actually there's no symmetry whatever in the two situations. First of all it should be taken into consideration the fact that in case of objects moving within a liquid, friction plays a fundamental role mainly in the different liquid-liquid thin layers slipping over each other rather than in the solid–liquid interface relative movement. In fact in laminar flow regime the inner liquid layer adheres to the solid surface and moves with it.

In addition to this the role played by the above mentioned thin film of air has to be carefully examined. Since air viscosity is lower than water one, it could be in fact hypothesized that the layer of tiny air bubbles may have a fundamental importance in reducing friction occurring between the fluid and the superhydrophobic surface. This is true in the laminar flow case (where the extremely thin air layer acts as a lubricant, similarly to what happens in hovercrafts), but not in turbulent flow regime where paradoxically superhydrophobicity may result even counterproductive! The drag from air bubbles is actually due to two components: friction and pressure. The fact that air viscosity is lower than water one may reduce friction but on the other hand may add to pressure up to the point that in turbulent motion the presence of a layer of air bubbles due to superhydrophobicity may actually impair motion. The Laplace equation on pressure gradient at the interface VS surface curvature proves that the smallest the bubble radius and the greatest the difference of pressure on the two sides of the air/water interface. It has been calculated that the 0,10 mm radius of a champagne bubble entails a pressure gradient of 1,5 kPa: enough to sustain a water column approx 15 cm high.

Therefore it may not be so wrong after all the hypothesis according to which air acts as a sort of sustaining cushion rather than a lubricant with a global effect of impairing the object motion

within the fluid.

Liquid Marbles

As an alternative it has been proved possible to reach a very high hydrophobicity and motion improvement by nano structuring the liquid surface rather than the solid one. This is obtained covering the drops with superhydrophobic powders. We are actually talking of the so called "liquid marbles". Behaving as moving liquid micro reservoirs and exhibiting a dramatic reduction of adhesion they can easily roll over and sometimes even bounce off the surfaces. They behave as *soft solids* whose elasticity comes from surface tension. Thanks to the missing liquid/solid contact line it is possible to obtain extremely fast movements. Moreover leaking issues are minimized and the force needed to move them is extremely week even in case of tiny droplets where usually the balancing between surface adhesion and gravity favors the movement of weightier particles. All these properties are particularly interesting for microfluidic applications.

Due to hydrophobicity the dust particles, instead of mixing with the liquid, migrate at the water-air interface forming a monolayer. Since the grain size is much smaller than capillary length, gravity is overwhelmed by capillary forces. However to produce *liquid marbles,* grains whose size is much smaller than the drop dimension are needed: typically for drops a few millimeters in diameter the grains size has to be between 1 and 50 μm. Suitable powders may be soot, graphite, lycopodium powder or even silica spheres specifically treated to become hydrophobic.

Thanks to the superhydrophobic coating the drop shape is not dependent on the substrate and, generally speaking, in static conditions it will be stable in time.

L*iquid marbles* can be employed in transporting liquids both on a solid substrate and on other liquid surfaces. Tests have been made where, according to the substance and the way in which the encapsulated drop is deposited on the liquid surface, before merging the drop will float as long as 1 minute. This is much longer than a simple water droplet which, in presence of surfactants, exhibits an average life of 0.3 seconds. If on the contrary the drop is deposited on the surface of a liquid wetting the powder (such as oil or alcohol) then it is immediately destroyed. This could be exploited at the end of the process to terminate the drop encapsulation and release the liquid at the predesigned spot. The liquid final release is in fact one of the major issues in implementing such innovative microfluidic systems. Ideally it would be highly desirable to be able to either open or close the drop at the desired time, to have the liquid substance released exactly on the chosen spot or, even, to be able to add new substances and chemical reagents to the already existing drop.

In *liquid marbles* case the contact area is not limited to one point as it would be expected in a superhydrophobic situation. In fact owing to weight the drop center of mass is lowered thus forcing the liquid-solid contact. Surface tension obviously opposes the creation of such contact area since it would increase the drop global surface.

There are actually two possibilities:

a) If the radius is larger than the capillary length gravity dominates, and the drop takes over the shape of a cap. The resulting motion along an incline is asintotically stable, with a final speed not

dependent on the drop size but only on the viscosity level and the incline angle.

b)If the radius is smaller than the capillary length then the effect is rather counterintuitive: the smallest the drop, the fastest the rolling. Quite differently from what happens to tiny droplets on usual surfaces. This is an extremely anomalous type of friction also because viscous spheres [4] moving under gravity action usually follow Stokes law, that is speed increases with dimensions. But liquid marbles are *'soft solids'* so even if contact angle is 180 ° there's still a slight deformation generating a contact area with the substrate which is proportional to R^2. If the speed is not too high, the fluid internal dissipation (viscous friction) which has a braking effect, acts mainly in the contact area. Bigger drops have a larger contact area. This is progressively increasing with R much faster than volume and it ultimately leads to a much higher friction. On the other hand small viscous pearls (made out of either honey or glycerol) behave as solid rotating spheres, minimizing viscous dissipation. As they roll down the incline they reach speeds which are sometimes comparable to those obtainable under zero friction conditions! The constant final speed is due to the balancing of gravitational force and viscous friction and its value is inversely proportional to the radius. Just to set the picture while a millimetric drop one thousand times more viscous than water, such as glycerol, rolls down the incline at a speed between 1 mm/s and 1 cm/s, *liquid marbles* of similar size and viscosity roll from 100 to 1000 times faster (approx. 1 m/s). Such apparently counterintuitive result had already been anticipated by theoretical studies, but since a short time ago there was no experimental proof of it.

As a rule liquid marbles are driven by gravitational field, but it is possible to exploit also electrostatic or magnetic weak fields. The effect of an electrostatic field has been tested on a liquid bead deposited on a metallic substrate (but the material doesn't seem to be so determinant) by approaching a Teflon rod charged through rubbing: the drops move according to their distance from the rod. Some Australian researchers are actually studying 'liquid marbles' coated with magnetite superhydrophobic nanograins (approx 10 nm in diameter) which could be driven by magnetic fields. If successful this could bring to the drops manipulation and control, such as opening and closing it, through electronic devices.

Further research

Outreach materials

- Michael Nosonovsky, Bharat Bhushan - *"Green Tribology: Biomimetics, Energy Conservation and Sustainability"*, Springer 2012
- Application of superhydrophobic coatings and nanostructured surfaces to collect drinking water

[4] N.B. Viscosity is a main factor: when its value is low (such as inwater) speed increase with radium!

- Magnetic **liquid marbles** as an alternative to microchannel fluidics- Nanowerk (February 2010)
- Liquid metal marbles as a novel platform for developing soft electronics Nanowerk blog (August 2012)

Research papers

- Properties of liquid marbles P. Aussillous e D. Quèrè
- Non–Stick Droplets P. Aussillous e D. Quèrè
- Michael A Nilsson, Robert J Daniello and Jonathan P Rothstein A novel and inexpensive technique forcreating superhydrophobic surfaces usingTeflon and sandpaper J. Phys. D: Appl. Phys. 43 (2010)
- *Advanced Materials* ("Magnetic Liquid Marbles: Manipulation of Liquid Droplets Using Highly Hydrophobic Fe_3O_4 Nanoparticles"), Tong

Videos

- Short but spectacular videoclips on superhydrophobic surfaces and liquid marbles *http://wn.com/Water_droplets_on_a_superhydrophobic_surface*

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