Ferrofluid oscillator: Pre-reading

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Overview

In this work, dissipative forces acting on a ferrofluid droplet moving on a superhydrophobic surface are determined by measuring damping oscillations of the droplet in a harmonic magnetic potential. The potential is created by a cylindrical permanent magnet underneath the superhydrophobic surface. The droplet is placed on the surface away from the minimum energy position (the magnet axis). When the droplet is released the magnetic force pulls it into an oscillatory motion (Fig. 1), which is recorded with a high-speed camera and analyzed with Matlab. Two dissipative forces are identified: one proportional to droplet velocity and one independent of it.[1] You will conduct the measurements in the lab using a premade superhydrophobic surface. Afterwards you will analyze the data and write a report. All work is done as a group with 2 members.

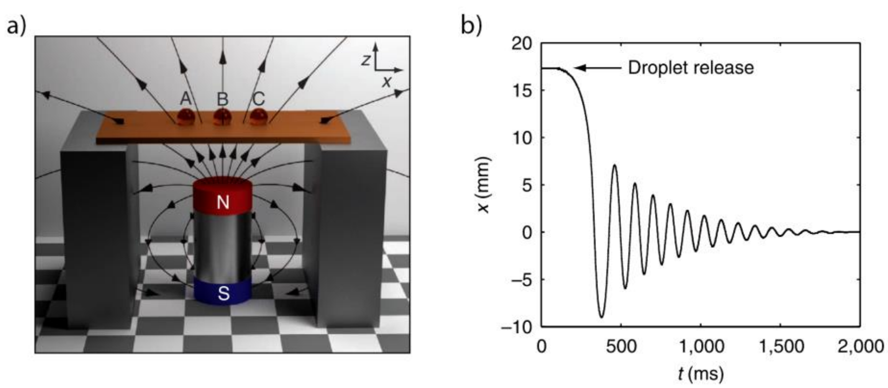

Figure 1: a) *schematic figure of the setup* ***b)*** *droplet position as a function of time*

[1] J. V. I. Timonen, M. Latikka, O. Ikkala, and R. H. A. Ras, "Free-decay and resonant methods for investigating the fundamental limit of superhydrophobicity", *Nature Communications*, vol. 4, pp. 2398, 2013.
See also videos: http://www.youtube.com/watch?v=76hzbbRYms0, http://www.youtube.com/watch?v=Z-Nrv_N04ug

Background

Water on *superhydrophobic* (i.e. extremely water-repellent) surfaces acts in a peculiar way: it can form almost spherical, remarkably mobile droplets. Superhydrophobicity results from a combination of hydrophobic material and nanoscale roughness. Water on such a surface is supported by the roughness and thus rest partly on air, which greatly reduces adhesion between water and the surface.

This phenomenon has been observed in nature for thousands of years. Some plants (e.g. lotus) have evolved superhydrophobic, self-cleaning leaves from which water rolls away taking dust and impurities with them.[2] However, research of superhydrophobic surfaces really started as late as the end of 20th century, and commercial applications, such as superhydrophobic sprays[3], have not been in the market for long.

Wetting characterization

Wetting properties of a surface can be measured with the help of quantities called *contact angle* and *contact angle hysteresis*. Contact angle is the angle between the liquid-air interface and the solid (Fig. 2a). It is used to quantify water-repellency: the higher the contact angle, the more hydrophobic the surface is. *Contact angle hysteresis* on the other hand describes how easily the droplet moves on a surface. If the surface is tilted slightly, the droplet does not move but is deformed by gravity instead. This deformation changes the contact angles: the angle on the lower edge increases and the angle on the higher edge decreases. The more the surface is tilted, the more the contact angles change, until the droplet starts to slide across the surface. The maximum angle is called *advancing contact angle* (because it is observed on the advancing edge of the moving droplet) and the minimum angle *receding contact angle* (on the receding edge) as shown in Fig. 2b. The difference between advancing and receding contact angles is called *contact angle hysteresis*. Droplets on superhydrophobic surfaces have high contact angles (over 150°, which means the droplets are almost spherical) and low contact angle hysteresis (which means the droplets move very easily).

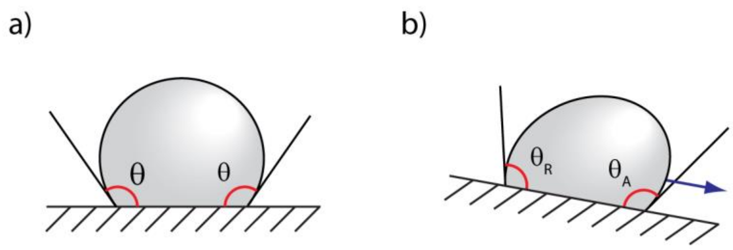

Figure 2: a) *contact angle* θ ***b)*** *receding* θ_R *and advancing* θ_A *contact angles*

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[2] Peter Forbes, "Self-Cleaning Materials", *Scientific American*, vol. 299, pp. 88-95, 2008.
[3] Ultra Ever Dry, "Ultra-Ever Dry ® - Superhydrofobinen ja oleofobinen nestepinnoite", http://www.ultraeverdry.fi, (Accessed 11.4.2018).
See also video: http://www.youtube.com/watch?v=IPM8OR6W6WE

Wetting characterization is usually done using optical contact angle goniometry, where the shape of a droplet on the surface is analyzed to determine the contact angles. However, this method is not well-suited for superhydrophobic surfaces, because it is very sensitive to errors when measuring high contact angles (Fig 3). In addition, this method does not give direct information on the dynamic properties of moving droplets, which would often be important for applications. Ferrofluid oscillator used in this lab work helps to overcome both these limitations.

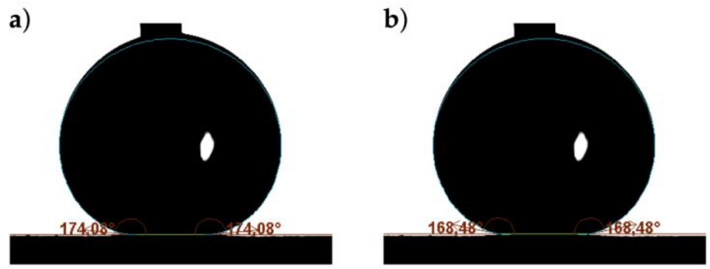

Figure 3: *Contact angle measurement errors:* ***a)*** *measured contact angle, 174°* ***b)*** *same image with 1 pixel error in solid interface position, 168°.*

Dissipative forces

Despite the extremely high mobility, there are still small frictional forces that dissipate kinetic energy of droplets on superhydrophobic surfaces. These forces can be divided in two categories: those proportional to the velocity of the droplet and those independent of it. The first category includes forces due to internal flows inside the droplet. These losses are represented as *viscous dissipation force* F_η, which is proportional to droplet *contact area* (i.e. liquid-solid interface, Fig. 4a). The second category relates to energy losses happening at the moving *contact line* where all the three phases (solid, liquid and gas) meet (Fig. 4b). This force is proportional to contact angle hysteresis, and thus it is called *contact angle hysteresis force* (*CAH-force*) F_μ. It is analogous to normal dry friction between two solids (i.e. it is independent of the velocity of the droplet).

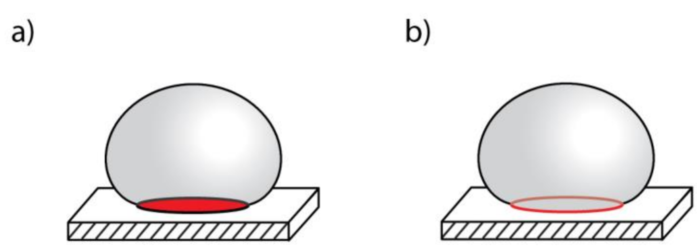

Figure 4: ***a)*** *contact area* ***b)*** *contact line*

These dissipative forces can be conveniently investigated by observing an oscillating droplet. This is realized by adding a small amount of superparamagnetic iron oxide nanoparticles in water and using a permanent magnet to create a harmonic potential well. A small amount (0.2% in volume) of nanoparticles is enough to make the droplet controllable with the magnetic field, while leaving other physical properties (density, viscosity, surface tension) of water essentially unaltered.

The movement of the droplet in the potential well obeys the equation of general harmonic oscillator (Fig. 5):

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = F_{ext} - F_{\eta} \pm F_{\mu}$$

where m is the mass and x the position of the droplet, t is time and F_{ext} is the external driving force. In the case of harmonic magnetic potential $F_{ext} = -kx$, where k is the magnetic spring constant. The direction of the F_{μ} is always opposite to the direction the droplet is moving.

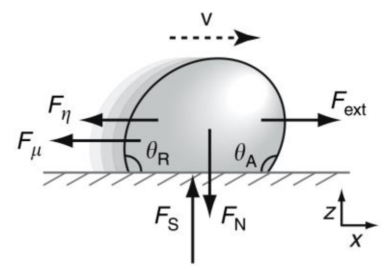

Figure 5: *Forces acting on moving droplet*

In addition to lateral force, the magnet also induces a downward force on the droplet. This *normal force* F_N can be used to deform the droplet and thus to control the contact line length and contact area. F_N is opposed by *support force* F_S exerted by the substrate on the droplet. The strength of magnetic field affecting the droplet can be tuned by changing the distance between the droplet and the magnet. This way the relationships between the dissipative forces and the droplet shape can be investigated. For more information see our article ”Free-decay and resonant methods for investigating the fundamental limit of superhydrophobicity”.[4]

[4] J. V. I. Timonen, M. Latikka, O. Ikkala, and R. H. A. Ras, ”Free-decay and resonant methods for investigating the fundamental limit of superhydrophobicity”, *Nature Communications*, vol. 4, pp. 2398, 2013.

Experimental Work

Safety

The magnets used in this work are extremely strong! Be careful, don't rush, and follow the safety rules:

- **INFORM THE ASSISTANTS IF YOU WEAR A CARDIAC PACEMAKER OR A SIMILAR MEDICAL DEVICE**
- **DO NOT DETACH THE MAIN MAGNET FROM THE HOLDER**
- **DO NOT BRING THE MAIN MAGNET AND THE AUXILIARY MAGNET CLOSE TO EACH OTHER. The magnets are brittle, and can shatter if allowed to slam together. Eye protection must be worn when handling these magnets.**
- **KEEP THE MAGNETS AWAY FROM METAL OBJECTS, CELL PHONES, DEBIT/CREDIT CARDS ETC.**
- **ASK HELP FROM THE ASSISTANTS WHEN YOU HAVE QUESTIONS**

The ferrofluid used in this work contains non-toxic nanoparticles. However, long-term health effects of such particles are not yet extensively studied. Thus:

- **USE GLOVES**
- **WEAR EYE PROTECTION**

READ THE INSTRUCTIONS BEFORE DOING ANYTHING!

Demonstration: Superhydrophobic Soot Surface

A recent paper[5] (March 2014) describes a remarkably easy method for creating superhydrophobic surfaces using only a candle and a glass slide. Incomplete combustion of the candle creates soot that contains hydrophobic carbon nanoparticles. These particles are bound to the glass surface and to each other with paraffin wax (also from the candle), and create a hydrophobic nanoporous network, which gives the surface superhydrophobic properties (Fig. 6). Preparation of such a surface is demonstrated in the lab, but this can also be easily tried at home.

Figure 6: a) *Superhydrophobic soot surface with some defects (little white marks and reflective areas near the edges).* ***b)*** *Scanning electron microscope image of the coating showing the nanoporous soot structure (reproduced from [5]).*

Instructions:

1. Take a clean glass slide and rub one side thoroughly with candle to cover the glass with paraffin wax. A thin uniform layer is enough.
2. Attach the slide to a clothespin.
3. Use candle flame to vaporize the wax on the glass slide and attach soot to it in the following way:
   - Keep the glass slide horizontal near the center of the flame (~1 cm from the tip of the wick “kynttilän sydänlanka”).
   - Move the slide back and forth horizontally over the candle flame to obtain a uniform soot coating.
   - Continue until the slide is entirely covered with soot (~70 seconds). The coating should be opaque and matte.
4. Let the glass slide cool down. Do not touch the coating at any point, it is fragile.
5. Test with water droplets!

Please note that the glass gets **very hot** during preparation! The procedure works also on other substrates than glass slides, but thermal expansion can break fragile substrates. Preparation also produces some smoke.

[5] K. Seo, M. Kim, and D. H. Kim, “Candle-based process for creating a stable superhydrophobic surface”, *Carbon*, vol. 68, pp. 583 – 596, 2014.

The Setup

In this work you will record damping oscillations of a ferrofluid droplet with different separations between the droplet and the magnet. Droplet coordinates will be extracted from the videos with Matlab and analyzed at home. The work is carried out with a ready-made setup consisting of the following main parts (Fig. 7):

1. Base plate
2. Superhydrophobic surface
3. Main magnet (attached to a holder)
4. Small auxiliary magnet (attached to a holder)
5. LED-panel
6. Camera (attached to a lab jack)

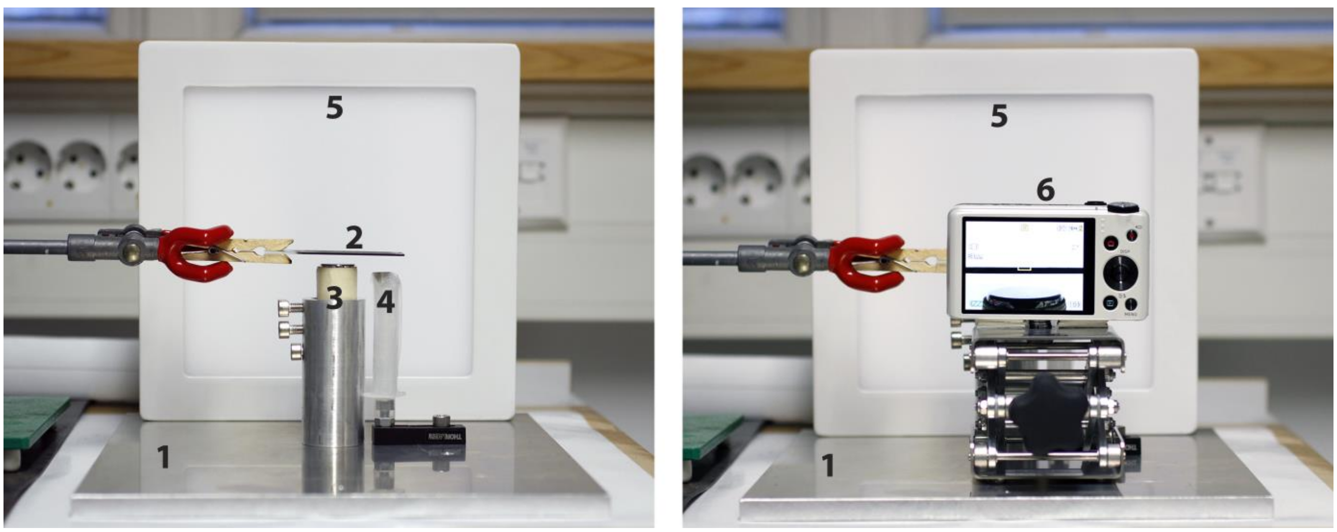

Figure 7: *The experimental setup:* ***1****. Base plate* ***2****. Superhydrophobic surface* ***3****. Main magnet* ***4****. Auxiliary magnet* ***5****. LED-panel* ***6****. Camera*

In addition you will use:

- Safety gloves
- Protective eyewear
- Ruler
- Pipette
- Pen and paper
- Computer and USB-cable

The Test Surface (Hydrobead)

You will perform the oscillatory measurements on a glass slide that has been coated with a commercial superhydrophobic spray, Hydrobead.[6] If you accidentally damage the coating or notice any defects on the surface, please let the assistants know. Success of the experiments depends on the coating quality.

Pipetting

You will use a Finnpipette (Fig. 8) to place a droplet with fixed volume on the superhydrophobic surface. Follow these instructions:

1. Finnpipette has a first stop when you press the operating button gently, and a second stop when you press fully. Make sure you feel the difference before pipetting!
2. Set the volume by turning adjustment and/or fine adjustment knobs.
3. Push the tip cone gently into a disposable tip.
4. Press the operating button to first stop.
5. Dip the tip under the water (~1 cm) and slowly release the operating button.
6. Bring the tip where you want to pipet the droplet.
7. Gently press the operating button to first stop. Wait ~1 second and press the button all the way down. The tip is now empty.
8. Release the operating button.
9. Press the tip ejector to discard the used tip.

Important things to keep in mind:

- **KEEP THE PIPETTE UPRIGHT WHEN IT IS FILLED WITH LIQUID!** Otherwise the liquid in the tip might get inside the pipette, contaminating it.
- **DO NOT LEAVE THE FERROFLUID BOTTLE OPEN.** Evaporation will change the concentration of the nanoparticles and invalidate the measured magnetization data.
- Use both hands when pipetting to increase precision and to reduce shaking. Keeping your elbow(s) on the table will also help.
- **BE CAREFUL NOT TO TOUCH THE SURFACE WITH THE PIPETTE**. Even a slight touch will create a defect on the superhydrophobic coating.
- If you need to pipet a very small ferrofluid droplet away from the substrate, you can first add some water to it. Larger droplets are easier to pipet away than small ones. Remember that you can adjust the volume of the pipette.

[6] Hydrobead, "Hydrobead | Superhydrophobic Water Repellent Spray Coating", http://www.hydrobead.com/, (Accessed 11.4.2018)