

# Some Physics Inside Drying Droplets

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Droplets are of great scientific interest because studying their formation and dynamics is important in many technologies such as in microfluidics [1, 2]. Evaporation of droplets is another interesting aspect that has caught much scientific attention. An example of an evaporating droplet is a coffee droplet spilled on a table. After evaporation the coffee droplet leaves a ring-like stain called a coffee ring or coffee stain [3]. This phenomenon, known as the ‘coffee ring effect’, occurs not only with coffee droplets but also with all droplets containing non-volatile solutes. There are a number of interesting physical processes going on within the droplets during evaporation to form the ‘coffee stains’. In this article, we will see what they are.

## Introduction

Studying wetting phenomena is important in many cases ranging from the moisture of your eyes to many industrial applications in food, biochemical or soil sciences. Spreading of a droplet placed on a solid surface (sessile droplet) depends on the wetting properties of the liquid on that surface. Depending upon the wetting nature, a droplet can fully or partially spread over a solid surface. In the case of total wetting, the droplet spreads completely on the surface. On the other hand, in partial wetting, the droplet has a spherical-cap shape. A characteristic measure of the droplet shape is its macroscopic equilibrium contact angle  $\theta_Y$  on the solid surface (see *Figure 1*). The contact angle depends on the interfacial tensions between the liquid, solid and the ambient medium which is usually air (see *Box 1*). When the contact angle of a water droplet  $\theta_Y < 90^\circ$ , the surface is



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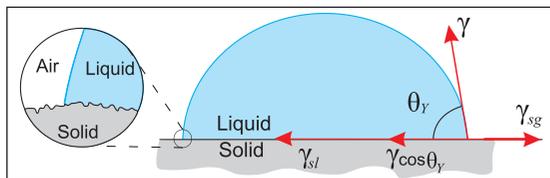
To the memories of Jais Tom, my former student and friend.

### Keywords

Drying droplets, surface tension, coffee stain effect, electro-wetting.



**Figure 1.** A droplet placed on a solid surface. A zoom-in reveals that the contact line is pinned on the microscopically rough surface.



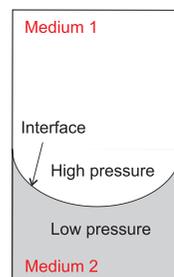
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said to be hydrophilic (*water loving*) and otherwise, if  $\theta_Y > 90^\circ$ , it is said to be hydrophobic (*water hating*). When the surface is rough or textured the contact angle of water on the hydrophobic surfaces can exceed even  $150^\circ$ . Such surfaces are called super-hydrophobic surfaces (see *Box 2*) on which the droplet sits partially on air as illustrated in *Figure 2*. The lotus leaf is an example of a naturally existing super-hydrophobic surface. This non-wetting property acts as a cleaning mechanism for these leaves because water droplets roll off easily taking dirt with them.

When the surface is wetting, the contact line (i.e., the edge of the droplet) gets pinned onto microscopic hydrophilic regions. As a result, the droplets are not mobile on wetting surfaces. However, when the contact line is pulled in one direction, for example by tilting the solid

### Box 1. Surface Tension

The surface excess energy per unit area of liquid surfaces when it is in contact with another material is called surface tension or interfacial tension. When a liquid droplet is in contact with a solid (see *Figure 1*), the equilibrium forces due to the interfacial tensions at the liquid-gas ( $\gamma$ ), the solid-gas ( $\gamma_{sg}$ ) and the solid-liquid ( $\gamma_{sl}$ ) interface determine the contact angle,  $\theta_Y = (\gamma_{sg} - \gamma_{sl})/\gamma$  of the droplet on the solid. Droplets placed on solid surfaces, therefore, adopt spherical to flat shapes depending upon the interfacial tensions. The lower the surface tension  $\gamma$ , the higher the tendency of a liquid to spread on a given solid surface. Another consequence of the surface tension is the excess pressure (compared to the outside pressure) inside a droplet or a bubble (see also *Figure A*). This is called Laplace pressure given by  $\Delta P = P_{\text{inside}} - P_{\text{outside}} = 2\gamma/R$ , for a spherical droplet of radius  $R$ . The smaller the droplet, the greater its inner pressure. For a water droplet of  $1 \mu\text{m}$  radius,  $\Delta P$  can be as high as atmospheric pressure\*.



**Figure A.** Pressure varies across a curved interface separating two fluid mediums. The low- and high-pressure regions are shown (relative to each other).

\* Pierre-Gilles de Gennes, Françoise Brochard-Wyart and David Quéré, *Capillarity and wetting phenomena: drops, bubbles, pearls, waves*, Springer, Chapter 1, 2004.

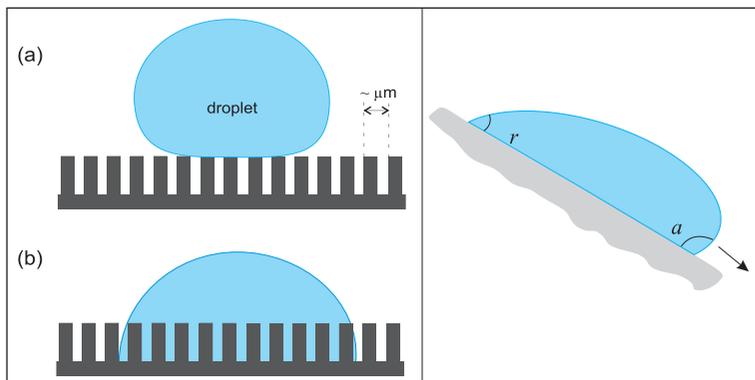
### Box 2. Super-Hydrophobic Surfaces

Super-hydrophobic surfaces are hydrophobic surfaces with some textures on them. Due to these textures, droplets sit partially on air as illustrated in *Figure 2*. Such surfaces consist of an array of pillars having a few micrometers height and separation between them. Once this array of pillars is coated with a thin film of hydrophobic material (often Teflon), a super-hydrophobic surface is obtained.

In laboratories such surfaces are made using nano-fabrication techniques. You can make super-hydrophobic surfaces at home! Take a metal spoon (or any other surface that does not burn) and hold it above a candle flame for a few seconds to form a black layer of carbon soot on the inside surface of it. Place a very small water droplet on this black layer. You can see that the droplet is spherical and rolls over the surface when you move the spoon. Here, the tiny carbon particles act as the pillars\*.

\* Xu Deng, Lena Mammen, Hans-Jürgen Butt and Doris Vollmer, Candle Soot as a Template for a Transparent Robust Superamphiphobic Coating, *Science*, Vol.335, pp.67–70, 2012.

surface at an angle, the droplet tends to slide down the incline. In this case, the contact line of the droplet is pulled in one direction by gravity. During this process, the contact angle increases locally with the pulling force until it reaches an advancing angle ( $\theta_a$ ) whilst on the opposite side it decreases to a receding angle ( $\theta_r$ ) and the droplet slides on the surface (*Figure 3*). This is a common scene on the wind-shield of your car when it rains. The small droplets stick to the glass, however larger ones flow down when their weight (gravitational force) cannot be balanced by the pinning forces. The advancing and the receding angles depend on the microscopic roughness of the surface where the droplet sits.



**Figure 2 (left).** Structure of a super-hydrophobic surface where a droplet sits partially in the air (Cassie Baxter state). Under certain conditions (see text) the droplet fills in between the pillars (Wenzel state).

**Figure 3 (right).** A droplet flowing down on a tilted surface by gravity. The advancing and the receding contact angles are shown.



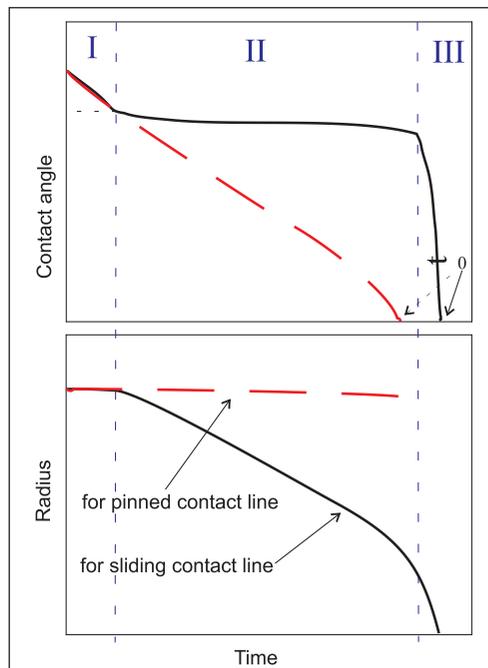
The difference between the advancing and receding contact angles is called the 'contact angle hysteresis', which is a parameter that represents the roughness of the surface.

The difference between the advancing and receding contact angles is called the *contact angle hysteresis* ( $\theta_a - \theta_r$ ). It is a parameter that quantifies the roughness of a surface. On low hysteresis surfaces, i.e., on (super-) hydrophobic surfaces where there are only a few pinning sites, the contact line slips easily. Therefore, droplets are very mobile on a (super-) hydrophobic surface. Moreover, liquid flow on super-hydrophobic surfaces does not obey the accepted no-slip boundary condition [4].

### Evaporating Droplets

The wetting properties and the contact angle hysteresis are important parameters determining the dynamics of an evaporating sessile droplet. Evaporation is the escaping of liquid mass from the droplet surface. As a result of that the droplet becomes smaller and smaller in time. During this process the contact line (also the contact angle) undergoes three distinctive phases as illustrated in *Figure 4*. Immediately after the droplet is placed on

**Figure 4.** Schematic (not to scale) of the contact angle and the radius of an evaporating droplet with time. The solid curve represents a sliding contact line and the dashed curve represents a pinned contact line during the evaporation. The evaporation time  $t_0$  is shown. When the contact line is pinned (e.g., on a hydrophilic surface) the evaporation is quicker. The dashed vertical lines separate different phases of the evaporation.



the surface it has a contact angle that equals  $\theta_Y$ . In the first phase, the contact line stays fixed (constant droplet radius) while the contact angle decreases from  $\theta_Y$  to the receding angle  $\theta_r$ . In this phase, the height of the droplet also decreases. Once the receding angle is reached, the contact line starts to slip over the surface as the evaporation proceeds. In this second phase, the contact angle stays fixed while the radius of the droplet decreases. The movement of the contact line may not be smooth, however, and can involve stick and slip-like motion. In the third phase both the radius and the contact angle decrease sharply. Depending upon the contact angle hysteresis of the surface the duration of each phase can vary. On a highly hydrophobic surface the second phase dominates and the third phase can be very short at the end of the evaporation. On a highly hydrophilic surface the second and the third phases can be absent since the contact line pins at the early stage of the evaporation.

Some simple scaling arguments can be applied to predict the retraction of the contact line quantitatively during the evaporation process. When only controlled by diffusion, the evaporation rate is proportional to the perimeter of a droplet. This implies that  $dV/dt \propto -2\pi R(t)$ , where  $V$  and  $R$  are respectively the volume and the radius of the droplet. Assuming a sliding contact line, i.e., a constant contact angle, one can derive that the radius decreases with time as  $R \propto (t_0 - t)^\alpha$ , where  $\alpha$  is an exponent that depends on the ambient conditions and  $t_0$  is the time at which the droplet vanishes. When the evaporation is controlled only by diffusion,  $\alpha = 0.5$ ; however, when convection above the droplet is significant then the evaporation rate is proportional to the surface area of the droplet and the value of  $\alpha$  can be 1. [5].

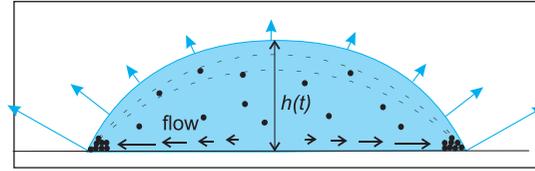
Along with shape and size changes, there are a few other processes going on within the droplet during the evap-

The evaporative mass loss near the contact line must be balanced by new liquid flowing to there from the bulk of the droplet.

The temperature on the droplet surface is not the same everywhere. The top of the droplet is the coldest part due to the longer conduction path from the isothermal substrate.



**Figure 5.** An evaporating droplet with the contact line pinned on the surface. The arrows above the droplet represent the evaporation flux which diverges at the contact line. The radius of the droplet is constant while the height  $h$  decreases with time. The flow of liquid to compensate for the evaporated liquid from the edge is represented with the arrows inside the droplet. This flow brings the dispersed particles to the edge forming the 'coffee ring' at the end of the evaporation.



oration. The temperature on the droplet surface is not the same everywhere. The top of the droplet is the coldest part due to the longer conduction path from the isothermal substrate. As a result, the evaporative flux from the droplet tends to diverge in the vicinity of the contact line. When the contact line of the droplet is pinned on the surface, the evaporative mass loss near the contact line must be balanced by new liquid flowing to there from the bulk of the droplet (see *Figure 5*). Therefore, a capillary flow can exist within an evaporating sessile droplet. This flow is directed radially outward towards the edge of the droplet. The flow velocity near the edge can be several tens of micrometers per second. On top of that, the non-uniform evaporative flux leads to temperature gradients over the droplet surface, which in turn produce differences in the surface tension. Consequently, an additional flow called the *Marangoni flow* is generated especially in the vicinity of the contact line (see *Box 3*).

### Box 3. Bénard–Marangoni Convection

Gradients in surface tension can be caused by local temperature variations or presence of chemical species. Such chemical species are in general called surfactants (for example soap) which lower the surface tension. When there are gradients, the regions with higher surface tension pull the interface with lower surface tension. As a result the liquid locally flows towards regions of higher surface tension. This is called Bénard–Marangoni convection or simply Marangoni flow.

The direction of the Marangoni flow in sessile droplets is determined by the ratio of thermal conductivities between the solid substrate and the liquid. If the thermal conductivity of the substrate is at least a factor of 2 greater than that of the liquid, the droplet is warmest at the contact line and the Marangoni flow is directed radially outward along the substrate. On the other hand, when the thermal conductivity of the substrate is much less than that of the liquid, droplet is coldest near the contact line and the Marangoni flow is directed inward along the substrate to the center of the droplet.



## The Coffee Ring Effect

Consider an evaporating sessile droplet with its edge pinned on the solid surface. If the liquid contains dispersed non-volatile solute particles in it the radially outward capillary flow or the Marangoni flow (only very small contribution especially for water droplets) can carry these particles towards the drop edge and deposit them there (see *Figure 5*). At the end of the evaporation process a ring-like residue of the particles is left on the solid surface. Such stains are often seen with coffee droplets spilled on a table. Therefore, residue patterns from drying droplets are in general called *coffee stains* or *coffee rings*.

Observing the ring-like deposition very closely, one may find many interesting things. The particle deposition in the early stage of the evaporation creates well-ordered structures at the contact line. In the beginning, the deposition speed is low and the particles have enough time to get arranged by Brownian motion. This ordering can be visualized clearly by putting fluorescently labelled particles inside the droplet. At the final stage of the evaporation, the contact angle approaches zero and the evaporation rate near the contact line diverges. This causes a sharp increase in the arrival of the particles towards the contact line. This rush arrival of particles causes unordered accumulation of them. Finally, after completion of the evaporation, the deposition particle has square packing close to the contact line followed by hexagonal packing and finally unordered packing [6,7].

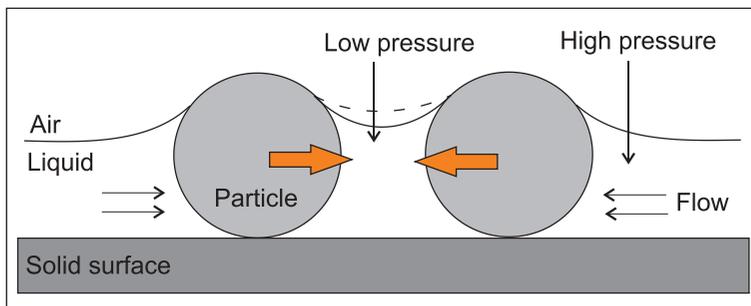
The ordering of the particles and the formation of the crystalline structures near the contact line are influenced by the capillary forces between the particles. The reason for the capillary forces is the deformation of the liquid-air interface, which is supposed to be flat in the absence of the particles. The larger the interfacial deformation produced by the particles, the stronger the

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**Figure 6.** The capillary attractive force between two particles is illustrated. The liquid evaporation between the particles causes the meniscus to be curved more, thereby creating a low pressure region there. Consequently, the liquid flowing in from the sides brings the meniscus back to the normal shape (dash line). This flow pushes the particles towards each other.



capillary forces between them. Therefore, the capillary force is in general sensitive to the wetting properties of the particle surface. When the particles are floating freely on the liquid-air interface, the force between two similar particles (often attractive) is driven by gravity and buoyancy forces. This attraction occurs because the liquid meniscus deforms in such a way that the gravitational potential energy of the two particles decreases when they draw close to each other. For particles resting on a solid surface, the ordering starts when the thickness of the water layer containing them becomes approximately equal to the particle diameter. The mechanism of this capillary attraction is illustrated in *Figure 6*. The evaporation of the liquid from the concave menisci between two particles increases the local curvature there and hence creates a low pressure region compared to the thicker parts of the liquid layer. This results in a liquid influx which pushes the particles towards each other [8]. Eventually, particle deposits formed near the contact line are of well-ordered structures. The deposit shape can also be affected by electrostatic and van der Waals forces between the particles or between the particle and the solid substrate. Electrostatic forces are unavoidable since mostly the particle surfaces are charged in liquids.

One interesting scenario where no coffee rings are formed, is when the liquid evaporates much faster than the particle movement. In this case the droplet evaporates fully before the particles get deposited at the contact line. This situation occurs when the droplet is very small, say only a few micrometers in diameter.

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## Suppressing the Coffee Ring Effect

The coffee ring effect on your coffee table is not a big issue; however, its ubiquitous presence is a nuisance in many industrial applications such as in microelectronics, inkjet printing, bioassays and paints. This is because the coffee ring effect prevents formation of homogeneous residues. For example, when paints dry unwanted thicker edges can appear; printing dots can be formed as rings instead of spots; after drying, bioassays get randomly distributed, which causes difficulties in analysing them. Therefore, many technological applications require the coffee ring effect to be suppressed.

There are many ideas introduced to suppress the coffee ring effect. Adding some chemical components (for example, ethanol) into the aqueous droplets brings forth surface tension gradients and consequently the Marangoni effect. When the substrate–liquid thermal conductivities are selected appropriately, a radially inward Marangoni flow towards the center of the droplet is produced which ensures a spot-like uniform particle deposition. Adding chemical species to the liquid may not be desirable in some cases like in the analysis of biological samples.

The shape of the suspended particles inside the droplet itself can be used to eliminate the coffee ring effect. For example, ellipsoidal particles are deposited uniformly during evaporation. This is because the ellipsoids are carried to the air–water interface by the same outward flow that causes the coffee ring effect. Once the ellipsoids are at the air–water interface, they significantly deform the interface. As a result, strong inter-particle capillary interactions are produced which lead to the formation of loosely packed or arrested particle structures at the air–water interface. These structures prevent the suspended particles in the droplet from reaching near the contact line and ensure a uniform deposition [9].

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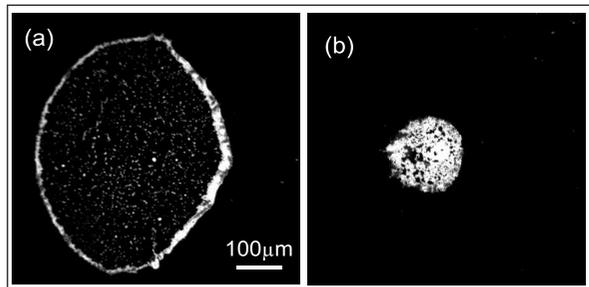


Knowing that the coffee ring effect occurs from the pinning of the contact line, one can depin the contact line continuously during the evaporation. This can be achieved by placing the droplet on a super-hydrophobic surface. On such surfaces the evaporation is in constant contact angle mode and the contact line jumps over the pillars as the droplet evaporates. Since the contact line is always moving during the evaporation (see *Figure 4*), such surfaces do not cause a ring-like deposit. However, the droplet may not always stay on top of the pillars during the evaporation. When the droplet size becomes small, depending upon the surface roughness, the liquid can fill in between the pillars (see *Figure 2*). It may disrupt the suppression of the coffee ring effect. Another method to induce slipping contact line without using a super-hydrophobic surface is electrowetting (EW) [2,10] (see *Box 4*). In electrowetting with AC (alternating current) voltage, the droplet spreads and retracts as the voltage oscillates. Therefore, the contact line periodically detaches from small pinning sites and the contact angle hysteresis is reduced considerably. No contact line pinning means no particle deposition. Additionally, the periodic disturbances of the contact line in AC electrowetting generate strong circulating flows within the droplet. These flows remove any sporadically deposited particles near the contact line. Therefore, upon evaporation the droplet does not make a ring-like, rather a

#### Box 4. Electrowetting

Electrowetting (EW) refers to the wetting of a droplet by the application of an electric potential. In a typical electrowetting setup a droplet is placed on a hydrophobic dielectric layer (often Teflon) coated on a conductor (electrode). A voltage  $U$  is applied between the droplet and the conductor. The system acts like a parallel plate capacitor where  $C$  is the capacitance per unit area of the dielectric layer between the droplet and the conductor. The resulting electric force  $f_{el} = CU^2/2$  (per unit length) pulls the contact line until it balances with the opposing surface tension force,  $(\gamma \cos \theta + \gamma_{sl} - \gamma_{sg})$ . As a result, the contact angle is decreased given by the Young–Lippmann equation,  $\cos \theta(U) = \cos \theta_Y + f_{el}/\gamma$  [2, 8]. When  $U$  is periodic, the contact line also moves periodically on the dielectric layer. Since  $f_{el} \propto U^2$ , the contact line moves outwards in every half cycle of the voltage.





**Figure 7.** (a) A 'coffee ring' formed after evaporation of a droplet containing fluorescent particles of diameter  $5 \mu\text{m}$ . (b) When the coffee ring effect is suppressed (for example, by AC electrowetting) a spot-like deposition is obtained upon evaporation.

spot-like deposition of particles in it at the center, as shown in *Figure 7*.

So far, we have discussed drying of sessile droplets in ambient conditions. Drying of a droplet placed on a very hot surface involves additional interesting phenomena like the Leidenfrost effect [11] in which the droplet is separated from the hot surface by a thin layer of vapour due to the extremely fast evaporation. This vapour under the droplet can push it upward. When the weight of the drying droplet cannot balance the pushing force the droplet takes off from the hot surface. You may observe this phenomenon by throwing water droplets onto a hot cooking pan.

In short, the evaporation process of droplets involves many interesting physical phenomena and studying them is beneficial in many technological applications.

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