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Capillary surfaces modeling liquid drops on wetting phenomena

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Wetting and spreading phenomena appear in a variety of industrial and engineering processes (e.g., automobile manufacturing, textile production, ink-jet printing or colloid-polymer mixtures) when a liquid is deposited on a solid substrate. It is of interest to understand the physics and chemistry theory lies behind them, and many experiments consist to modify the characteristics of liquid and the solid until to attain the desirable wetting/spreading properties [3, 5]. A simple, but illustrative example, appears when a given amount of an incompressible liquid is deposited on a solid substrate. Under idealized conditions (constant pressure and temperature, low viscosity or purity), the only forces acting on the liquid molecules are of order of a few nanometers and are determined by the van der Waals and electrostatic interactions. These forces are balanced except for the liquid molecules on the liquid-air interface Σ of the drop which, to be in contact with the air phase, are mainly attracted inward and to the sides so the attraction energy at the interface is less than at in the interior.

In thermodynamic equilibrium, the interface Σ is free to change of shape in order to minimize its total free energy G. Part of this energy is formed by the surface energy to create the interface and that it is proportional to the number of interfacial molecules, that is, its surface area $A(\Sigma)$. The energy per area of Σ is called the *surface tension* σ and, assuming small scale, the surface tension dominates the gravitational forces, so the gravity can be neglected. Thus the energy G can be expressed as $G = \sigma A(\Sigma) + \lambda V$, where V is the volume of the droplet which is a fixed value, and the coefficient λ is a Lagrange multiplier, indeed, λ is the pressure difference between the inside and the outside across the drop. In the given system, there are present three different phases, namely, liquid-air, solid-liquid, and solid-air, and three surface tensions σ, σ_{SL} and σ_{SA}, respectively; see Fig. 1, left. According to the principle of virtual work, the system will be in equilibrium if the work made by the surface tension and the work made by the pressure are equal, resulting the Laplace's equation

$$P_L - P_A = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \sigma(2H),$$

where $P_L - P_A$ is the pressure difference across Σ, R_i are the curvature radii and H is the mean curvature at each point of Σ. A second condition is the Young's equation $\sigma_{SA} - \sigma_{SL} = \sigma \cos\theta$ that establishes that the drop makes a constant angle θ with the substrate along the liquid-solid-air contact line [4, 8]. As a conclusion, *the liquid-air interface Σ of a liquid droplet is modeled by a surface in Euclidean space where the mean curvature is the same at every point and that it makes a constant contact angle with the support surface.* These surfaces will be called *capillary surfaces.*

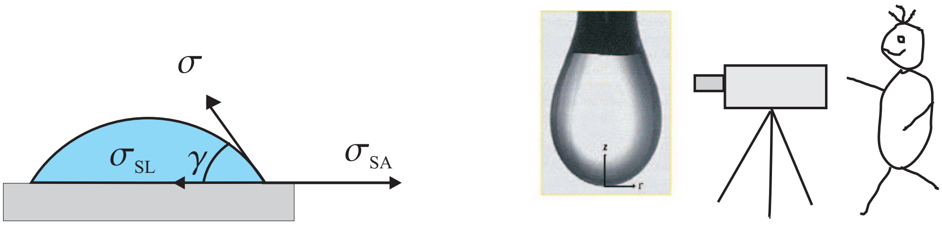

FIGURE 1. Left: the contact angle θ and the equilibrium between the three surface tensions. Right: the pendant drop method to measure the surface tension for an axisymmetric droplet

In a specific problem, the wetting state follows once it is known the three surface tensions. In general, it is difficult to determine them, although the difference $\sigma_{SA} - \sigma_{SL}$ is a property of the solid, and independently of the liquid used. Among numerous measurement techniques for the surface tension σ, we point out the sessile and pendant drop method ([1]). A drop is sitting (or hanging) on a horizontal plane which is taken aside-view photographs of the profile and use the snapshot to determine the angle θ (or the shape of Σ) by comparing the actual shape of the drop with theoretical simulations based on the parameter σ; see Fig. 1, right. However, in order to use the Young's equation, the liquid can be easily contaminated so the contact angle θ can be difficult to compute explicitly. Other procedure consists to determine the mean curvature H adequating the profile shape of the drop to a well-controlled geometry, extracting σ from the Laplace's equation.

The constant mean curvature equation $H = ct$ is a PDE of order two that cannot be integrated and only be numerically approximated by analytic methods. In this sense, it is useful to reduce this equation into an ODE if, owing to symmetries, the equation depends only on one coordinate, so the computer calculations became easy and fast. The most common situation is assuming rotational symmetry because the axisymmetric solutions of $H = ct$ are known (Delaunay surfaces) and can be represented by elliptic integrals. In addition to the well-known sphere and cylinder, they consist of unduloids, nodoids and catenoids (Fig. 2, left). Usually, experiments utilize symmetric devices to deposit the droplet or to connect a liquid channel. This is the case when a drop hangs from a circular disc or a liquid bridge is formed between two horizontal coaxial circular discs, where the observed interface is assumed to be a surface revolution (Fig. 1, right).

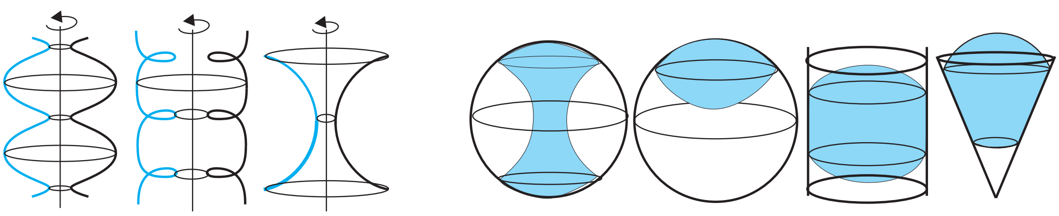

FIGURE 2. Left: an unduloid, a nodoid and a catenoid. Right: different configurations of capillary surfaces supported on a sphere, a cylinder and a cone

The aim of the present work is to contribute and relate the shapes of liquid drops obtained in experiments with the mathematical models of capillary surfaces. This is our starting point, asking whether the geometry of the support S imposes restrictions to the possible configurations of a capillary surface Σ, such as, if the symmetries of S are inherited by Σ. Reciprocally, an important driver has been the recent interest and the progress in experiments done for liquid drops deposited on (or between) a cone, an assembly cylinders and spherical rigid bodies (e.g., [6, 7, 9, 10, 15]), which allow to consider new theoretical problems in the field of capillary surfaces. The possibility of implementation numerical analysis as well as modeling software, needs again to model droplets as Delaunay surfaces where the geometry associated is relatively simple.

We study different settings for S, as for example, that S is a sphere, a cylinder and a cone, obtaining conditions that assure that Σ shows some symmetries. The topology of S limits possible shapes as for example, if a Delaunay surface is a capillary surface on a cylinder or a cone, then the boundary of the surface must be homologous to the circle that defines the cylinder or the cone. One of the main ingredients in the proofs is the Alexandrov reflection principle [2], but with an original use respect to the standard one. Usually the very surface is used as a barrier in a process of reflection across a uniparametric family of parallel planes and next apply the maximum principle to the mean curvature equation. In our results, reflections about planes use the symmetry of the support surface, as for example, that the planes have a common straight-line: [11, 12, 13, 14]. We also employ a method due to McCuan of spherical reflection method by inversions across spheres that, although they are not isometries of the ambient space, can give a certain control of the mean curvature for the inverted surface.

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