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# Determination of contact angle of droplet on convex and concave spherical surfaces

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ABSTRACT

Experimentally measuring the apparent contact angle on a curved surface usually requires a specific instrument, which could be costly and is not widely accessible. To address this challenge, we proposed a simple wetting model to theoretically predict the apparent contact angle of a droplet on convex and concave spherical surfaces, which requires knowing the volume of the droplet, surface curvature and intrinsic contact angle. Using this theoretical model, we investigated the influence of radius and hydrophobicity of curved surfaces on wetting behaviors. For a concave surface, the droplet on it could exhibit a convex or concave morphology depending on the detailed parameters. The critical volume for a droplet changing from convex to concave shape was determined in this study. Employing this model, the contact angle on curved surface with microstructures was also investigated. The model may contribute to the understanding of natural wetting phenomenon and better design of related structures.


## 1. Introduction

The contact angle of a droplet on a curved surface is widely involved in the fields of engineering [1,2], biomedicine [3], and natural world [4,5]. For example, curved microstructures fabricated on a surface can modify the hydrophobicity of the surface through affecting droplet-surface interactions [6,7]; changes of droplet shape can be used to characterize the sensitivity and specificity of biomembranes [8]; and some plant leaves and insect wings are capable of high water repellence (e.g., lotus leaf, morpho butterfly) [9–11]. Investigation of droplet contact angle not only contributes to assessing the wettability of the surface (i.e., hydrophilic or hydrophobic ability) and understanding the related natural phenomena, but also promotes the better design of functional surfaces and improves the intellectualization of related structures. For instance, novel artificial materials with super water- or oil-proof capability have been designed through designing special curved surfaces [12,13].

With the contact surface assumed absolutely smooth, stiff, homogenous and inert (i.e., an ideal surface), the relation between contact angle and interfacial tension of a droplet was firstly described by Young's equation [14,15]. Further, whilst the Wenzel equation determined the contact angles on a rough surface for homogeneous wetting regime [16], the Cassie–Baxter equation developed the theories for heterogeneous wetting regime (e.g., porous contact surface) [17]. However, these studies mostly focused on the contact angle of a droplet on flat surface, Fig. 1(a). Recently, a theory of wetting on ideal spherical surfaces, proposed by Extrand and Moon [18] demonstrated that the wetting equation $\theta = \theta(\theta_0, a, R)$ could determine the apparent contact angle $\theta$ by experimentally measuring the contact radius $a$ and the intrinsic contact angle $\theta_0$, $R$ being radius of the solid spherical surface, Fig. 1(b). In addition, $\theta$ could be quantified through another proposed equation $\theta = \theta(\theta_0, r, R)$, where the droplet radius $r$ is experimentally measured [19]. Besides spherical surfaces, a recent study extended the theory to concave surfaces and proposed a different wetting equation $\theta = \theta(V_L, a, R)$, where the droplet volume ($V_L$) could be manually controlled in the experiment [20], Fig. 1(c). However, it is technically challenging to measure the horizontal contact area between the droplet and nonplanar surface, the center of the hemispherical droplet, and the intrinsic contact angle on nonplanar surface, which has limited the practical applications of these theories on convex and concave spherical surfaces. Therefore, there is still an unmet need for a wetting model that

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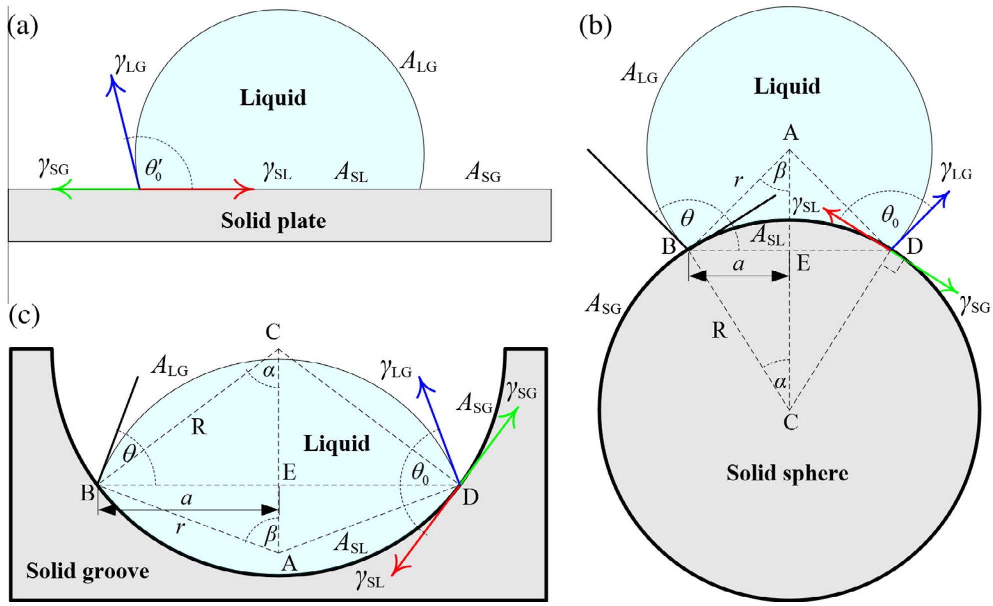


**Fig. 1.** Schematic of a droplet on different surfaces. (a) Flat surface. (b) Convex surface. (c) Concave surface. $A_{LG}$, $A_{SL}$ and $A_{SG}$ are separately areas of liquid–air, liquid–solid and solid–air interfaces; $\gamma_{LG}$, $\gamma_{SL}$ and $\gamma_{SG}$ are related coefficients of surface tension.

can be readily employed to determine the contact angle of a droplet on convex and concave spherical surfaces.

Measuring the apparent contact angles on the curved surfaces could be expensive, and usually the specific instruments are necessary. In this study, we proposed a simple wetting model to predict the apparent contact angle on curved surfaces $\theta = \theta(\theta'_0, V_L, R)$, which describes the quantitative relation between the apparent contact angle $\theta$ and the intrinsic contact angle on flat surface $\theta'_0$, the curvature $R$ and the droplet volume $V_L$. For the intrinsic contact angle, $\theta'_0$, it is a known constant parameter for the droplet and the ideal curved surface made of known materials. For most material, $\theta'_0$ is already available in handbooks. The curvature of the convex or concave (i.e., $R$) is measured with ease, and the droplet volume $V_L$ is known as the liquid could be controlled when dripping it. Thus, it avoids the need for the specific equipment. This theoretical model was verified by performing a set of experiments on contact angles of droplets on spherical and concave surfaces. Then it was employed to investigate the influence of different parameters on the apparent contact angles. In addition, this model was extended to discuss the contact angle on curved surfaces with microstructures.

As for the applicability, predicting the apparent contact angle and thus the morphology of the droplet on curved surface could be significantly important. Wetting behavior on ideally flat surfaces merely occurs in lab experiments. However, curved surfaces are more widely encountered in nature and industrial process. For instance, cactus' spines could collect fog from the air due to the wetting behavior on curved surfaces [25]. This is much favorable for the cactus to survive in the desert. Some research has shown that the wetting behavior on curved surface can be used to separate oil from water [26], which is significant as we are now facing a more and more critical energy crisis. Thus studying the wetting behavior on curved surfaces could help understanding the nature and may have potential applications in engineering.

## 2. Theoretical model

When a drop spreads on an ideal solid surface (Fig. 1), the contact area between the liquid and the solid surface (i.e., liquid–solid interface), $A_{SL}$, becomes larger. Meanwhile, the contact area between the solid surface and air (i.e., solid–air interface), $A_{SG}$, decreases, as $A_{SG} + A_{SL} = \text{constant}$. However, dependent upon the apparent contact angle $\theta$, the changing trend of the contact area between the liquid and air (i.e., liquid–air interface), $A_{LG}$, varies. According to Young's theory on interface energy and with the effects of gravity ignored [21], thermodynamic equilibrium of the system dictates:

$$\frac{dA_{LG}}{dA_{SL}} = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \tag{1}$$

where $\gamma_{SG}$, $\gamma_{SL}$ and $\gamma_{LG}$ are separately the coefficients of surface tension amongst the three objects. Depending only on the materials, temperature and pressure, these parameters remain constant in experiments. Eq. (1) is valid for flat, spherical and concave surfaces. For a flat surface, Eq. (1) reduces to Young's equation: $dA_{LG}/dA_{SL} = \cos\theta'_0$. For a spherical surface, by considering small changes $d\beta$ and $d\alpha$, the area of liquid–air interface is determined by the integral equation $A_{LG} = \int_\beta^\pi 2\pi r^2 \sin\beta d\beta$ while the area of liquid–solid interface is calculated by $A_{SL} = \int_0^\alpha 2\pi R^2 \sin\alpha d\alpha$. Based on the assumption of liquid incompressibility and the geometrical relations among the angles of curvatures ($\alpha$, $\beta$), radius of droplet ($r$) and contact angles ($\theta$, $\theta_0$), we arrived at (see Appendix):

$$\frac{dA_{LG}}{dA_{SL}} = \cos\theta_0 \tag{2}$$

It has been demonstrated that Eq. (2) also holds true for a concave surface. Because $\gamma_{SG}$, $\gamma_{SL}$ and $\gamma_{LG}$ are constant for given materials and environment, regardless of the shape of the contact surface, Eqs. (1) and (2) suggest that the intrinsic contact angle on an ideal curved surface equals the one on an ideal flat surface, i.e., $\theta_0 = \theta'_0$, which are both constant. In other words, $\theta_0$ could be determined by measuring the contact angle of a droplet on a flat surface.

By systematically analyzing the geometrical variables shown in Fig. 1(b) and (c) and adopting the relation between $\theta_0$ and $\theta'_0$, we obtained the dimensionless wetting equation for convex and concave spherical surfaces as: