Contact angle hysteresis of Newtonian fluid

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Abstract. Contact angle hysteresis of Newtonian fluid is a fundamental and complicated phenomenon related to wetting and dewetting. This article reviews typical research progress of contact angle hysteresis and proposes some critical directions deserved to be investigated. The traditional measuring methods are not accurate to measure the contact angle, and the conventional definition is not suitable for the Wenzel, Cassie, or the intersection of the two states. The surface roughness and droplet size are important factors affecting the hysteresis. Effective roughness scale for hysteresis could be at nanoscale. The difference between microscopic and macroscopic contact angle leads to different hysteresis at microscopic scale, which is valuable for nanodevice.

1. Introduction
Ideally, the droplet at equilibrium state will form a unique contact angle in the vicinity of the triple-phase contact line. On the basis of this principle, Young equation links the contact angle and the force balance among the solid-liquid-gas three interfacial tensions at horizontal direction. However, this equation is only based on the absolutely smooth and chemically homogeneous surface. On the most of real solid substrate, the contact angle is often in a range. The advancing static angle is defined as the maximum value of this range, similarly, the minimum value as the receding static angle. This universal phenomenon is known as the hysteresis of contact angle. From the perspective of thermodynamics, the hysteresis is because of the existence of different energy metastable states caused by energy barrier on real solid surfaces. In the macroscopic concept, this phenomenon is closely related to the pinning force at the triple-phase contact line, affected by the surface roughness, liquid penetration, surface deformation and so on. Also, the long-range interactions between molecules, such as van der Waals force, play a non-negligible role in contact angle hysteresis at nanoscale.

Contact angle hysteresis exists widely in production and life, such as self-cleaning material, oil extraction, coating and mineral processing. The investigation of this phenomenon will not only help to transform properties of materials, but also contribute to industrial applications. Given the complex nature of non-Newtonian fluids, this article summarizes the basic scientific problems existing in contact angle hysteresis of Newtonian fluid and puts forward several valuable directions of specific research.

2. Measurements and definitions of contact angle hysteresis
2.1. Measurements of static advancing/receding angle
In experiments, the traditional methods of measuring contact angle to denote hysteresis mainly include two methods: the needle injection method and the tilting plate method.
The needle injection method is to add or remove liquid slowly through a micro syringe to a drop which places on a flat substrate (Figure 1). Initially, the contacting area between the liquid and the solid substrate remains unchanged, and the contact angle increases or decreases with the liquid’s volume. When the liquid droplet gradually increases to a specific volume causing the contact line moving outward, the maximum boundary value of the angle between the solid and liquid is recorded as the advancing static angle. In a similar way, the receding static angle is captured as the contact line from stillness to inward movement with removing liquid.

![Figure 1. The needle injection method](image)

(a) Add liquid

(b) Remove liquid. $\theta_a$ is the advancing static angle, and $\theta_r$ is the receding static angle.

The tilting plate method uses the spontaneous movement of the liquid droplet along the slope under the action of gravity. At first, the drop is placed slowly on a level plate, and the solid substrate is gradually inclined up to a certain angle of roll that the entire droplet moves down along the plate (Figure 2). Before moving, the contact angle of droplet at the uphill point increases until reaching the advancing angle; otherwise, the receding angle is measured as the static contact angle of droplet at the downhill point decreases to the minimum.

![Figure 2. The tilting plate method](image)

$\theta_a$ is the advancing static angle, and $\theta_r$ is receding static angle.

Nevertheless, both of the traditional measuring methods mentioned above exist some errors in practice. For the first one, the wetting of the syringe's wall affects the contact angle, especially the receding angle. Because the tip of the syringe needs to be embedded in the droplet to extract liquid, which destroys the geometry of the droplet. For the other, in some cases, only the front part of the droplet moves, while the back part of the droplet is stationary, which leads to the error between the real contact angle and the apparent contact angle. Krishnan, et al. through the experiment presented that the advancing angle gauged by the tilting plate method is in consistence with the real advancing angle, but the measured receding angle is significantly larger than the actual value due to the phenomenon of triple-phase contact line pinning requiring the whole liquid to overcome the energy barrier. In addition, this method is influenced by the size of the droplet and limited in some situation. For example, the sample surface is inclined to 90 °, while the droplet does not roll down with the slope.

In molecular dynamic simulations, these two methods are not appropriate to measure the micro droplets at nanometer scale. Firstly, increasing or decreasing molecules from nano-droplet will seriously affect the efficiency of simulation. Secondly, because the droplet is so small that its gravity is almost negligible compared with the surface tension, the droplet will not move with tilting the surface. Therefore, Wang, et al. proposed a new method of measurement suitable for simulation. By applying a force to the equilibrium liquid drop on the substrate to overcome the energy barrier of contact line movement, the shape of the droplet is changed until the contact area increases. It is similar to the tilting plate method, because both rely on the external force that causes the drop to roll down...
and reaches to the advancing and receding static angles. However, the new method avoids some situations that the drop does not slide along the inclined plane.

2.2. Definitions of contact angle hysteresis

The above two conventional measurement methods in experiment and the new method in simulation can provide data for the traditional definition of contact angle hysteresis. However, the above information also shows that the error of tilting plate method is too large to represent the characteristics of solid surface. Thus, in the experiment, researchers tend to use the needle injection method to gauge the advancing and receding angle, and put these measured values into the traditional definition of hysteresis. The traditional definition of hysteresis introduces a simple arithmetic difference between the advancing angle and receding angle. This definition uses the advancing angle and receding angle to compare the hysteresis of drops under the same contact area. However, it is obvious that the traditional concept of hysteresis ignores the influence of droplet in different states, such as two common states on rough surfaces: Cassie state and Wenzel state. In Cassie state, the liquid drop contacts with the compound surface including peaks of the rough surface and trapped air in depressions between the peaks. For the Wenzel state, the drop completely contacts with the profile of rough surface. So, the traditional definition is not universal.

![Figure 3. Droplets in (a) in Young equilibrium state, (b) in Cassie state and (c) in Wenzel state.](image)

Recently, Koishi, et al.\(^1\) introduced a new definition to quantify contact angle hysteresis caused by droplets in different states. This definition measures the contact angle of droplets under the same volume but different initial conditions, like different contact areas and different states, and compares the hysteresis of contact angle between the Cassie state and Wenzel state.

Although the new definition can be used flexibly in computer simulation, it is hardly to measure by using the above two traditional measurement methods in experiments. Because the new definition needs amount of continuous data of contact angle in different states. Considering the remarkable development in microscope, the researchers can solve this problem by means of laser scanning confocal microscope. By adding or reducing the liquid and vibrating the surface to change the volume and the initial state of the liquid drop respectively, the dynamic contact angle can be recorded, so as to quickly obtain a variety of contact angle data. Then the contact angle derived from the macro fitting of the contour is introduced into the new definition to compare the hysteresis across different states.

3. Influencing factors for hysteresis of contact angle

The roughness of solid surface and the size of droplet have a non-negligible impact on the hysteresis.

The hysteresis of contact angle results from defects pinning to the contact line, so it is obvious that the scale of the defects will influence the magnitude of hysteresis. The physical characteristics of defect are usually described by roughness. On a homogeneous, rough surface, the hysteresis increases with the roughness, which is due to the increase of energy barrier hindering liquid motion. Jaroslaw, et al.\(^4\) found that all surfaces show obvious hysteresis in their experiments, even the smoothest surface, which is different from the Extrand's conclusion that when roughness \( r < 100 \text{ nm} \), this factor has a weak influence on hysteresis\(^5\). Therefore, the effective scale of defects for contact angle hysteresis is still controversial. On the other hand, only qualitative analysis was carried out because of insufficient surface characterizations in Jaroslaw's experiment. Then, the researchers tried to add parameters to explore the relational expression between roughness and hysteresis. The experimental results of Dettre

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\(^1\) Koishi, et al.
\(^2\) Extrand
\(^3\) Jaroslaw et al.
\(^4\) Dettre
and his coworkers showed that the hysteresis and surface roughness are not monotonic functions. Ramos, et al. also agreed with this view and cited the areal density of defects as the parameter. When the is smaller than radius of droplet, the hysteresis increases with the roughness, and the droplet is fixed by the pinning force of a single defect, while the hysteresis begins to decrease with the further increase of roughness, which is caused by the collective pinning effects. However, the specific reasons need more study in the future. Moreover, this experiment needs to measure and verify this relationship in high density defect surfaces in the following study, because the defects concentration used in this experiment, even in the highest density surface, is too low to reduce its homogeneity by adding new defects. Besides, because the adhesion is affected by the surface roughness away from the contact line and is directly associated with the energy dissipation during the droplet movement, hysteresis of contact angle. Some researchers proposed to use adhesion, that is, the pull-out force needed to separate the droplet from the solid surface, as the parameter to reflect the hysteresis. However, the determination of surface adhesion is still problematic. At present, there are two main different adhesion models. One theory emphasizes that the adhesion is determined by the contact area between the drop and the substrate. The other focuses on the impact of triple-phase line of contact on the adhesion. Also, these two models still need to be proved by further experiments.

The formulas of Wenzel and Cassie have some limitations in describing the contact angle on roughness surfaces, because the liquid size is much larger than the defect size. This exposes to another factor that needs to be considered in the study of hysteresis—droplet size. In the experiment, it can be observed that the contact angle of liquid drop on the horizontal surface increases with the decrease of droplet size, which leads to the change of hysteresis. The line tension was introduced in contact line zone to revise the relation between the contact angle and droplet size. This concept was first proposed by Gibbs, which refers to the free energy per unit length of the triple-phase contact line in one-dimensional space. Many researchers used line tension to revise Young equation, unfortunately, the calculation of the line tension is still under debate, which is related to the interfacial potential. For one thing, the assumption of "moderate curvature" inherent in the modified Young’s expression may not be applicable when the triple-phase contact line is twisted. For another, there is subjective influence in the process of measuring the contact angle.

To sum up, in the process of analysing hysteresis, many factors should be considered, such as surface roughness, surface deformation, liquid adsorption and size effect. However, the point is to describe these factors accurately. For surface roughness, its effective scale and characteristic parameter for hysteresis should be investigated carefully. For droplet size effect, how to add the line tension into contact angle hysteresis is another open question.

4. Microscopic hysteresis of contact angle

More and more microscopic experimental results showed that there are differences between apparent contact angle and microscopic contact angle. The solid substrate is superhydrophobic one when the contact angle of water droplet on it is more than 150° according to traditional optical measuring method. However, it is not accurate to judge whether a surface is superhydrophobic one in this way. By obtaining the confocal microscope video of the droplet on a liquid-repellent surface, Frank, et al. proved that the advancing angle is equal to or even larger than 180° at the micro scale due to the concave curvature of the liquid surface, which is quite different from the traditional conclusion of the apparent contact angle. In recent years, with the rapid development of microfluidic devices, atomic force microscopy (AFM) has been widely used. Yu, et al. used the tapping mode of the atomic force microscope to scan the thin film around the contact line region. He found that in the range of several to tens of microns, the film profile is highly linear with a constant slope. Compared with the macro contact angle measured by the traditional optical method, it is still valid with the AFM measurement results when the thickness of the thin film is large. However, AFM shows that the film profile no longer displays the linearity relationship and exists a transition region with different microscopic contact angle when the thickness of liquid film is below 100nm, which means that the concept of macroscopic or apparent contact angle is unsuitable under the circumstances of less than submicron.
Therefore, it can provide new results or deep insight by investigating the hysteresis at microscopic scale\textsuperscript{12}.

With the exploration of the microscopic contact angle, the precursor liquid film attracts the researchers' interest. In the process of droplet wetting, the contact line will produce micro film at the front end under the action of separation pressure, which is called precursor liquid film. The formation of precursor liquid film is usually in completely wetting droplets\textsuperscript{13}. The precursor film is first spread on the surface at a higher speed, and then the droplet is spread on the precursor film. Therefore, the paradox of energy dissipation is relaxed in this way. However, the precursor film was also revealed in partially wetting water droplets in an advanced molecular dynamics simulation. So, it is necessary to study the role of precursor liquid film in hysteresis of contact angle.

5. Conclusions and outlines

In this paper, the hysteresis of droplet on solid surface is reviewed. Long-standing controversial issues and critical directions are summarized. Further fundamental studies of contact angle hysteresis should address the following questions.

- Some methods of measuring contact angle are not accurate to infer the hysteresis, and the state of droplets including the Wenzel, Cassie, or the intersection of the two state is not considered in the traditional definition. Although the new definition considers the initial state of droplets, it isn't applicable to current traditional measuring methods. In the future, researchers can propose a more accurate and universal definition or measurement such as using the confocal microscope.
- The surface roughness and droplet size are important factors affecting the hysteresis. The effective scale of defects, collective pinning effects as a reason of hysteresis, and the parameter surface adhesion of the surface roughness and the line tension of droplet size are still controversial and remain to be studied.
- At the micro scale, the difference between the micro contact angle and the macro contact angle indicates that the traditional conclusion of the apparent contact angle is not applicable, and the influence of precursor film on contact angle hysteresis is considered as a new research direction.

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