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Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

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Roughness effects on contact angle measurements

Bernard J. Ryan and Kristin M. Poduska[a)]
Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada

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We have developed a simple and economical procedure to demonstrate the effects of roughness and wetting fraction on the equilibrium contact angles of liquid droplets on solid surfaces. Contact angles for droplets placed on a rough surface, which wet only a portion of the surface, are larger than the contact angles of droplets formed by condensation of steam, which wet the surface more completely. These contact angle data facilitate assessments of changes in true surface area, due to surface roughening, as well as changes in the fractional contact areas of the water droplets, due to the formation of air pockets between the rough surface and the droplet.

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I. INTRODUCTION

Much recent research has been devoted to understanding how to design surfaces that repel water. One of the goals of this type of research is to develop self-cleaning surfaces.[1,2] Nature gives us one of the best examples of this kind of surface in the leaves of the lotus plant.[1] The way in which droplets of liquid bead up on a solid surface, whether it is a nonstick coating or a lotus leaf, is related to the physical properties of the surface.

The contact angle, which provides a measure of the angle between surface of the droplet and the solid surface, has been used for many years to assess surface wettability. Contact angles less than 90°, as shown in Fig. 1(a), are associated with hydrophilic surfaces, while hydrophobic surfaces have contact angles larger than 90°, as shown in Fig. 1(b). Neglecting the effects of gravity, Young's contact angle can be explicitly related to solid–vapor (γ_{SV}), solid–liquid (γ_{SL}), and liquid–vapor (γ_{LV}) interfacial surface energies:[3]

$$\cos\theta_Y = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}. \tag{1}$$

The contact angles are thus influenced by the specific kinds of atoms and surface terminations present at the liquid–solid–vapor interfaces.

Surface roughness plays an equally important role in the wettability of a surface, and reported values of the Young's angle have traditionally shown a wide range of variability when they have not been corrected for roughness effects. When a water droplet completely wets a rough surface on which it sits, as shown in Fig. 2(a), the impact of surface roughness on contact angle is given by the Wenzel equation:[4]

$$\cos\theta_W = r\cos\theta_Y. \tag{2}$$

The Wenzel equation relates the observed contact angle on a rough surface, θ_W, with the roughness ratio r of the surface and the contact angle on a smooth surface, θ_Y. Since the roughness ratio compares the true surface area of a rough surface with the surface area of a comparably sized smooth

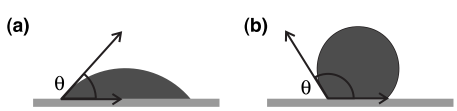

Fig. 1. A schematic illustration of the contact angle θ between a fluid drop and a solid surface for (a) hydrophilic and (b) hydrophobic surfaces.

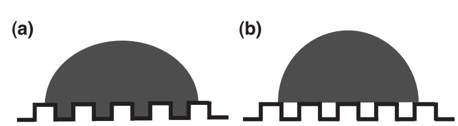

Fig. 2. A schematic illustration of the difference between (a) the homogeneous (Wenzel) and (b) the heterogeneous (Cassie–Baxter) wetting regimes.

surface, this ratio will always be larger than one. Wenzel's relation thus shows that surface roughness will decrease the contact angle for a droplet on a hydrophilic surface and increase the contact angle for a droplet on a hydrophobic surface.

If a liquid droplet does not entirely wet the rough surface and leaves pockets of air between the droplet and the substrate, the observed contact angle, also called the heterogeneous contact angle, is influenced by the fraction f of the droplet that is actually in contact with the surface, as shown in Fig. 2(b). The heterogeneous contact angle θ_{CB} is given by the Cassie–Baxter equation:[5]

$$\cos \theta_{CB} = f \cos \theta_W + (1 - f) \cos \theta_{air}. \tag{3}$$

Since water droplets have a 180° contact angle with air, the Cassie–Baxter equation can be simplified:

$$\cos \theta_{CB} = f \cos \theta_W + (f - 1). \tag{4}$$

It is thus possible to have hydrophobic-range contact angles from intrinsically hydrophilic surfaces when heterogeneous wetting occurs.

To illustrate the effects of roughness and wetting fraction on chemically homogeneous surfaces, we have developed a simple and economical method to measure contact angles that is appropriate for an undergraduate laboratory experiment. In this paper, we describe the instrumentation and setup, useful software for data treatment, and examples of analyses that students can do to verify the existence of homogeneous and heterogeneous wetting regimes.

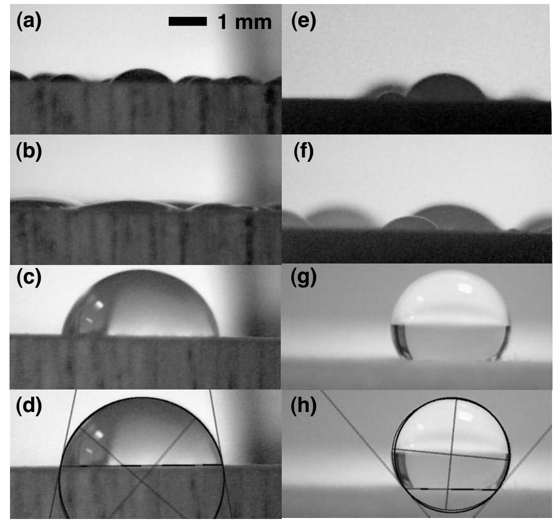

Fig. 3. Representative images of water droplets in contact with smooth and roughened plastic surfaces. Images (a)–(d) were obtained with a PMMA surface, while droplets shown in (e)–(h) were obtained on a PTFE surface. The top images (a, e) show condensed droplets on smooth surfaces. Images (b, f) show that condensed droplets on roughened surfaces have lower contact angles. In contrast, pipetted droplets on the same roughened surfaces have substantially larger contact angles due to heterogeneous wetting, and can lead to either hydrophilic (c) or hydrophobic (g) contact angles. An example of contact angle fits from ImageJ, applied to the images shown in (c, g), are displayed in (d, h).

II. EXPERIMENTAL DESIGN

Contact angle measurements that are suitable for undergraduate laboratories have been reported, but none have emphasized the role of roughness on contact angles. Some studies have focused on determining numerical[6] or analytical expressions[7] to describe the shape of the fluid interface. Experimental investigations have addressed the effect of surface chemistry on contact angle values.[8–13] These earlier reports have used microscopes or other more specialized optical equipment to view the droplets.[12,14] In contrast, the heart of our contact angle measurement setup is a webcam connected to a standard personal computer.

The digital camera used for this study (Labtec Webcam Plus, retail price $25) has manual focus and automatic contrast adjustment capabilities, and produces images with a 640×480 pixel resolution. The webcam was mounted on a lab stand with a movable clamp to adjust its relative height and levelness for true edge-on views of water droplets. To enhance the contrast to allow more precise measurements of the contact angles, the sample was placed on a black surface with a white backdrop. Regular room lighting in conjunction with shadowing directly above the droplet offered excellent contrast options, and no special lighting was required.

The best surfaces for observing roughness effects on contact angles with our setup were plastics, including fluorinated plastics, such as polytetrafluroethylene (PTFE, including Teflon), and acrylic glasses, such as polymethyl methacrylate (PMMA, including Plexiglas). Sheets of these materials were generally smooth enough as-purchased to be used to determine Young's angle. For subsequent measurements, some samples were roughened with sandpaper (wet–dry, 100–400 grit) to obtain uniform surface features with dimensions on the order of tens to hundreds of μm. (It is useful to note that grit sizes are related to average particle sizes. The distribution of particle sizes, which has a more pronounced impact on surface roughening, will vary among manufacturers.) A figure-eight sanding pattern reduced the possibility of directional sanding grooves which could pin the droplets. All samples, whether still smooth or manually roughened, were rinsed thoroughly with ethanol and distilled, filtered water to remove any coatings or particulate matter prior to contact angle measurements.

Water droplets can be formed on surfaces by using a pipette to place a single droplet, or by condensing steam to obtain many droplets. This laboratory experiment employs both preparations, since recent research has shown that contact angles vary considerably between drops prepared by each method.[2] Because condensation promotes nucleation of small droplets—even in deep and narrow surface crevices—it tends to allow more complete wetting of rough substrates, and thus lower contact angles. Therefore, we used condensed droplets on smooth substrates to determine θ_Y (equilibrium contact angle on a smooth surface), and condensed droplets on roughened surfaces to determine θ_W (equilibrium contact angle on a rough surface in the homogeneous wetting limit). Condensed droplets were formed on our surfaces when they were held (inverted) over a beaker of heated water for a period of seconds to minutes, with longer times yielding larger droplets. Pipetted droplets on rough surfaces yield θ_{CB}, which is the equilibrium contact angle on a rough surface in the heterogeneous wetting regime.

Representative droplet images on smooth and roughened surfaces are shown in Fig. 3. Droplet volumes of 0.5–10 μl were easiest to view with the working distance of 5 mm between the droplet and our camera window. To minimize the effects of evaporation and spreading of the droplets (due to airborne particulates), images of the droplets were cap-

Table I. Representative contact angles, given in degrees and measured on PTFE and PMMA surfaces, for the smooth wetting (θ_Y), rough homogeneous wetting (θ_W), and rough heterogeneous wetting (θ_{CB}) regimes. The quoted uncertainties reflect the range of variations among different droplets formed on the same surface. For these data, all roughened surfaces were prepared with 400 grit sandpaper.

	θ_Y (°)	θ_W (SD)	θ_{CB} (°)
PTFE	61 ± 2	52 ± 5	125.6 ± 0.4
PMMA	55 ± 2	32 ± 9	77 ± 2

tured within a few seconds of their placement on the surface. Drops that appeared asymmetric when placed on a level surface were most often pinned by grooves or other imperfections in the surface. Such droplets were removed easily and quickly by wicking them away with a paper towel.

To measure the contact angles from the captured images, a variety of public domain software packages can be used to simplify and increase the accuracy of the measurements. All data analyzed for the work described in this paper utilized the public domain software ImageJ[15] with a Contact Angle plug-in.[16] Other algorithm implementations, such as Drop Shape Analysis,[17] are also freely available. The ImageJ software allows the user to make cursor marks at the air-droplet-surface interface, as well as along the air-droplet interface. These points are then fit to a circle or ellipse, as shown in Figs. 3(d) and 3(h), from which the resulting contact angle was calculated. It was very easy to identify by eye when there was a poor correspondence between the fitted circle and the air-droplet interface due to misplaced cursor marks. Our best results were obtained from black and white images, or images on which edge detection schemes were applied for clear delineation of the droplet outline. Representative contact angle values are given in Table I. We note that uncertainty estimates tend to be higher for flatter droplets whose contact angles are closer to 0°.

III. DATA ANALYSIS AND INTERPRETATION

Once contact angles are obtained, students can use Eq. (2) to extract roughness ratios r by using the rough (θ_W) and smooth (θ_Y) contact angles of condensed droplets. Representative results are shown in Table II. Based solely on the changes in the contact angles of condensed droplets, students can confirm that both plastics show comparable increases in surface area after manual roughening with the same kind of sandpaper. For example, the data in Table II show that there is a 40% increase in surface area after roughening PTFE or PMMA with 400 grit wet–dry sandpaper. Students can also compare their extracted roughness ratios with the surface area increase one would obtain from close-packed hemispheres, which could be considered a crude approximation to the sandpaper surface. The roughened plastics investigated in this experiment have a roughness ratio of $r=1.4$, considerably lower than the ratio $r=1.9$ one would expect to see for monodisperse close-packed grains. This suggests that the grains in our sandpaper are less densely packed.

By comparing the contact angle differences between pipetted and condensed droplets on surfaces of the same roughness, students can determine the fractional contact area f of heterogeneously wetted samples. Calculated with the assistance of Eq. (4), the f_{smooth} and f_{rough} values shown in Table II relate the difference in fractional contact areas between condensed drops and pipetted drops on smooth and roughened surfaces, respectively. The data clearly show that the fractional contact areas are less for the rough surfaces than for the smooth surfaces, as the schematic picture in Fig. 2(b) would suggest. These data also highlight the importance of considering surface chemistry when wettability is a concern: Even though the roughness ratios are similar for both plastics, PTFE, which is widely used in nonstick coatings, has substantially lower fractional contact areas compared to PMMA.

Table II. Representative roughness ratios and fractional coverages on PTFE and PMMA surfaces. The quoted uncertainties reflect the range of variations of measured contact angles for different droplets formed on the same surface. For these data, all roughened surfaces were prepared with 400 grit sandpaper.

	r	f_{rough}	f_{smooth}
PTFE	1.3 ± 0.2	0.26 ± 0.01	0.52 ± 0.04
PMMA	1.5 ± 0.2	0.66 ± 0.05	0.76 ± 0.05

Utilizing our simple and straightforward contact angle measurement procedure, students can pursue a number of more advanced lines of inquiry:

- Study contact angles as a function of droplet volume.[1,2]
- Investigate how contact angles change with other fluids or surfaces.[8–13]
- If research interests and facilities of the course instructors allow, other kinds of surface roughening techniques, such as plasma etching or colloidal particle layers, or other surface roughness measurement methods, such as a profilometer or atomic force microscope, could be used.

When contradictory or unexpected results appear, it is useful to remind students that the physics of hydrophobic and hydrophilic surfaces is often more complicated than the simple Wenzel and Cassie–Baxter models of surface wetting. Recent literature has shown that pressure can be used to induce homogeneous wetting on rough surfaces, and that there is significant hysteresis before reverting back to heterogeneous wetting.[2] Other studies on lotus plant leaves have shown that, when droplet sizes are comparable in magnitude to the surface roughness features, the apparent contact angles do not match the true local contact angles of the droplet with the surface.[1] Subsequent theoretical analyses have highlighted the need to understand the assumptions of the Wenzel and Cassie–Baxter models in order to identify limits for their applicability.[18] It is this active interplay between experimental and theoretical results that continue to make studies of contact angles on rough surfaces a vibrant area of scientific investigation.

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[a]Electronic mail: kris@mun.ca

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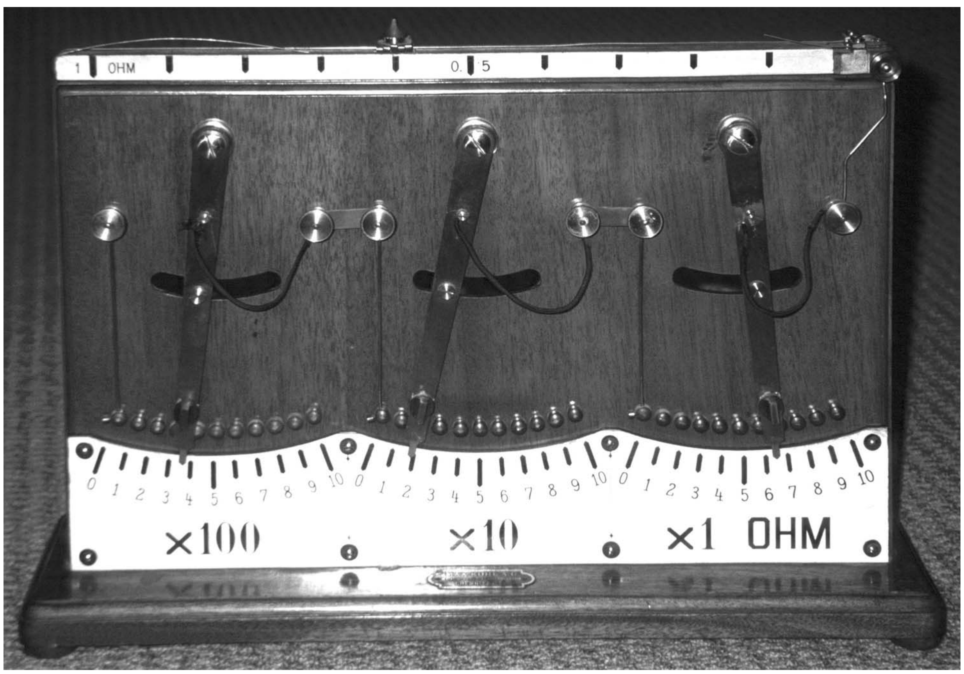

Variable Resistance. This five decade variable resistor made by Max Kohl of Chemnitz is in the physics museum at Washington and Lee University in Lexington, Kentucky. The 0.1 and 1 ohm resistors are slide wires along the front and back of the top, and the three upper ranges use coils of low-temperature coefficient resistance wire (probably constantan). Soon after this device was made the familiar dial-type resistance boxes began to be made by firms such as Leeds & Northrup. (Photograph and Notes by Thomas B. Greenslade, Jr., Kenyon College)