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We report a simple technique for moving water droplets on a hydrophilic aluminum surface containing a hydrophobic copper background. A surface tension gradient due to a triangular-shaped wedge moves the droplets towards the end of the wedge which contains more Al surface area. Movement on both horizontal surfaces and surfaces oriented vertically against gravity has been observed. The mode of droplet motion was found to depend on the wedge angle, and the speed was found to depend on both the wedge angle and the droplet contact angles on the Al and Cu. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4802926]

There is a large array of engineering applications, especially in the heating, ventilation, air conditioning, and refrigeration (HVAC&R) industries that are influenced by the management of water droplets on metallic surfaces. For example, the condensate retained on the surface of a heat exchanger has hydrodynamic effects by changing the surface geometry and the airflow pattern.[1–3] Furthermore, a water layer on the surface increases the local surface heat transfer resistance. Thus, retained condensate can degrade heat transfer by occupying surface area and blocking airflow.[4,5] In applications like the "lab-on-a-chip," it is important to move droplets from one place to another in a controlled manner. Thus, using water droplets, rather than a continuous flow, also has significant advantages in some microfluidics and biotechnology applications.[6–8]

In HVAC&R systems, most heat exchangers are made of aluminum and/or copper, which are naturally hydrophilic (i.e., water loving). In air-cooling systems, this can lead to water condensing on the heat exchanger surface in the form of droplets. It is important in this context to eliminate or move these water droplets in desired directions, or even to specific positions,[9] before they are carried away by the air flow into the occupied space or before they freeze on the surface of the heat exchanger. For this reason, the study of water droplets on metallic surfaces (and not just silicon and glass substrates) is especially important.

Various surface-tension-gradient schemes have been proposed and used to manipulate water (as well as other fluid) droplets on flat surfaces.[10] Surface tension effects dominate at small droplet volumes, making it possible to engineer the surface tension force at the triple-phase contact line to induce motion in desired directions.[11]

In this letter, we report a process that produces strongly hydrophilic Al and strongly hydrophobic Cu regions on a surface by using oxygen plasma exposure followed by a hydrophobic self-assembled monolayer (SAM) that selectively forms on Cu. We demonstrate the movement of water droplets on flat surfaces oriented horizontally (as well as vertically) by fabricating wedge-shaped hydrophobic Cu regions on hydrophilic Al blocks. This geometry creates a surface tension gradient that exerts a net force on deposited droplets which span both regions. Droplet fronts are observed to move multiple centimeters due to the capillary force that is created as a result of the variation in the surface tension force around the periphery of the droplet.

Figure 1 shows the behavior of water droplets placed on horizontal Cu and on Al surfaces at different stages of the process. Both the Cu and Al surfaces are mirror-finish-grade thin blocks that initially contain a plastic protective layer on the polished side. Industrial grade Alconox detergent is used to clean the surfaces after peeling off the protective plastic cover. Fig. 1(a) is a picture of a droplet on a clean Cu surface. The surface is hydrophilic with a contact angle of about 45°. Exposing the surface to oxygen plasma makes it even more hydrophilic with a contact angle close to 25°, as shown in Fig. 1(b). The Cu block is then immersed in a 0.1M hepta-decafluoro-1-decanethiol (HDFT) solution for 6 min and dried to create a strong water-repelling self-assembled monolayer on the Cu.[12] Water droplets show a strong hydrophobic behavior in this case even though the surface was very hydrophilic before the application of the SAM. The contact angle in Fig. 1(c) is about 140°. Fig. 1(d) is a normal color picture (using a Pentax camera) of the droplet in Fig. 1(c). Performing the same steps on Al, however, reveals a distinctly different behavior at the last step of the fabrication. Initially, the cleaned Al surface is almost identical to Cu with a contact angle slightly below 50°, as shown in Fig. 1(e). Oxygen plasma exposure (or Alconox cleaning) makes the Al super-hydrophilic for a period of a couple of days, with a contact angle less than 8°.[13] The most striking difference between the Cu and Al surfaces is that the immersion of the Al into the HDFT solution just after oxygen plasma exposure does not make the surface hydrophobic. Rather, water droplets placed on the surface exhibit a contact angle of about 25°, as shown in Figs. 1(g) and 1(h). This suggests that the HDFT SAM layer is not formed on the Al, possibly due to the insulating aluminum oxide film that exists on the

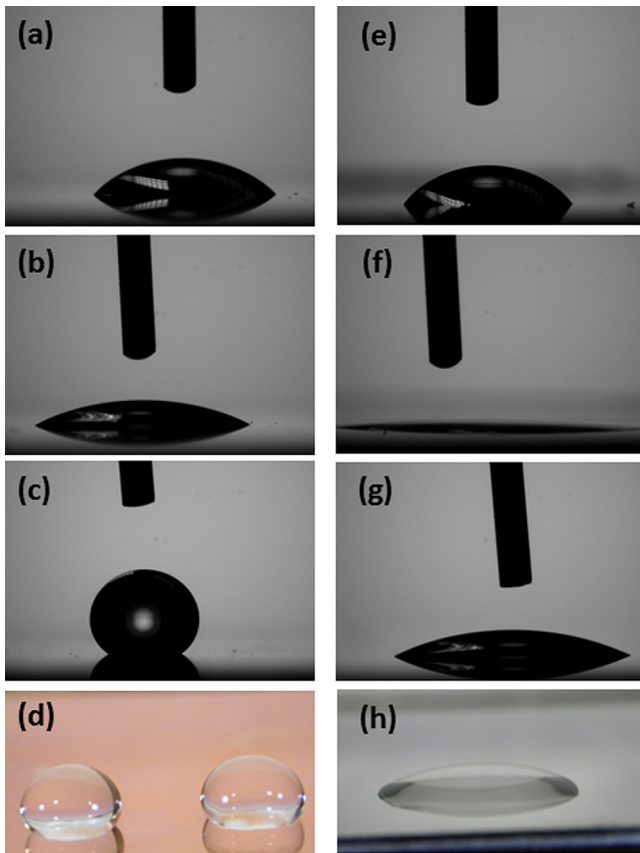a)Author to whom correspondence should be addressed. Electronic mail: eidkf@miamioh.edu.

FIG. 1. CCD-camera pictures of 6-μl water droplets placed on horizontal copper and aluminum surfaces at different stages of the surface fabrication process. (a) Droplet on an Alconox-cleaned Cu surface showing hydrophilic behavior. (b) After cleaning and oxygen plasma exposure, Cu becomes more hydrophilic. (c) Immersion in HDFT makes Cu strongly hydrophobic with a contact angle of about 140°. (d) Color picture of water droplets on Cu after immersion in HDFT. (e) Alconox-cleaned Al surface is moderately hydrophilic just like Cu. (f) After oxygen plasma exposure, Al becomes superhydrophilic. (g) After immersion in HDFT, Al remains strongly hydrophilic unlike Cu. (h) Color picture of a water droplet on Al after immersion in HDFT.

surface. This difference in behavior between the Cu and Al surfaces allows for the fabrication of Cu/Al features on the same surface but with very different wetting characteristics. This property in turn can be used to manipulate water droplets. For example, creating Al channels on Cu leads to a strong capillary effect that causes droplets (which span both regions) to deform significantly in order to wet the Al and minimize contact with the Cu. Resulting droplets often deviate substantially from a circular base contour shape.

In this work, we create a wedge-shaped surface tension gradient by depositing Cu on a thin Al block using a simple shadow mask and then treating the surface to induce a larger difference in wettability between the Cu and Al.[14] To begin,

a piece of aluminum foil is cut with scissors to form multiple triangles each possessing a different head angle, ψ. The foil is then used as a shadow mask to thermally deposit a $\sim$100 nm Cu film on a mirror-finish Al block giving the pattern shown in Fig. 2(a). Fig. 2(b) shows two water droplets, one placed on the Cu and one on the Al after deposition, plasma etching, and immersion in the HDFT solution. It is clear that the wettability is identical to that shown in Fig. 1, with the Al and Cu regions exhibiting hydrophilic and hydrophobic behaviors, respectively. A water droplet placed at the tip of an Al triangle moves quickly towards the Al region to avoid contact with the water-repelling Cu surface. It is not necessary to place the droplet in a symmetric position centered along the axis of the triangle. If the droplet is placed to the side, but touches the Al slightly, it will quickly move in order to become centered on the Al region in addition to moving down the axis of the triangle.[15] Figs. 3(a)–3(h) show pictures of a 10 μl water droplet as it moves along the wedge-shaped Cu/Al interface. A ruler is placed near the surface to provide a direct visual estimate of the distance traveled, and the time is noted on each picture. As time progresses, the droplet is observed to move to the right (the "+" x-direction) and spread out due to the near-total wetting of the Al surface. One can see from these pictures that the front of the droplet is not smooth due to occasional surface imperfections that act as pinning sites for the "contact line" between the droplet and the Al surface. These pinning sites cause the motion of the droplet to be discontinuous at times and not always smooth. During tests, droplets ranging in volume from 2 μl to about 80 μl were examined.

The speed of travel of a droplet depends on the difference between the contact angles on the Cu and Al regions as well as the head angle of the triangle. It increases for larger differences in the contact angles and for wider triangle head angles. It is unfeasible, however, to treat the water droplet as a rigid body and expect the front and back to move by the same amount or to even define a unique speed for the droplet as a whole. The droplet's front moves faster than the back, and the droplet ends up assuming the shape of a triangle with rounded edges (i.e., tadpole shape)[16] in order to achieve maximum wetting of the Al and to avoid contact with the Cu. Nonetheless, it may be reasonable to assume that the contact line of the droplet is elliptical or circular initially in order to calculate the net surface tension force in the positive x-direction. Fig. 4(a) shows the circular three-phase contact line of a water droplet placed on a homogeneous surface. The x-component of the surface tension force for an element of length, ds, along the contact line is

$$dF_{sx} = \gamma \cos\theta \cos\emptyset \, ds = \gamma \cos\theta \cos\emptyset \, R \, d\emptyset, \qquad (1)$$
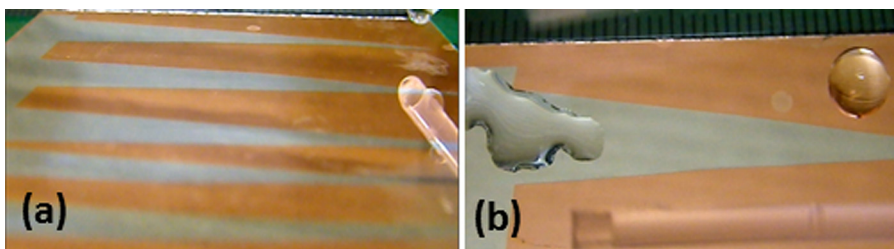

FIG. 2. (a) The Cu/Al surface with the wedge-shaped gradient patterns, (b) Image of $\sim$75 μl water droplets on the Al and Cu regions shortly after plasma exposure and immersion in the HDFT solution. The Al is hydrophilic, and the Cu is hydrophobic.
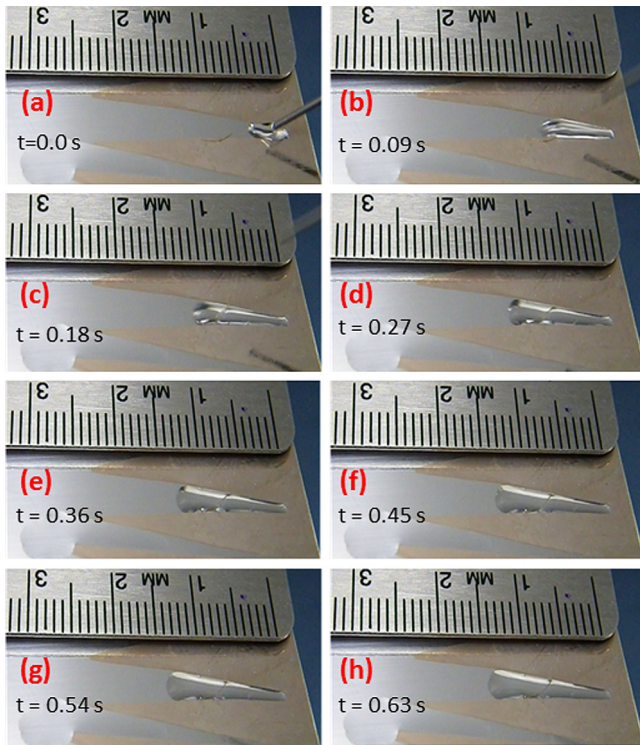
FIG. 3. Snapshots showing the motion and spreading of a 10 μl water droplet on a horizontal wedge. A ruler is placed near the droplet as a visual indication of the traveled distance, and the time is displayed on each picture. The droplet front starts moving fast then slows down before it eventually stops.

where γ is the surface tension per unit length, θ is the contact angle at the position of ds, R is the radius of the circle, and ϕ is the angle that the line connecting ds with the center makes with the x-axis. The total surface tension (or capillary force) in this case is zero due to the circular symmetry of the contact line. Yet, there will be a net force in the x-direction if
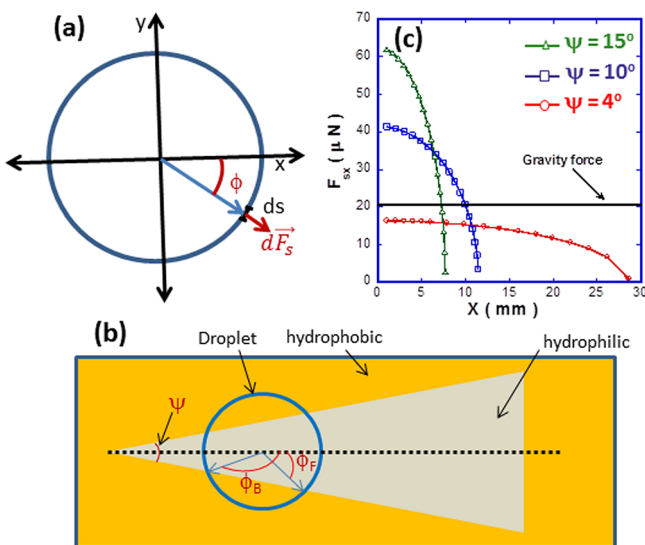

FIG. 4. (a) Surface tension force on a circular three-phase contact line. (b) Droplet placed on an Al wedge surrounded by Cu. (c) The net surface tension force (i.e., capillary force) of a circular droplet with radius 1 mm for three different wedge angles. A large wedge angle produces a significantly larger net force in the x-direction for a shorter distance. The horizontal line gives an estimate of the gravitational force (weight) of the droplet for comparison.

the droplet is placed on a surface containing a wettability gradient such as the wedge shown in Fig. 4(b). The net capillary force on the droplet in this case is obtained by integrating the surface tension force acting along the three-phase contact line of the droplet.[17]

If the contact angle is assumed to change abruptly (i.e., in a stepwise manner) at the boundary between Cu and Al,[18,19] then it can be shown that the net force is

$$F_{sx} = 2\gamma R\{\cos\theta_{Al} - \cos\theta_{Cu}\}[\sin\emptyset_B - \sin\emptyset_F], \quad (2)$$

where θ_{Al} is the contact angle on Al (which is about 25° in these samples) and θ_{Cu} is the contact angle on Cu (which is about 140°). In this equation, ϕ_F represents the azimuthal angle to the first Cu/Al boundary at the front of the droplet, and ϕ_B represents the azimuthal angle to the second Cu/Al boundary at the back of the droplet. Equation (2) shows that in order to move droplets, both large contact angles on the hydrophobic side and small contact angles on the hydrophilic side are desired. Furthermore, if the contact angle is the same on both the Al and Cu, then the net force is zero. This is different from the traditional capillary effect in thin tubes, where the contact angle associated with the tube wall determines the total capillary force. It is also important to note that Eq. (2) only gives the contribution of the surface tension force acting on the droplet. There are other forces that act as retention forces on the droplet to hinder its motion such as contact angle hysteresis, pinning forces due to surface defects, and the hydrophilic/hydrophobic discontinuity line.[20,21] The shape of the front of the droplet does not affect the gradient force, as long as the width perpendicular to the axis of motion remains the same.[22] Thus, approximating the contact line as a circle does not invalidate the conclusions made in this study. As the droplet moves forward, more of its contact line is over the Al and the net force becomes smaller because of the finite size of the droplet. Fig. 4(c) shows the variation of the net capillary force in Eq. (2) as a function of travel distance x for a droplet of radius 1 mm placed on a triangular wedge for three different angles—namely, 4°, 10°, and 15°. It is seen from this figure that the capillary force induced by the wedge-shaped gradient can be significantly larger than the gravitational force on the droplet. Although the gravitational force plays no direct role in the horizontal motion of droplets on flat surfaces, it is crucial when considering motion on inclined surfaces.

The mode of motion of the water droplet is distinctly different for narrow triangles (i.e., smaller wedge angles) than for wide triangles (i.e., large wedge angles) as observed in Fig. 3. This might be because the net capillary force is too small to overcome the other retention forces and produce an overall motion of the droplet initially. As shown in Fig. 5, in the case of small wedge angles, a thin precursor film moves forward wetting the whole Al triangle, while the main part of the droplet stays in place without moving. Then, the main droplet begins shrinking as it gets pulled by the precursor film and slowly consumed by the water already over the Al. This process takes significantly longer and is quite similar to a process called "droplet coarsening."[14,23] During coarsening, two droplets placed close to one another on a wetting surface merge together through a thin wetting film that
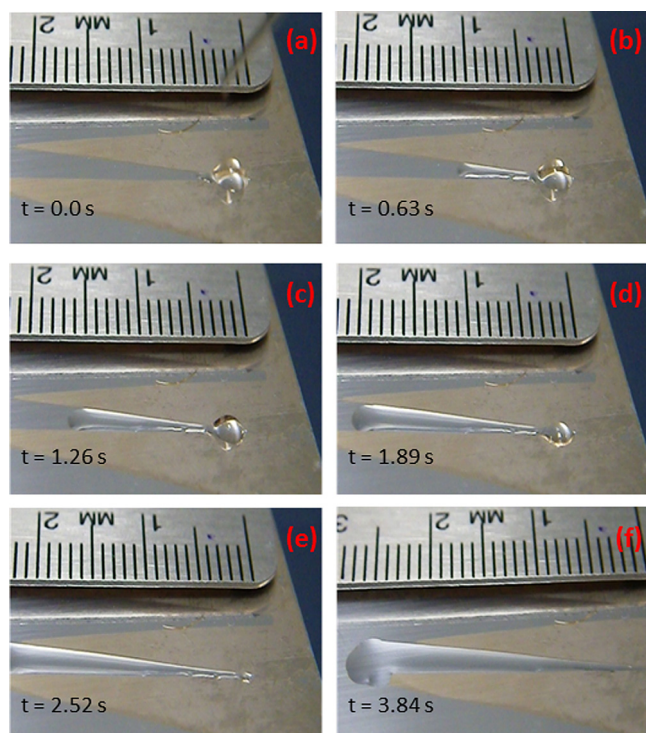
FIG. 5. Pictures showing the precursor film linking the main droplet to the dispersed water film on a narrow wedge. This mode of water droplet motion is different from the motion of droplets on wide wedges and is similar to a process called "droplet coarsening."

extends between them. The droplet with the higher internal (Laplace) pressure flows into the one with the smaller pressure. Despite this difference in the mode of motion, similar travel distances of 2 to 3 cm are observed over a range of droplet sizes.[24]

    Water droplet motion was also observed vertically against gravity on these surfaces (not shown). This supports our analysis in Fig. 4(c) which shows that the capillary force resulting from these wedge-shaped gradients can be significantly larger than the gravitational force.

    In conclusion, we have developed a simple process for creating a shape-induced surface tension gradient on an Al/Cu surface. Cu is selectively made hydrophobic while Al

remains super-hydrophilic for several days with the difference in contact angles exceeding $110°$. Water droplets placed at the tip of an Al triangle spread out and move spontaneously towards the base of the triangle to avoid contact with the Cu, both on horizontal and vertical surfaces. Two different modes of water droplet motion have also been observed. Either all parts of the droplet move (at different speeds) or a precursor film forms and then slowly pulls the droplet towards the Al. This behavior was observed for droplets ranging in volume from approximately 2 to 80 μl.

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[24]See supplementary material at http://dx.doi.org/10.1063/1.4802926 for evidence of the precursor film and droplet motion for droplet volumes larger than 80 μl.