DROPS WITH A SENSE OF TOUCH

TEXT: CHRISTIAN SCHNEIDER

It is such a common sight that it seems downright banal: at some point, almost everyone has likely watched raindrops run down a windowpane. So, it may come as a surprise that there is still fundamental scientific knowledge to be uncovered about how drops travel over surfaces. Research on drops is precisely what a team from the Max Planck Institute for Polymer Research has succeeded in doing – and they've opened up surprising potential applications in the process.

A train ride in the rain: you've finally managed to get into your train seat after the frantic rush of the station; now you can catch your breath and watch how the raindrops dance on the windowpane. Initially, many of the drops stay wherever they land. Eventually they start to trickle. Once the train picks up speed, things really start to move. When does a drop start to run? Where will its trajectory head? Will it grow longer and become a small trickle, through which more rainwater will run down?

Hans-Jürgen Butt, Doris Vollmer, and Rüdiger Berger from the Max Planck Institute for Polymer Research in Mainz share a fascination for the movement of drops – it has inspired their work for over ten years now. "I already knew about the friction of two solids from school," says Rüdiger Berger, who heads a research group at the Max Planck Institute in Mainz. "But understanding the friction between a drop and a surface: that I found exciting." The researchers wanted to know, for example, whether drops roll or slide. They also wanted to understand the precise ways in which surface characteristics affect how drops move, as well as the tracks that drops leave on surfaces.

Director at the Mainz-based institute, Hans-Jürgen Butt, explains the solution to many of these questions: "The microscopic processes at the three-phase contact line are of particular interest to us." The three-phase contact line is the line where a liquid drop, such as water, meets a solid surface, such as glass, and a gaseous component, such as air. In scientific jargon, each of these three elements is referred to as a "phase."

The angle that the drop forms with the solid surface is strongly affected by the nature of the surface. While a water drop will lay flat like a flounder on a surface that is highly hydrophilic – that is, a water-loving surface – it will bead into a pearl on a surface that repels water. Which of these wetting properties are needed in each case depends on the application: "For printing or coating surfaces, and

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PHOTO: RÜDIGER BERGER / MPI FOR POLYMER RESEARCH

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Set the scene: Researchers at the Max Planck Institute for Polymer Research are studying the behavior of drops on surfaces. Among other things, they make water bead over slopes. To make the drops more visible on the photo, the water was dyed with two different colors.

also for 3D printing, the drop needs to remain in the same place until it dries," explains Doris Vollmer, who heads a research group in Butt's department. "Conversely, for eyeglasses, cameras, or even car windows, you want to have a clear view again as quickly as possible – so a water-repellent surface is better in these cases." A water-repellant surface is important for solar cells as well, to allow drops to roll off their surface quickly and carry away as much dirt as possible. A clean surface is a must in order to keep the electricity yield high, especially in desert regions with a lot of sand and little rain.

The lotus leaf literally takes such water-repellent qualities to the extreme: it is made up of tiny columns and, using this trick, drastically reduces the contact area with the drop. On the surface of the lotus leaf, water drops form an almost perfect sphere that can only be kept on the leaf with great skill: if the leaf tilts just a little, the drop rolls off. "Here, you can clearly see the connection between the contact angle and drop friction," Vollmer explains. "The more water-repellent a surface is, the more spherical the drop becomes – and the less friction there is with the surface."

It all comes down to the surface

To learn more about the interaction between drops and surfaces, the team employs a modified instrument that can measure contact angles between liquids and surfaces. The roughly half-meter-high device consists of a metal frame that resembles a portal and a sliding table about the size of a palm. The surface to be examined is attached to a plate. The researchers place a drop on this and fix it using a little trick: "We first tried to hold the drop with a pointed wire end while the table moved underneath," Berger says. "But this kind of needle is often just pulled through the drop. So, to hold it in place, we added a tiny ring to the end of it – it's a bit like putting a crown on a drop."

The wire bends elastically as the researchers move the table beneath the fixed drop, providing a measurement of the frictional force acting between the drop and the surface. The team measures how much the wire bends using a camera. The magnitude in bending provides a map of the surface showing where there is friction and how much. Rüdiger Berger demonstrates the measuring concept on a surface on which the team has written an M using a particularly water-repellent substance. The M is clear to see in the friction map because the drop pulls on the wire with less force there. No other technique is as direct and quick at mapping the wetting characteristics of any surface or liquid. This measurement concept is also interesting for technical applications, as Berger explains: "With the help of this microscope, for instance, we can see even the smallest imperfections on surfaces. These imperfections are about the size of a hair, or a tenth of a millimeter, and are too small to be felt by hand." This is relevant, for example, if you want to check the homogeneity of paint layers. The drop can be used here as a probe to detect cracks, for instance, because a crack produces more friction between the surface and the drop. "We use it to detect imperfections that are far smaller than the drop, because only the contact line sticks to it," Berger explains.

SUMMARY

The more hydrophilic a surface is, the more the friction between water drops and the surface increases. Drop friction increases at tiny cracks and other imperfections in surfaces making it possible to evaluate, for instance, the quality of coatings.

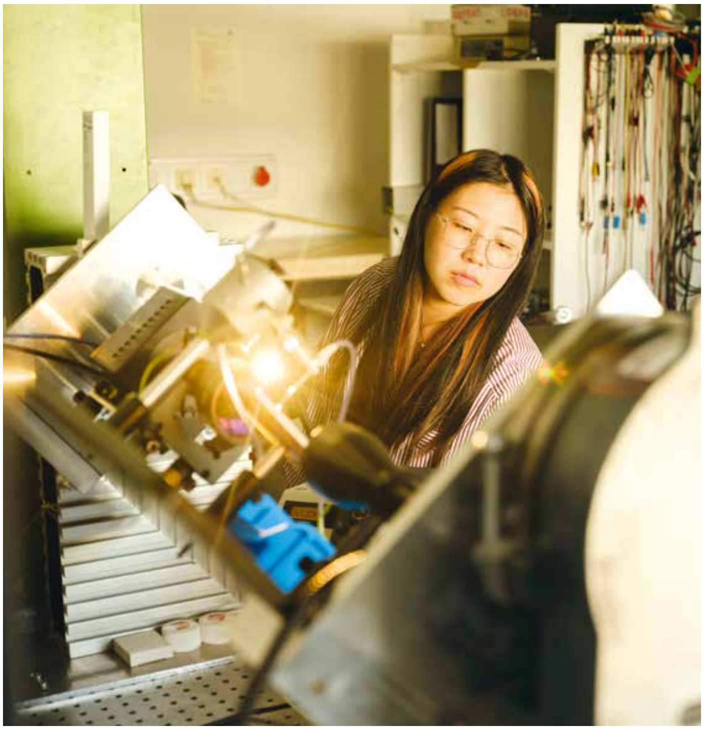
Water drops change many surfaces. For example, the outer layer of a glass pane swells, and some of its chemical components dissolve into a drop.

Sliding drops can generate charges on surfaces. This effect can be used for drop transport in microchip laboratories.

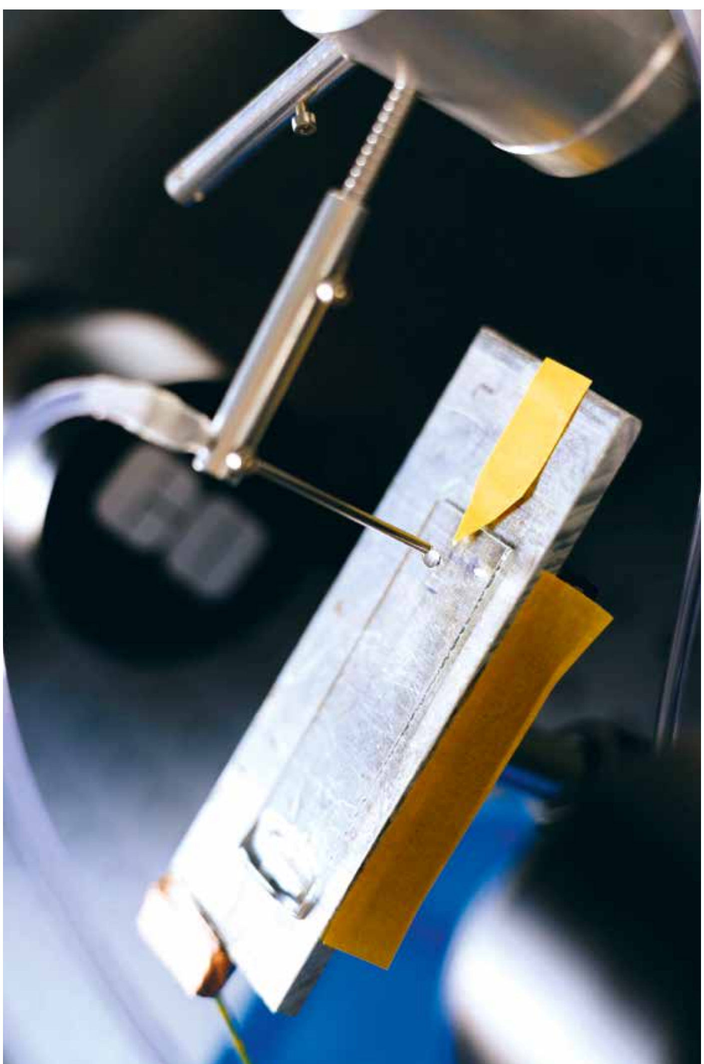
Hamburg-based company Krüss, which specializes in the creation of scientific measuring instruments, including those for surface analysis, has also acknowledged the benefits of the method. Krüss now wants to make a device based on Berger's team's research commercially available. According to Thomas Willers, Head of Applications Engineering and Science at Krüss, the research coming out of Mainz is exciting because it makes it possible to scan surface characteristics that cannot be measured with the company's other equipment. Measuring drop friction, he says, will result in new applications in surface analysis.

When exposed to water, some surfaces, like paint layers, remain stable, but other surfaces undergo processes that alter them. These surface alteration processes occur more often than one might think. The effect can be observed when it rains on a windowpane: if two drops flow down the pane, they will often take the same path. "This is because the glass surface changes when a drop runs over it," says Hans-Jürgen Butt. "You can think of it as the silicon dioxide surface swelling up a bit. It then becomes more water-loving." The result: the second drop takes the hydrophilic path defined by the first.

From a physical standpoint, describing these processes is anything but trivial: how does the surface adapt to a drop? And how quickly does it do this? To address these questions, the researchers developed a general model that can describe the interaction of drops with different surfaces. With the help of this adaptation model, they can better explain the effects of drops running



A slide for drops: Yuwen Ji measures the friction of drops on a surface that she has tipped with the bearing of a discarded lathe. This setup allows the team from Mainz to determine how quickly the surface and the liquid interact with each other.



At the end of a fine cannula, water slowly emerges and forms a drop. When this is heavy enough, it detaches and beads in a downwards direction on an inclined glass plate.

PHOTOS: KATRIN BINNER FOR MPG

over surfaces – and perhaps open up new fields of application at the same time.

Berger's team developed another instrument for the study by removing components from an old lathe and repurposing them. The first thing that catches the eye is a sizable black plate that can be tilted with the aid of the lathe's bearing. At its center is the core of the structure: a small plate attached to a holder, over which drops of water glide at regular intervals. Researchers are able to control how quickly the drops on the slope develop with the variable tilt angle. A high-resolution camera that records at 2000 frames per second records them on their way down. The images are used to measure the contact angle, both at the front and the back of the drop because the flow motion causes the two angles to differ. While the drop curves bulbously at the front, i.e. on its downward-facing side, it drags a kind of trail behind it at its end – unless the surface is extremely water-repellent.

A race down the slide

The researchers used their self-built drop-track to investigate, among other things, whether drops roll or slide. Do the water molecules in the drop rotate in a circle as though they were in a wheel, or is the drop motionless within itself as it glides over the surface? However, the experiments show there is no general solution to this question. How the molecules behave depends, among other things, on their position in the drop and on the surface. The drop's outer molecules rotate on surfaces that are more hydrophilic, as in a wheel. However, the further inside the particles are, the more they flow parallel to the drop path. The interaction between the various effects also influences friction, which in turn affects the drop's shape. The speed at which the surface is changed by the drop also plays a role. This gave the team an

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idea, which they worked out together with a group from the Vidyasirimedhi Institute of Science and Technology in Thailand led by Daniel Crespy, a former team leader at the Max Planck Institute in Mainz: could not the speed of the drops and their interaction with the surface determine the speed at which medical active ingredients dissolve from a carrier polymer in the body, for example, in the blood? "In the future, these special polymers could be used to create nanoparticles, such as those needed for medical therapies," explains Rüdiger Berger. The development of these particles depends significantly on how quickly the polymer delivers the active ingredient; however, this question cannot be resolved using standard analytical tools such as nuclear magnetic resonance spectrometers. These technologies are too slow to record some processes, which can sometimes be extremely fast.

With the drop slide, on the other hand, the team led by Rüdiger Berger and Daniel Crespy can precisely track the delivery of the active ingredient using a sophisticated indirect approach. The researchers repeatedly send drops across the surface, which they have previously coated with the active ingredient-loaded polymer. When doing so, they start with a relatively steep trajectory and gradually reduce its tilt angle, which causes the drops to become slower and slower. A drop eventually comes into contact with the surface for a sufficient amount of time for the active ingredient to dissolve. The remaining surface changes the contact angle, which the researchers image with their high-speed camera. "Adjusting the drop velocity provides a method for studying quick processes on surfaces, such as reaction rates."

Drops not only chemically interact with surfaces, but also electrically: depending on the material they roll over, they leave a more or less strongly charged track on the surface. "The underlying effect is not new, but the fundamentals have not yet undergone quantitative research," explains

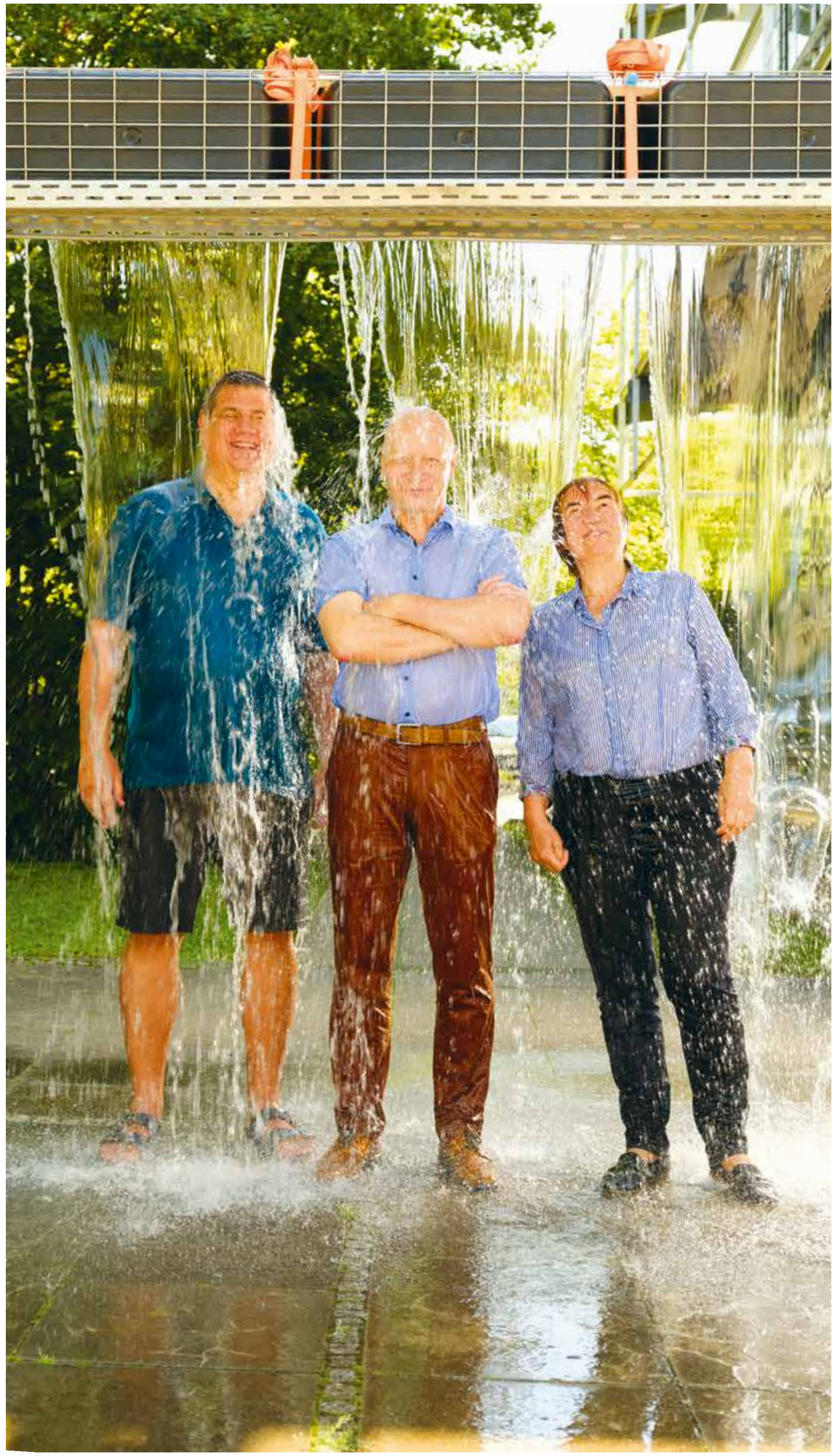


PHOTO: KATRIN BINNER FOR MPG

In their element: In a self-experiment, Rüdiger Berger, Hans-Jürgen Butt, and Doris Vollmer (from left) test their own wetting characteristics under an artificial waterfall.

Hans-Jürgen Butt. “Even before 1900, it was known that water drops can cause electrification in waterfalls.” This effect was not studied again until the mid-1990s, this time in the semiconductor industry. There, the charge generated by liquids used in manufacturing became a problem because it damaged the chips. Hans-Jürgen Butt and his team have been working on an EU-funded project since 2021, to better understand what exactly occurs during the electrical exchange between the drop and the surface. Here, findings could result in as yet unforeseen applications.

Electrifying drops

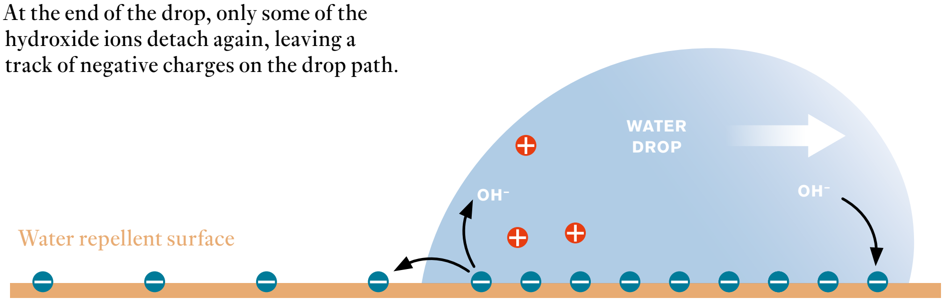
The researchers initially believed the first result of their study was an error. “At first, we thought we weren’t getting the measurement right,” Butt recalls. Each drop showed a different charge – in some cases the charges differed by a factor of three to four. But in the meantime, the team found out that the charge and behavior of drops are highly dependent on what has happened on the surface beforehand. How many drops have already run down the surface and in what time interval? How high is the humidity, for example? Humidity slowly degrades the charged track.

Hans-Jürgen Butt’s team has created a theoretical model based on experimental studies that accurately describes how strongly different liquids charge various surfaces and how this affects the liquids’ wetting characteristics. “The charge on a surface plays a much bigger role in wetting than we thought,” Butt says. In addition, the team demonstrated that drops hitting a water-repellent material leave charges on it. The generated charges depend on the falling height of the drop. The Mainz researchers and a team led by Xu Deng – a former doctoral researcher at the institute and current professor at the Chinese University of Chengdu – came up with the idea of dropping numerous drops close to one another from various falling heights in order to create a track of increasing or decreasing charges. This trail remains even when the surface dries. The result is a kind of conveyor belt that transports more drops at high speed between two points, and even over curved tracks or up a slope. The process virtually eliminates all liquid loss from the super water-repellent surface, allowing the electric drop transport to maneuver samples through a lab on a microchip. Many research institutions around the world are developing such tiny labs, as they could form the heart of small mobile devices for science or medicine. The miniature laboratories could make many examinations easier, particularly in medical diagnostics. On the other hand, it is uncertain whether slide electrification could ever be used to generate electricity. Even if sufficiently large charge differences could be generated using this method, it will not be easy to utilize them as a voltage source. That said, it might be worthwhile to experiment with appropriate technology for mobile power supply in tents, for example. And perhaps the drops’ electrical tracks will turn out the same way as other discoveries made by the Max Planck Institute for Polymer Research team, driven by their fascination with drops: they could result in applications that might not seem obvious at first, but in which the drop solution accomplishes the goal more effectively than alternative methods.

GLOSSARY

THREE-PHASE CONTACT LINE
is the name of the line where, for example, the water of a drop, a solid surface, and air meet. The more hydrophilic a surface is, the smaller the angle between the drop and the surface.

SLIDE ELECTRIFICATION
is the term used to describe the charging of a surface by friction, such as by a drop of water.



Electric tracks: When a drop slides over a surface, negatively charged hydroxide ions deposit on the surface, while the positively charged protons remain inside. At the end of the drop, only some of the hydroxide ions detach again, leaving a track of negative charges on the drop path.

GRAPHIC: GCO BASED ON A TEMPLATE BY BUTT, H.-J. AND BERGER, R., PHYSIK JOURNAL 20 (2021) NO. 4, WILEY-VCH GMBH.

"Freedom of teaching and of opinion in book or press is the foundation for the sound and natural development of any people." This quote by Einstein is on display at the Shanghai World Expo Museum – in a country that has severely restricted academic freedom in recent years.

PHOTO: ANNA L. AHLERS / MPI FOR THE HISTORY OF SCIENCE