

## TECH BEAT

Dr. Neil Canter / Contributing Editor

# Drop friction

*Researchers explore how friction affects the movement of liquids on a solid surface.*

**A** better understanding of friction at the macroscale and the nanoscale has been the subject of much research and a number of articles in TLT. We all know that a solid object placed on a surface can be moved once frictional forces are overcome.

The force needed to push the object is proportional to the object's weight or load. A heavier object has a greater contact area with the surface than a lighter one and, as a result, has more friction to overcome in order to move. This is the basis for Amontons' laws of friction.

In a previous TLT article, work was done to show that friction at the nanoscale is consistent with what is seen at the macroscale.<sup>1</sup> Both effects are dependent upon the roughness of the surface. In the case of the nanoscale, roughness is defined by the number of atoms that interact between two surfaces.

**An instrument called the Centrifugal Adhesion Balance can generate any combination of normal and lateral forces to assess the ability of an object (a drop in this study) to remain on a surface.**

An important aspect of friction that has not been explored is how friction affects the movement of liquid drops on a solid surface. As most of the lubricants we work with are liquids, this should be an important consideration in selecting a product for a specific application.

Rafael Tadmor, associate professor of chemical engineering at Lamar University in Beaumont, Texas, started looking into this issue after seeing a difference in performance between drops based on oleic acid compared to stearic acid. He says, "We were studying different coatings used for the stabilization of ferric oxide colloidal dispersions, which form magnetic fields utilized to seal computer hard drives. An oleic acid coating results in a stable dispersion in hexadecane, but a stearic acid coating cannot form a stable dispersion in the same medium."

"Placing a hexadecane drop onto a mica surface treated with the salt derivatives of two surfactants showed very different results: The drop wetted and spread on the oleic acid-derived surface but formed a well-defined drop on the stearic-derived surface. This showed that the oleic acid is solvated by the hexadecane while the stearic acid drop is not."

The structure of oleic acid and stearic acid only differ in that the former has a double bond between the ninth and tenth carbon. Yet, they produced markedly different wetting properties. This result prompted Tadmor to use drops as a sensitive tool for surface characterization and eventually to take a closer look at the frictional behavior of liquid drops on surfaces.

## KEY CONCEPTS

- **The effect of friction on the movement of liquid drops on a solid surface had not been previously examined.**
- **The Centrifugal Adhesion Balance measures the changes in friction for drops situated at any particular angle on a surface.**
- **The lateral forces needed to move pendant drops are higher than those for sessile drops. This differs from what occurs in moving a solid object on a surface.**

**‘We found that the lateral forces needed to move pendant drops are higher than those for sessile drops. This means that less force is required to move a droplet with a greater contact area on the surface, which differs from what we know about a solid object on a surface.’**

### **CENTRIFUGAL ADHESION BALANCE**

Tadmor and his research group built an instrument called the Centrifugal Adhesion Balance (CAB) that can generate any combination of normal and lateral forces to assess the ability of an object (a drop in this study) to remain on a surface. An image of the apparatus is shown in Figure 1.

The cylinder at the right end of the CAB is a closed chamber that contains a camera and a light source. In between the two is a surface on which a drop can be applied. To the left of the chamber is a control box that takes data from the camera and sends it wirelessly to a nearby computer. Further to the left of the control box is a counterbalance.

Underneath the table holding the CAB is a DC motor that is used to rotate the cylindrical chamber containing the drop.

By tilting the chamber, the normal and lateral components of the centrifugal force as well as those of gravitation force are varied. By controlling both the tilt and the centrifugal acceleration, any combination of normal and lateral force can be obtained.

The researchers measured the change in friction for hexadecane on various surfaces. Drops are situated initially at angles of 0 degrees and 180 degrees. This corresponds to a sessile drop and a pendant drop, respectively. The former is a drop that rests on a surface, while the latter is a drop literally hanging from the surface.

The drop is moved to a particular angle and allowed to rest for a specific time. Then the CAB arm is slowly rotated with a slowly increasing angular velocity until the drop starts to slide along the surface.

Tadmor says, “We found that the lateral forces needed to move pendant drops are higher than those for sessile drops. This means that less force is required to move a drop with a greater contact area on the surface, which differs from what we know about a solid object on a surface.”

In other words, greater friction is seen for a pendant drop than a sessile drop.

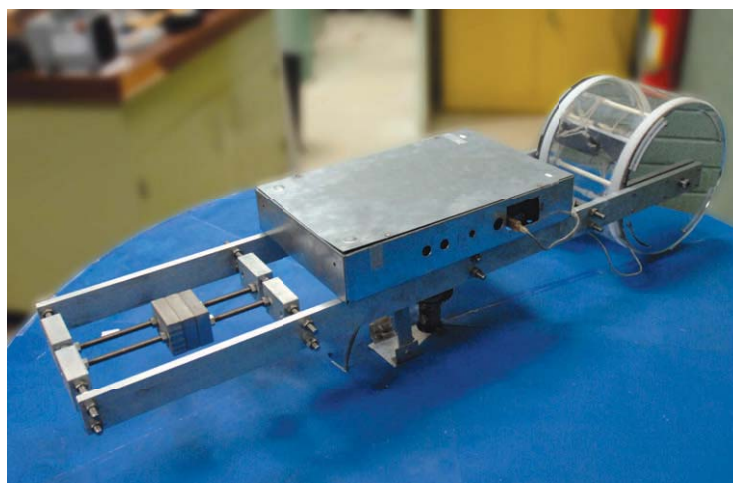
While seemingly counterintuitive, this result is consistent with current thinking about how drops move on surfaces. In the case of a pendant drop, the gravitational force works in the same direction as the pulling of the solid surface by the drop’s surface tension. This factor leads to a molecular

orientation that creates a stronger intermolecular interaction between the drop and the surface. On the other hand, when a drop is resting in a sessile fashion, the gravitational and surface tension forces act in opposite directions, resulting in a weaker drop-surface intermolecular interaction.

Some experimentation was tried with water drops, which seem to exhibit the same behavior but it was more difficult work with this material. Tadmor says, “We

worked with water, but factors such as evaporation made it very difficult to maintain fixed conditions. The high surface tension of the water also served to destroy some of our surfaces.”

Future work will be conducted in different media, including the use of silane grafted onto a silica surface. Additional details about this research can be found in a recent paper<sup>2</sup> or by contacting Tadmor at [rafael.tadmor@lamar.edu](mailto:rafael.tadmor@lamar.edu).



**Figure 1 | The Centrifugal Adhesion Balance is used to measure the lateral forces needed to move a drop at any particular angle to a surface. [Courtesy of Lamar University]**

### **REFERENCES**

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# Rapid dispersion of particles

*These solids are capable of dispersing quickly when placed in a liquid medium.*

## KEY CONCEPTS

- Solid particles quickly disperse when placed into a liquid medium.
- This phenomenon occurs because the particles pick up energy after displacing water from the air-water interface. This acquired energy enables the particles to rapidly oscillate, leading to the generation of repulsive hydrodynamic forces that cause the fast dispersion.
- Smaller particles disperse faster than larger ones. As a result, the speed of dispersion increases as the number of particles dropped into a liquid also increases.

**S**olid lubricants such as molybdenum disulfide and polytetrafluoroethylene are very effective at reducing friction and increasing the load-carrying capacity of lubricants. Due to the insolubility of these materials in oil and water, introducing them into liquid lubricants has proved to be a challenge.

This problem is overcome by placing the solid lubricants into stable dispersions in either oil or water. Typically, the concentration of the solid lubricant in the dispersion can range from 10% up to 35%.

With the increasing interest in nanotribology, researchers are looking to also find carriers or solvents to utilize these small nanoparticles in liquid lubricants. A recent TLT article discussed the development of a dispersion of nanoparticles of potassium borate in an ester matrix.<sup>1</sup> This borate-based lubricant additive can be used in oil- and water-based lubricants.

But not much is known about why solid particles quickly disperse when introduced into a liquid medium.

Figure 2 shows the process as a solid material such as flour introduced into water. Images are taken 0.033 seconds, 0.161 seconds and 0.363 seconds after the solid is added to the water shows the rapid rate of dispersion.

Pushpendra Singh, professor of mechanical engineering at the New Jersey Institute of Technology in Newark, N.J., says, “This is an experiment you can do at home in your kitchen by filling a dish with water, waiting a few minutes for the water to become still and then adding a solid such as flour or finely crushed pepper.”

Singh notes that a few milligrams of a solid can fill the entire surface of the water almost instantaneously. The reason for why particles react in this violent fashion has not been known until now.

## REPULSIVE HYDRODYNAMIC FORCE

Singh and his researchers determined that the rapid dispersion of particles is due to the development of repulsive hydrodynamic forces that arise because, as the particles are adsorbed at the interface, they move rapidly in the direction normal to the liquid surface. Glass and mustard seed particles ranging in diameter from 10 microns to 1.1 millimeters were dropped into water, corn oil and glycerin. The velocity of the particles was measured through the use of a video camera.

Singh says, “Once a solid particle comes into contact with a liquid, it is pulled

**‘Once a solid particle comes into contact with a liquid, it is pulled down into the liquid by a force due to the interfacial tension and establishes an equilibrium position of the particle at the interface between the liquid and the air.’**

## An interesting aspect of particle dispersion is that the speed of the particles increases as the number of particles dropped into a liquid also increases.

down into the liquid by a force due to the interfacial tension and establishes an equilibrium position of the particle at the interface between the liquid and the air. The extent to which the particle goes below the surface is dependent upon its weight, the interfacial force and the contact angle of the air-liquid interface.”

For example, Singh notes that a particle with a contact angle of 90 degrees must move downwards by a distance equal to its radius, assuming it is spherical. The particles will then oscillate up and down about their equilibrium height at the interface. He adds, “The particle oscillates in a similar fashion to an under-damped spring-dashpot system. The frequency of this oscillation for a mustard seed with a diameter of 1.2 millimeters is approximately 83 Hertz.”

This process leads to a decrease in the interfacial energy. Singh explains, “The decrease in the energy is due to the decrease in the area of the air-water interface, a part of which is replaced by the particle. A large fraction of the released interfacial energy is transferred to the particle.”

As the particle rapidly oscillates to dissipate the acquired energy, it forces the liquid around it to move away and give rise to repulsive hydrodynamic forces that cause particles to disperse. Singh says, “Particle velocity at the air-water interface can be as high as 47 meters per second (or 168 kilometers per hour).”

The speed of the particle, assuming all other parameters are fixed, is dictated by its size, according to Singh. As the radius decreases, the mass decreases to a much larger extent (decreases as the third power of the radius) than the interfacial energy acquired by the particle (decreases as the square of the radius), which means that smaller particles disperse at a faster rate than larger ones.

Fluid viscosity plays a factor in slowing down the speed of the particle. Singh says, “As the fluid viscosity increases, it acts to reduce the particle’s speed, which then lowers the rate of dispersion.” The researchers found that speed of the dispersion of glass particles in water is three times faster than in a solution of 60% glycerin in water. The latter exhibits a viscosity that is six times higher than water.

An interesting aspect of particle dispersion is that the speed of the particles increases as the number of particles dropped into a liquid also increases. Singh explains, “Repulsive hydrodynamic forces that arise as two particles are adsorbed near each other at the interface are stronger, because each particle creates an outward flow and the net sum of the flow is higher than for an individual particle. This result means that the rate of dispersion will increase, even more as the number of particles increases above two.”

Singh indicated that this phenomenon was determined not only through experimentation but also by the use of direct numerical simulation. When a cluster of particles is dispersed, the researchers found that the particles moved in a radial direction away from the center, as seen in Figure 2. The final radius reached by the particles also increases

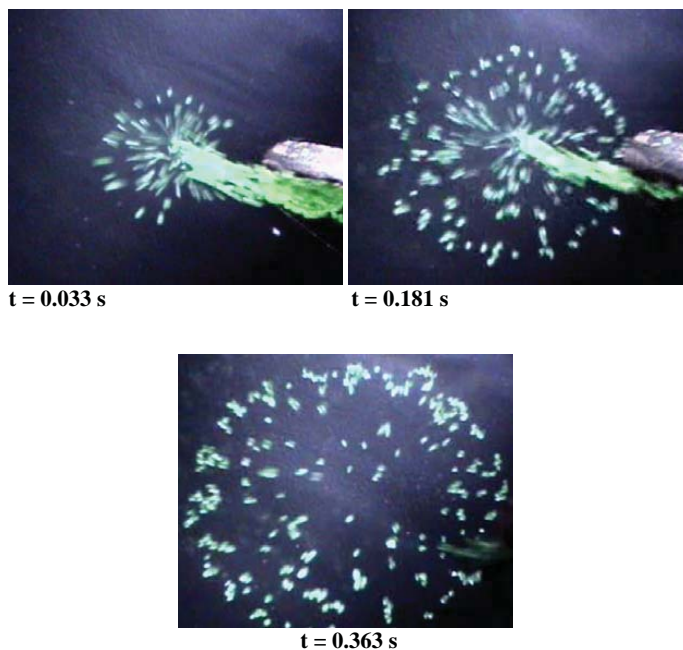


Figure 2 | The dispersion process is so explosive that after 0.363 seconds the solid has moved through the liquid. [Courtesy of the New Jersey Institute of Technology]

as a function of the number of particles.

The chemical structure of the particle and its polarity with respect to the liquid medium do not impact the rate of dispersion, but the addition of a surfactant can reduce dispersion speed significantly. Singh says, “Surfactants adsorbed in the interface act to reduce surface tension. This effect leads to a reduction in the energy that can be transferred to individual particles, thus reducing the rate of dispersion.”

Singh found that even using soap to wash the lab equipment used in the experiments adversely impacted the rate of dispersion. He says, “We had to clean the glassware without using surfactants in order to not affect the results.”

Further information can be found in a recent paper<sup>2</sup> or by contacting Singh at [singhp@njit.edu](mailto:singhp@njit.edu).

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# New blue pigment

*An unexpected process was found to develop a new, more environmentally friendly blue.*

## KEY CONCEPTS

- The current blue pigments have been used for a long time but are either environmentally hazardous or suffer from durability issues.
- An unexpected process has been found to develop a new blue pigment by incorporation of manganese dioxide into other metal oxides.
- These manganese-based oxides are not toxic, although they are quite stable and display good durability in initial testing.

In many cases, the last feature looked at in a lubricant is its color. At times we are so busy making sure that a specific product has sufficient lubricity, extreme pressure characteristics, corrosion inhibition and foam control to worry about such an aesthetic as appearance.

But the color of a lubricant can be important to the end-user. For example, an end-user working with metalworking fluids prefers to have products that are blue in color. If a supplier decides to have the identical fluid dyed red and evaluated by the end-user, the chances are the red-colored metalworking fluid will fail because of the preference for blue.

Typically, lubricant companies work with oil- and water-soluble dyes that are used in small quantities. In some cases, complaints are received about the durability of the dye, as it may change color during use.

The current types of blue pigments have been available for some time. For example, Egyptian blue (calcium copper silicate) has been known since the time of the pharaohs. Other blue pigments include Cobalt blue, Han Chinese, Maya blue, Ultramarine, Prussian blue and Azurite.

**‘Many of the currently used blue pigments are either environmentally hazardous or suffer from durability issues. Cobalt is highly toxic and Prussian blue evolves hydrogen cyanide under acidic conditions. Ultramarine and Azurite are not stable under high temperature and acidic conditions.’**

Mas Subramanian, Milton-Harris professor of materials science at Oregon State University in Corvallis, Ore., says, “Many of the currently used blue pigments are either environmentally hazardous or suffer from durability issues. Cobalt is highly toxic and Prussian blue evolves hydrogen cyanide under acidic conditions. Ultramarine and Azurite are not stable under high temperature and acidic conditions.”

Development of a new, more environmentally friendly blue pigment would be welcomed. Such a pigment has just been prepared.

## YITTRIUM INDIUM MANGANESE OXIDES

Subramanian found that preparation of solid solutions of yttrium oxide, indium oxide and manganese dioxide at temperatures between 1,100 C and 1,200 C produces a bright blue solid. He says, “This product is an unexpected result as yttrium oxide is a white solid, indium oxide is a yellowish white solid and manganese dioxide is a black solid.”

## 'We know that this new type of blue pigment is heat stable, but it is also not attacked by acids and bases. The color also appears not to fade after durability testing.'

Subramanian indicates that the blue solid was developed by accident. He explains, "We were originally looking to develop materials that display both ferroelectric and ferromagnetic properties. Materials that can be both photoelectric and magnetic simultaneously are not known."

Subramanian relates that a graduate student took a bright blue solid out of a hot furnace as he was walking through the lab. The intensity of the blue color made him realize that something unique had just been prepared.

As the stoichiometry of the metal oxides is changed, the color of the resulting pigment can change from blue to black. Figure 3 shows a number of images of the yttrium indium manganese oxides at various concentrations of manganese. In moving from left to right, the manganese concentration increases,

leading the color of the solid to darken. Finally, yttrium manganese oxide is found to be black, as noted by the image on the extreme right of Figure 3.

The intense blue color of the yttrium indium manganese oxides is due to the coordination of manganese atoms into an unusual trigonal bipyramid structure. Subramanian says, "This gives rise to splitting in energy levels in manganese's d orbitals that result in strong absorption in the red/green region of the visible spectrum and changes the color of the samples to intense blue."

Initial evaluation of the yttrium manganese oxides has been in pigment and paint applications. Subramanian says, "We know that this new type of blue pigment is heat stable, but it is also not attacked by acids and bases. The color also appears not to fade after durability testing."

Subramanian indicates that he knows of no conditions under which this new blue pigment fades. These metal oxides are not soluble in water but potentially could be dispersed in this medium. He speculates that some of the paint companies are using this approach.

The intense blue pigment can be prepared by introducing manganese into other metal oxides to prepare the trigonal bipyramid structure. Among the examples are scandium aluminum magnesium oxide, lutetium gallium magnesium oxide and indium gallium magnesium oxide. Subramanian adds, "We needed to add 5% manganese to these oxides to generate the intense blue color."

Another benefit of using this combination of metal oxides is that they are all more environmentally friendly than other blue dyes. Subramanian says, "Indium oxide, yttrium oxide and manganese dioxide are not toxic."

Future work will involve development of less expensive metal oxides that can act as blue pigments. Subramanian says, "We are particularly interested in preparing metal oxides that are more cost-effective by limiting

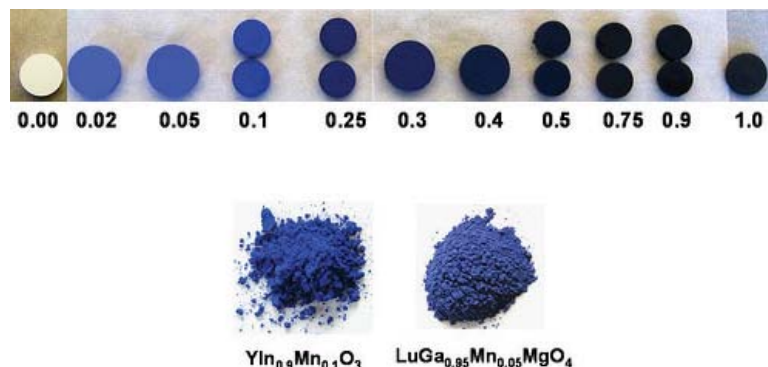


Figure 3 | Addition of manganese oxide into yttrium indium oxide leads to the preparation of a blue pigment. As the concentration of manganese increases in moving from left to right, the color of the pigment darkens until it becomes black as yttrium manganese oxide. [Courtesy of Oregon State University]

the indium content."

With the development of this new series of pigments, the possibility exists in the future that they can be utilized to provide an intense blue color that will be enjoyed by lubricant formulators and users.

More information on this work can be found in a recent paper<sup>1</sup> or by contacting Subramanian at [mas.subramanian@oregonstate.edu](mailto:mas.subramanian@oregonstate.edu).

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