Introduction

Liquid surfaces act as if they are in tension (Fig. 1). The thread is pulled into circular arcs. This pull, called surface tension, exists with all liquid surfaces and is uniform in all directions. Surface-tension forces affect the shapes and the motions of liquids that have open surfaces.

The film in Fig. 1 would contract if free to do so. It also will enlarge if the string is pulled down, as in Fig. 1b. The string performs work, pulling more molecules onto the surface to make it larger.

1. Soap film on wire frame pulls thread into circular arcs. The film can be enlarged by doing work, by drawing the string down. This pulls more molecules onto the surface to make it larger.
This tension of surfaces can be understood in terms of forces between molecules. Molecules repel each other when close, attract each other when farther away, and at some in-between distance neither repel nor attract. Inside a liquid, the molecules on the average usually repel each other slightly, just enough to counteract the pressure applied by the surroundings to the liquid. But molecules at the surface are farther apart than the neutral distance, and attract each other. This attraction, or surface tension, is necessary if surface molecules are to be kept from moving from the surface into the bulk liquid.

Since all phenomena in mechanics can be explained in terms of either forces or energies, the predictions one makes about surfaces are the same whether one starts with the concept of surface tension or surface energy. Surface energy results from surface molecules having more energy than molecules in the bulk liquid; they have had, in effect, half their neighbors removed from them. Dimensionally, surface tension, often expressed as dyne-per-centimeter, is the same as surface energy, which is often expressed as ergs per square centimeter (erg/cm² = dyne cm/cm² = dyne/cm).

**Magnitude of Surface Tension**

The surface tension of a film could be calculated by measuring the pull on the string in Fig. 1. A soap film would have a surface tension of about 20 or 30 dynes/cm on each of its two sides.

Reference 2 describes better techniques for measuring surface tension. Representative values obtained are given in Table I. It is useful to remember that:

- Water has a higher surface tension than most other liquids. (Liquid metals are an exception.)
- Other molecules in water usually lower the surface tension. (Some salts are an exception.)
- Increased temperature lowers surface tension.
- Electrical conditions at interfaces can raise or lower surface tension.

### TABLE I

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Surface Tension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>73 dynes/cm</td>
</tr>
<tr>
<td>Salt water</td>
<td>75</td>
</tr>
<tr>
<td>Soapy water</td>
<td>20-30</td>
</tr>
<tr>
<td>Ether</td>
<td>17</td>
</tr>
<tr>
<td>Alcohol</td>
<td>23</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>27</td>
</tr>
<tr>
<td>Lubricating oil</td>
<td>25-35</td>
</tr>
<tr>
<td>Mercury</td>
<td>480</td>
</tr>
</tbody>
</table>

2. Intersecting soap films, between two closely spaced glass plates. Only three-film intersections are observed, because intersections of four or more films are unstable. All angles are 120°, as required by symmetry.

**Surface Tension Boundary Conditions**

Since surfaces exert forces, they force liquids into shapes and motions that differ from what they would be in the absence of surface tension. The effects can be summarized by three general rules:

- **Contact angles.** Where surfaces meet, the contact angle is determined by the energies of the interfaces.
- **Pressures caused by curved surfaces.** A curved liquid surface has a higher pressure on the concave side:
  \[
  \Delta p = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right)
  \]
- **Shear forces caused by surface tension gradients.** Variation of surface tension along a surface is balanced by shear forces in the bounding materials:
  \[
  \nabla \sigma = \tau_A + \tau_B
  \]

\(\sigma\) is surface tension, and \(R_1\) and \(R_2\) are the two radii of curvature necessary to specify curvature at a point on a surface.

These three statements describe the boundary conditions that surface tension imposes on liquids and, together with the equations for fluid mechanics, are sufficient to determine the shapes and motions. All but a few simple cases, however, are difficult to solve mathematically. Free-surface boundaries introduce mathematical complexity even into cases that look as though they should be very simple, such as a static hanging drop.

**Contact Angles**

When soap films meet, they must meet symmetrically, at 120° angles (Fig. 2). Usually, however, liquid surfaces terminate on solid surfaces, and the contact angle can vary widely, as illustrated in Figs. 3 and 4.
3. A drop of water placed on wax by means of a hypodermic needle demonstrates a liquid angle greater than 90°. Water does not wet wax.

4. Water drop on a bar of soap. The angle included by the water at the edge is less than 90°.

Contact angles are usually "explained" by an equation called Young's equation:

$$\sigma_{\text{solid/gas}} = \sigma_{\text{solid/liq.}} + \sigma_{\text{gas/liq.}} \cos (\text{contact angle})$$

which is a statement that the three surface tensions pulling at the intersection of a gas, a liquid, and a flat solid should balance along that surface. Alternately, the $\sigma$'s can be regarded as the free energies of the three interfaces, and the equation then amounts to a statement that any perturbation of a stable intersection increases the total free energy of the surfaces.

Young's equation is not very useful in practice. The surface energies of real solids are often not known. The energy of a surface over which liquid is advancing is often different from that of the same surface if the liquid has retreated. (If it were not for such a hysteresis effect, water drops could not stand still on windowpanes.) The thermodynamically correct statement would be that the contact angle will be that angle which leads to the minimum available energy of the total system, a principle even more difficult to apply than Young's equation. Hence, since contact angles typically cannot be predicted, they are usually measured.

5. The capillary rise of water (in the tube on the right) is greater than of alcohol, showing that water has greater surface tension than alcohol.

6. Water rises in hyperbolic curve between two glass plates slightly separated at the left by paper clip.

Pressure Caused by Curved Surfaces

If an interface is curved, surface tension causes a pressure difference between the fluids on each side of the interface. The pressure causes the bulge, and is therefore always higher on the concave side. A force balance for a curved surface shows the pressure difference to be:

$$\Delta p = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right).$$

Such a pressure difference causes liquid to be sucked into a crevice or a hole if it wets the wall material. In a small tube, if the liquid wets the wall, as in Fig. 5, liquid is sucked up until its hydrostatic head, $\rho gh$, balances the pressure difference, $2\sigma \cos \theta/r$, where $\theta$ is the contact angle. The capillary rise can therefore be calculated to be: $h = 2\sigma \cos \theta/\rho g r$. Between the two glass plates, Fig. 6, the liquid rises least where the glass surfaces are farthest apart. Liquid will suck itself into holes only if $\theta < 90°$, that is, if it wets the material.
7. Water drops on waterproofed cloth. Because the contact angle of the water with the treated fibers is greater than 90°, the water will not penetrate the holes in the fabric.

For that reason, the water in Fig. 7 does not penetrate the quite porous fabric.

Applied to a cylindrical jet of liquid of radius \( r \), the equation for pressure drop indicates that the pressure inside is \( \sigma / r \) higher than outside. As \( r \) gets smaller, the pressure gets higher. Irregularities in a jet therefore amplify themselves; the higher pressure in any smaller region forces liquid away, into adjacent bigger regions. Since there are always irregularities, a jet is always unstable, and pinches itself into drops. Lord Rayleigh calculated that the most unstable disturbance wavelength is about four and a half times the diameter of the jet, which is about what one sees in Fig. 8.

Other examples of increased pressures are the interiors of bubbles or drops, where \( R_1 = R_2 = r \), and the pressure excess is \( 2\sigma / r \). A soap bubble, with both an inner and an outer surface, has an excess pressure of \( 4\sigma / r \). In Fig. 9, it is that excess pressure that blows the smoke out of the soap bubble.

9. The higher pressure inside a soap bubble on the end of a glass tube expels the smoke used to blow it up, converting surface energy of the film into kinetic energy of the smoke jet.

**Bubble Nucleation**

Until recently, people have found it difficult to understand how bubbles can be generated in boiling water and other bubble nucleation systems. New bubbles, to start from a zero size, would require an initially infinite internal pressure \( (p = 2\sigma / r_{\text{in}} = \infty) \). Even an assumption that bubbles start from statistical voids, of sizes near the intermolecular distance, would require that initial vapor pressures be thousands of pounds per square inch, a situation likely only under such conditions as those accompanying collisions of high-energy particles; nuclear bubble chambers do provide new bubbles. The more common bubble sources, such as boiling and electrolysis, remained a puzzle until about 1955, when people began to adopt the idea that new bubbles are simply pinched-off enlargements of old bubbles remaining in cracks on solid surfaces. Subsequent research has supported this now generally accepted idea. Bubbles in boiling come from sites where

8. A jet of water from a faucet is unstable, and pinches itself into separate drops.

10. Bubbles in beer do not form on smooth glass, but do form at the numerous vapor-filled cavities on the roughened end of a glass rod.
vapor cavities already exist. A roughened end of glass rod has many such sites, and nucleates many new bubbles in the glass of beer shown in Fig. 10.

**Break-up of Sheets of Liquids**

A free edge of a liquid sheet moves into the sheet, pulled by surface tension. An example is a soap bubble touched by a pencil that has been dipped in alcohol (Fig. 11). A hole appears and rapidly grows larger, consuming the bubble. The alcohol ruptures the liquid sheet by reducing the surface tension of a small portion of the surface. The higher surface tension of the surrounding surface stretches the weaker region until its thickness reduces to about that of the distance between molecules, and a hole appears. Its rolling-up edge is pulled by surface tension at a velocity determined by the rate at which the momentum flux of liquid into the edge equals the pull of surface tension.

If a water jet is deflected by the end of a cylinder,

![Image 11. Soap bubble a moment after rupture by a pencil dipped in alcohol.](image11)

as in Fig. 12, the resulting liquid sheet breaks up into droplets. The rolling-up edge is unstable. The deflected sheet can have different forms, such as the water bell in Fig. 13. It can even bend back sharply upon itself, as in Fig. 14; the sheet cannot go out beyond the radius where the surface tension is equalled by the radial momentum flux of the liquid, and it is at that radius that the water changes direction sharply.

![Image 12. A water jet impinging on the end of a cylinder forms a liquid sheet. The edge of the liquid sheet continuously breaks up into droplets.](image12)

![Image 13. The liquid sheet of Fig. 12 can form a water bell, illustrating that surface tension can cause a moving liquid sheet to bend.](image13)

![Image 14. A moving liquid sheet bends back sharply upon itself, apparently violating conservation of momentum.](image14)

**Impact of a Milkdrop**

The interplay of surface forces and inertia forces is shown well in high-speed photographs of a drop of milk hitting a thin layer of water (Fig. 15). The depth of water is about half the radius of the drop. A sequence of events occurs. The impacting drop spreads sideways, meets the stationary sheet of water, and sends up a cylindrical sheet of liquid, the base of which increases in radius at a rate approximately half that of the original drop velocity. The sheet projected upwards has a leading edge, which is pulled back by the surface tension of the two sides, causing a rolled-up
surface must move in the direction of higher surface tension pull at such a velocity as to produce viscous forces in the two fluids, just balancing the gradient of surface tension:

\[ \nabla \sigma = \tau_A + \tau_B. \]

These shear forces produce movement in the fluids adjacent to the moving surface, and the moving surface in this way drags along its bounding fluids.

**Motions Caused by Concentration Gradients along Surfaces**

A simple example of surface-tension variation occurs with a limp loop of thread on water. It snaps into a circle when the water inside is touched by soap (Fig. 16).

Continuous, rapid motion is experienced by bits of camphor scraped onto water. Camphor molecules lower the surface tension. Each particle dissolves unevenly, and the higher pull on the side where it dissolves least pulls the particle along the surface. A bit of wood with camphor at one end moves like a boat (Fig. 17).

15. A drop of milk hitting a thin layer of water spreads radially, and sends up a cylindrical sheet that surface tension changes into a coronet (a). Surface tension pulls the liquid downward, some impacting at the center to send up a spike of liquid, (b), which in turn is pinched off by surface tension. All this happens in a fraction of a second.

edge. This edge is unstable, and its tendency to become drops results in a coronet-like shape of surprising regularity. This coronet is pulled down, by surface tension, and about half of its liquid moves inwards, focusing on the center where it becomes a liquid spike. This spike, like all liquid cylinders, is unstable, and the top pinches off to form a drop. Because of its upward momentum, the drop continues to move up, but the remainder of the spike is pulled back down by surface tension.

**Motions Caused by Surface-Tension Gradients**

Liquids must move when the surface tension changes along their free surfaces. A liquid cannot stay still with unbalanced forces acting on it. Consideration of the forces on a unit area of interface between a liquid, \( A \), and another fluid such as gas, \( B \), indicates that the

16. Loop of thread on water snaps into a circle when surface tension inside is reduced by soap.

17. A bit of wood with camphor at one end moves like a boat. The greater surface tension on the bow pulls the boat ahead.
18. Wine tears. Surface tension differences continually pump alcohol-water mixtures up the sides of cocktail glasses.

Another continuous motion occurs in cocktail glasses. A water-alcohol mixture sloshed around in a glass leads to "wine tears," drops that move up and down the sides of the glass (Fig. 18). Evaporation of alcohol lowers the alcoholic content of the liquid film on the glass and increases its surface tension. The surface is therefore continuously pulled from the bulk liquid up the side of the glass, pumping up liquid which accumulates to form the wine tears.

This is also why one can blow bubbles with soapy water, but not with a pure liquid. The soap film in Fig. 1 holds itself up against gravity by continuous self-adjustment, to maintain a lower proportion of soap, and therefore a larger surface tension, in the upper region of the film.

Motions Caused by Electrical and Chemical Effects at Surfaces

Electrical charges also affect the magnitude of surface tension. Electrical charges usually concentrate at surfaces where their repulsive forces on each other subtract from the surface tension. For example, mercury and dilute sulphuric acid with a bit of potassium dichromate added will form a chemical battery if another metal, an iron nail, is brought in as a second electrode. When the two metals touch, the battery is short-circuited and the charge density on the mercury surface is reduced. The mercury drop pulls up because of increased surface tension. With just the right position of the nail, the mercury will set itself into oscillation, repeatedly short-circuiting the electrical charges that build up when the mercury is not touching the nail (Fig. 19).

Mercury, in nitric rather than sulphuric acid, experiences electrical and chemical effects at the surface that cause the mercury to swim toward potassium dichro-

20. A pool of mercury in nitric acid reaches out to touch a crystal of potassium dichromate.

mate crystals (Fig. 20), at times so rapidly that it fragments itself into several drops. Surface motions are so violent that the mercury drop acts as an effective agitator, forcing convection and diffusion of the potassium dichromate throughout the liquid.

Motions Caused by Temperature Gradients along Surfaces

21. Liquid film on a thin sheet of metal is pulled away from hot spot above soldering iron by higher surface tension of surrounding, colder liquid.

Temperature gradients cause surface-tension gradients. If a layer of silicone oil is put on a thin metal plate, a hot soldering iron moved underneath the plate causes a bare spot in the liquid above. As the iron is
moved around under the plate, the bare spot moves along with it (Fig. 21). Increasing the temperature always lowers the surface tension, because it becomes easier to pull molecules up into the surface. Above the soldering iron, the hot liquid has a lower surface tension than the cold liquid around it, so the hot sur-

face is pulled to the cold regions. In moving, the surface drags away the underlying liquid, leaving the bare spot. An ice cube instead of a soldering iron causes the liquid film above to hump up over the cold region (Fig. 22).

Air bubbles will "swim" in a liquid that is uneven in temperature. The cold side of the bubble will have a higher surface tension than the warm side. It will therefore pull surface from the warm side, where surface will be generated, around the bubble to the cold end, where the surface will disappear. This movement of surface, with its viscous drag upon the boundary fluid, will pick up a sheet of liquid and jet it off the cold back end. By jetting liquid one way, the bubble propels itself the other way. It will swim up the temperature gradient. Thermodynamically, such a self-propelling bubble is a heat engine. Wherever surface is created, heat is absorbed, and wherever surface is destroyed heat is given off. Therefore a swimming bubble absorbs heat at its hot end and rejects heat at its cold end, and becomes a self-propelling heat engine. As an example of swimming bubbles, air bubbles in silicone oil in a horizontal glass tube move themselves toward the hot end of a soldering iron held against the glass (Fig. 23).

An electrically-heated horizontal wire in a mixture of acetone and about 2% water generates bubbles of acetone and water vapor at nucleation sites along the wire. At low heating rates, the bubbles, instead of rising off the wire at the nucleation sites, swim along the wire, jetting hot liquid away from their cold ends (Fig. 24). Once bubbles start moving, the wire is colder where they have been and hotter where they are going, so they just keep going to where it is hotter.

When Surface Tension Is Important

When dimensionless groups such as the Bond number, \( \rho g L^2/\sigma \), reflecting the ratio of gravitational to surface forces, and the Weber number, \( \rho V^2 L / \sigma \), reflecting the ratio of inertial to surface forces, are small, surface effects can be expected to dominate. There are situations, such as in fuel tanks of orbiting space vehicles, where \( L \), the characteristic length, can be measured in feet, yet because of a much reduced \( g \), surface tension can be a controlling force. As a general rule, however, surface tension is controlling only in small systems, of which only a few representative cases have been described above.

References