An Essay on Surface Tension

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Introduction

When a small drop of liquid is placed on a flat surface[1] it may spread out into an infinitesimally thin sheet or remain where it is placed and gather into a regular shape. There are many common examples of this. A water drop placed on a sheet of glass will often spread out continuously, wetting the surface, or it can gather into a shape resembling a plano-convex lens – a circular disk with a flat bottom and a curved top. A drop of the liquid metal mercury, on most surfaces, collects into a near spherical ball that can appear to roll across the surface quite efficiently. Water can also can do this, when it is placed on a polymer surface or when placed carefully on the surface of water that is saturated with detergent. The behaviour can be surprising. What is the physical process that determines what happens?

The answer lies in the phenomenon of surface tension. It is not confined to liquids, but it is most often noticed in systems involving a liquid component. It arises because all substances are internally bonded by molecular forces, so that the molecules within attract each other and hold the entire system together. Sometimes these forces are strong enough to make the substance solid and hold its shape when external forces or high temperatures are applied. Sometimes the forces are so weak that the molecules are easily separated from each other by a gentle increase in temperature. These systems are gases. For intermediate strength inter-molecular forces, the molecules attract one another but are unable to hold the bulk substance into a fixed shape. This is the liquid state. The different states of matter: solids, liquids and gases, are therefore distinguished by the strength of the inter-molecular forces within. But note that in all cases, the forces are attractive.

A molecule deep in the bulk substance experiences forces from all directions. On average these forces are symmetrical, which means the molecules are not pulled in any particular direction. However, molecules near a surface, with no substance on the other side, experience a greater attraction towards the bulk than towards the void. This means molecules at the surface are preferentially pulled inwards and the surface becomes stiffer as a result. This is the phenomenon of surface tension. This effect can also occur at an interface between two different substances: the molecules near the interface (on both sides) experience a different force from across the interface than they do from their own bulk, so in this case as well, an inter-facial tension will inevitably arise.

How can we define surface tension so we can treat it mathematically and make quantitative measurements? There are two physically equivalent approaches, which we now describe.

Surface Tension – a Surface Force Description

The first definition requires us to draw a line on the surface and imagine the forces acting on either side it. Normally these forces would be equal and opposite, so there is no bulk motion. In this case the surface tension is defined as the force that acts to

1 Note that throughout this essay, we will not consider the effects of gravity upon the drop.

one side of the line drawn on the surface. Using this definition, the force T acting to one side a line of length L is given by the formula:

$$T=-\tau L, \tag{1}$$

where τ is the coefficient of surface tension i.e. the force per unit of length. It is an intrinsic property of the substance constituting the surface and can be determined by relatively simple experiments, most notably using the phenomenon of capillarity. Note that the surface tension T is considered to act in a direction that it perpendicular to the line L. It is also considered to be a negative force, since it it resists a pulling force.

In the case where the surface is an interface between two different substances (say i and j) equation (1) is better expressed by the equation

$$T_{ij}=-\tau_{ij}L_{ij}, \tag{2}$$

In which τ_{ij} specifies the interface tension between layers i and j. Note that the interface can be between solids, liquids or gases in any combined pair.

Surface Tension – a Surface Energy Description

The second approach to defining surface tension is through surface energy. The surface is under tension, therefore any increase in surface area requires work and work is a measure of energy. In effect, increasing the surface area does work on the surface and increases its energy. See Figure 1.

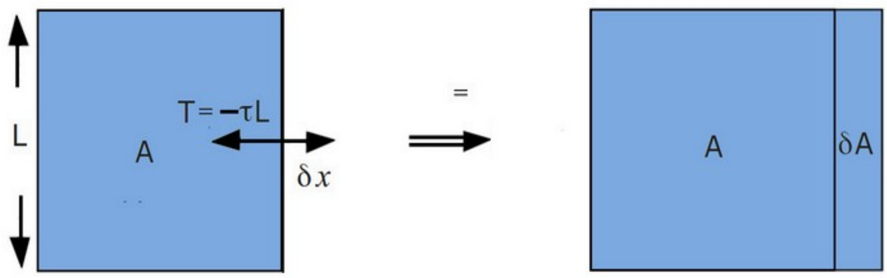

Figure 1

In Figure 1 a square area A of a surface is increased by an amount δA by pulling the right hand edge a distance δx against the surface tension $T=-\tau L$. The pulling force is in the opposite direction to the surface tension and so the work done on the surface is $\delta W=\tau L\delta x$. This is the increase in the energy of the surface, which can be written as $\delta E=\tau\delta A$. In general the energy of the whole surface can be written as:

$$E = \tau A, \quad (3)$$

or in the case of an interface:

$$E_{ij} = \tau_{ij} A_{ij}. \quad (4)$$

In Figure 1 it is evident that the surface tension resists an increase in surface area and therefore surface energy. It follows that free surfaces will always ensure that the surface energy is at a minimum. Note that in equations (1) and (2), τ and τ_{ij} are defined in units of force per unit length, while in equations (3) and (4) they are defined in units of energy per unit area. Dimensionally, these are the same (MT^{-2}), so τ (or τ_{ij}) has the same value in each case.

The Contact Angle

With these two definitions of surface tension in mind, let is return to the drop of liquid on a flat surface.

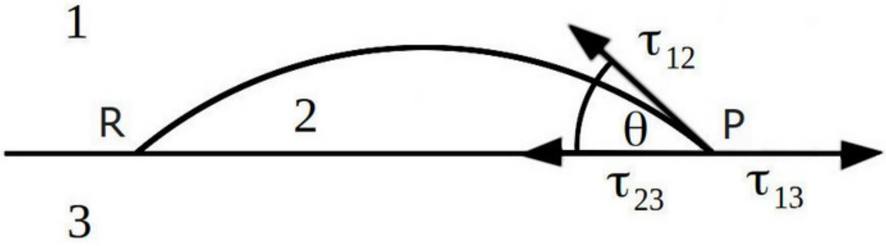

Figure 2

In Figure 2 we show a drop of liquid on a solid surface. Three different substances are involved here. Firstly there is the air, which we assume surrounds the system. This is labelled 1 in the figure. Next there is the liquid, which lies on the surface and is labelled 2. Finally there is the solid surface, which is labelled 3. Therefore three surface tension coefficients are necessary to describe this system: τ_{12}, for the interface between the air and the liquid; τ_{23}, for the interface between the liquid and the solid surface; and finally τ_{13} for the interface between the air and the solid surface.

The first thing we can determine is the contact angle of the drop on the surface, which is the angle θ shown in Figure 2. Wherever the liquid drop joins the solid surface, such as points P and R, is a place where all three substances are in mutual contact. Therefore at every point on the edge of the drop on the solid surface, three surface tension forces are acting and, provided the drop is stable on the surface, these forces must be in equilibrium. By considering a small horizontal line δl at a typical point like P it is easy to see that the forces balance in the following way:

$$\tau_{13} = \tau_{23} + \tau_{12}\cos\theta. \quad (5)$$

From this we easily obtain

$$\theta = \cos^{-1}\left(\frac{\tau_{13} - \tau_{23}}{\tau_{12}}\right). \quad (6)$$

This is the contact angle and it is an important property of the drop, but it does not tell us anything more without further assumptions. It seems logical that the overall shape of the drop on the actual surface must be circular, since no particular direction on the surface is favoured by the acting forces. However it is easy to imagine that a drop that has a non-circular shape might nevertheless satisfy equation (6). To resolve this, we must adopt a surface energy approach.

The Shape of the Drop

We shall assume that the shape of the drop is determined by the minimum energy surface, which equations (3) and (4) show is equivalent to a minimum surface area. The minimum surface area for a free spherical drop is a sphere. In the case of a drop lying on a surface it is reasonable to assume that the preferred shape would be a section of a sphere, provided it satisfies the contact angle as determined by equation (6). This is a *boundary condition* that the drop must satisfy.

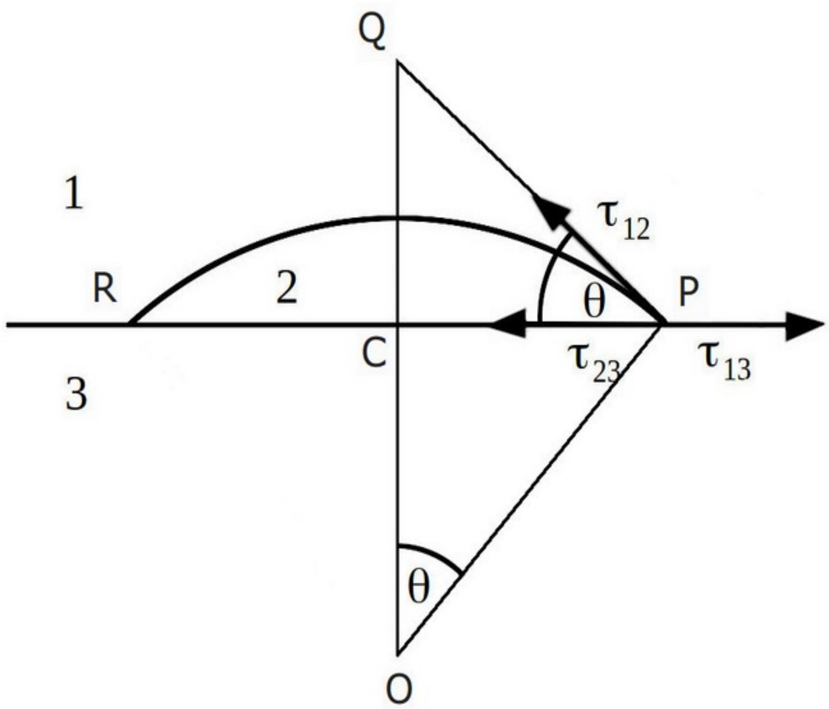

Figure 3

In order to factor in the boundary condition we need to develop Figure 2 further, in the manner shown in Figure 3.

As seen in Figure 3, if the surface of the drop (the arc drawn from R to P) is a section of a sphere, then the surface tension at contact point P (labelled τ_{12}) must lie in the air-liquid interface and must therefore be tangential to the sphere at P. A normal to the surface at P must pass through the centre of the sphere at O and also be perpendicular to the surface tension force vector. Point O can be found where the perpendicular bisector of the line RP on the solid surface (i.e. the drop diameter) intersects the normal drawn from P. The bisector also intersects the solid surface at C and the tangential surface tension force vector at Q. Angles $O\hat{P}Q$ and $Q\hat{C}P$ are right angles and triangles OPQ and QCP are right angled triangles. From this it follows that angle $Q\hat{O}P$ is equal to θ.

We now need to determine the dimensions of the drop. This is defined by the volume V of the initial drop of liquid, which we shall assume is a known quantity. The volume of the drop is the volume difference between two conical cones. The first is the flat bottomed cone that has its vertex at O and its circular base is the disk of the drop in contact with the solid surface. The second cone has the same apex, but its base is the curved surface of the drop, which we know is spherical. The volume of the drop is then

$$V=\frac{2\pi}{3}r^3(1-\cos\theta)-\frac{\pi}{3}r^3\cos\theta\sin^2\theta, \qquad (7)$$

in which r is the radius of the sphere and θ is the contact angle. The first term on the right is the volume (V_{sc}) of the cone with the spherical base and is obtained from the integral

$$V_{sc}=\int_0^r\int_0^{2\pi}\int_0^{\theta} r^2\sin\theta\, d\theta\, d\phi\, dr, \qquad (8)$$

which is simply the integral of the standard spherical volume element over the required ranges. The second term on the right is the volume V_{fc} of the flat based cone given as

$$V_{fc}=\frac{1}{3}base\,x\,height=\frac{1}{3}\pi(r\sin\theta)^2 r\cos\theta=\frac{\pi}{3}r^3\cos\theta\sin^2\theta. \qquad (9)$$

Equation (7) is easily expanded and rearranged to give

$$V=\frac{\pi}{3}r^3\left(\cos^3\theta-3\cos^2\theta+2\right). \qquad (10)$$

In equation (10) V and θ are known quantities and we need to know the radius r. Rearranging gives the following formula for r :

$$r^3=\frac{3V}{\pi}\left(\cos^3\theta-3\cos\theta+2\right)^{-1} \tag{11}$$

from which we can calculate the radius.

Knowledge of the radius permits a complete specification of the geometrical properties of the drop on the surface, so we have the following.

The diameter of the drop D_{drop} is given by

$$D_{drop}=2r\sin\theta. \tag{12}$$

The height of the drop H_{drop} is given by

$$H_{drop}=r(1-\cos\theta). \tag{13}$$

The area of liquid in contact with the solid surface A_{23} is

$$A_{23}=\pi(r\sin\theta)^2 \tag{14}$$

The area of liquid in contact with the air is

$$A_{12}=r^2\int_0^{2\pi}\int_0^{\theta}\sin\theta\,d\phi\,d\theta=2\pi r^2(1-\cos\theta). \tag{15}$$

The energies associated with the surfaces of the drop can be obtained by multiplying areas A_{12} and A_{23} by τ_{12} and τ_{23} respectively.

Proving the Surface Energy is Minimized

It is assumed above that the shape of the liquid drop on the surface is portion of a spherical sphere and that the contact angle this makes with the solid surface is given by equation (6), but we have not proved this. Here we do so using the minimization of the surface energy. The total surface energy is given by the equation

$$E=A_{12}\tau_{12}+(A-A_{23})\tau_{13}+A_{23}\tau_{23}. \tag{16}$$

In this equation A_{ij} is the area of the interface between substances i and j *etc*. and τ_{ij} is the corresponding coefficient of surface tension. Area A is the area of the solid surface and is an arbitrary constant such that $A>A_{23}$. The first and third terms on the right of equation (16) are the interface energies of the liquid drop with the air and the solid surface respectively, while the second term is the interface energy of the air with the solid surface. The areas A_{23} and A_{12} are given by equations (14) and (15) respectively.

Differentiating the total surface energy (16) with respect to θ gives

$$\frac{dE}{d\theta}=(\tau_{23}-\tau_{13})\frac{d}{d\theta}A_{23}+\tau_{12}\frac{d}{d\theta}A_{12}. \tag{17}$$

Differentiating (15) gives

$$\frac{d}{d\theta}A_{12}=4\pi r(1-\cos\theta)\frac{dr}{d\theta}+2\pi r^2\sin\theta, \tag{18}$$

while differentiating (14) gives

$$\frac{d}{d\theta}A_{23}=2\pi r\sin^2\theta\frac{dr}{d\theta}+2\pi r^2\sin\theta\cos\theta. \tag{19}$$

Substituting (18) and (16) into (17) and rearranging gives

$$\frac{dE}{d\theta}=(\tau_{23}-\tau_{13})\left(2\pi r\sin^2\theta\frac{dr}{d\theta}+2\pi r^2\sin\theta\cos\theta\right)+\tau_{12}\left(4\pi r(1-\cos\theta)\frac{dr}{d\theta}+2\pi r^2\sin\theta\right). \tag{20}$$

At maximum or minimum the derivative (20) should be zero, hence we have after rearrangement

$$\left((\tau_{23}-\tau_{13})\sin^2\theta+2\tau_{12}(1-\cos\theta)\right)\frac{dr}{d\theta}+\left((\tau_{23}-\tau_{13})r\sin\theta\cos\theta+\tau_{12}r\sin\theta\right)=0. \tag{21}$$

The derivative $dr/d\theta$ is obtained from (11) and is

$$\frac{dr}{d\theta}=-\frac{\pi}{3V}r^4\sin^3\theta. \tag{22}$$

So (21) becomes after rearrangement

$$\left((\tau_{23}-\tau_{13})\sin^2\theta+2\tau_{12}(1-\cos\theta)\right)\frac{\pi}{3V}r^3\sin^2\theta-\left((\tau_{23}-\tau_{13})\cos\theta+\tau_{12}\right)=0. \tag{23}$$

Inserting (11) into (23) and rearranging gives

$$\left((\tau_{23}-\tau_{13})\sin^2\theta+2\tau_{12}(1-\cos\theta)\right)\sin^2\theta-\left((\tau_{23}-\tau_{13})\cos\theta+\tau_{12}\right)(\cos^3\theta-3\cos\theta+2)=0. \tag{24}$$

In (24) we may replace $\sin^2\theta$ by $\cos^2\theta-1$ and then define $x=\cos\theta$ and expand to obtain

$$\tau_{12}x^3-(2\tau_{12}-(\tau_{23}-\tau_{13}))x^2+(\tau_{12}-2(\tau_{23}-\tau_{13}))x+(\tau_{23}-\tau_{13})=0. \tag{25}$$

We can solve this equation by Newton-Raphson, Cardano or graphically, but all we need do here is prove that the solution given in equation (6) for the contact angle is also a solution for (25). Writing (6) in the form

$$x=-\frac{(\tau_{23}-\tau_{13})}{\tau_{12}} \tag{26}$$

and substituting this into (25) leads to

$$\begin{gathered}-(\tau_{23}-\tau_{13})^3-2\tau_{12}(\tau_{23}-\tau_{13})^2+(\tau_{23}-\tau_{13})^3-(\tau_{23}-\tau_{13})\tau_{12}^2+\\ 2(\tau_{23}-\tau_{13})^2\tau_{12}+(\tau_{23}-\tau_{13})\tau_{12}^2=0.\end{gathered} \tag{27}$$

Where it is apparent that all the different terms cancel out. This proves that contact angle given in (6) is a solution of the minimum energy equation (25) and is therefore consistent with the minimum energy surface.