

On the demonstration of the Young-Laplace equation in introductory physics courses

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The Young-Laplace equation is usually introduced using mechanical rather than thermodynamic arguments when teaching surface phenomena at an elementary level. We discuss here three mechanical methods to deduce this equation, and we intend to avoid certain misunderstandings that are found in these derivations, providing thus the correct demonstrations.

It has long been recognized that in order to make an infinitesimal increase in the surface area Σ of a single component liquid-vapor interface, keeping constant the temperature and the volume of the whole system, an infinitesimal reversible work

$$\delta W = - \gamma d\Sigma \quad (1)$$

is required, where γ is the surface tension, which is always positive and depends only on temperature. The physical dimensions of γ are energy per unit area (and also force per unit length). It is worth remarking that in eq. (1) we have used the notation δW to indicate that the work is not a total differential. The fact that work is required to increase the surface area provides evidence for the existence of a pressure difference between the two sides of a curved surface. Its value for a spherical surface was deduced in 1805 independently by Thomas Young (1773-1829) and by Pierre Simon de Laplace (1749-1827), and is given by

$$p_{\alpha} - p_{\beta} = \frac{2\gamma}{r} , \quad (2)$$

where p_{α} and p_{β} are the internal and external pressures of the spherical surface and r is its radius. The Young-Laplace equation shows that the pressure inside a spherical surface is always greater than the pressure outside, but the difference decreases to zero as the radius becomes infinite (when the surface is flat). On the contrary, the pressure difference increases

if the radius becomes smaller and tends to infinite when r tends to zero. However, eq. (2) breaks down before r reaches zero, and so in practice this problem can be avoided.

The subject of surface phenomena is relevant not only to physics but also to neighbouring disciplines such as physical chemistry, life and health sciences, as well as chemical engineering. The study of these phenomena should be done using the formalism of thermodynamics (Pellicer *et al* 1995) not only because this formalism is closer to the currently accepted viewpoint (Woodruff 1973, Shaw 1992, Tabor 1993), but also because it is free from misleading results that occasionally arise when mechanical arguments are used. However, since the thermodynamic approach requires full understanding of certain thermodynamic functions, it is useful in intermediate physics courses (surface science, physical chemistry, thermodynamics) for scientists and engineers, but may not be appropriate for an introductory physics course.

The Young-Laplace equation is usually introduced when teaching surface phenomena at an elementary level (Young 1992). In this case, the surface phenomena are often described by using mechanical rather than thermodynamic arguments. To obtain a better understanding of the physical meaning of the Young-Laplace equation we discuss three mechanical methods to deduce it. The simplest method is based on the equilibrium condition of a single component liquid drop surrounded by its own vapor (Becker 1967, Temperley and Trevena 1979, Young 1992, Somorjai 1994, Pellicer *et al* 1995). The second method considers a liquid drop suspended from a syringe (Pippard 1964, Reiss 1965, Adkins 1968). The last method is based on a drop of liquid immersed in its own vapor, the entire system being enclosed in a cylinder (Reiss 1996, Jaycock and Parfitt 1986).

A simple method to deduce the Young-Laplace equation

Liquids tend to minimize their surface area. As the sphere is the geometrical form with the smallest surface/volume ratio, drops are spherical in the absence of gravity. Consider a single component liquid spherical drop of radius r and internal pressure p_{α} in equilibrium with its

vapor at pressure p_β and temperature T . Since the surface tension acts to reduce the surface area and hence the volume of the drop, while the pressure difference between the liquid phase α and the vapor phase β acts to increase the volume of the drop, the equilibrium condition is achieved when these two tendencies counterbalance each other. If only a hemisphere is considered (fig.1), the force due to surface tension is equal to $2\pi r\gamma$, where $2\pi r$ is the length of the circumference of the hemisphere. The force due to pressure difference is $(p_\alpha - p_\beta)$ times the projected area of the hemisphere, i.e., $(p_\alpha - p_\beta) \pi r^2$. Therefore, the equilibrium condition

$$(p_\alpha - p_\beta) \pi r^2 = 2\pi r \gamma, \quad (3)$$

leads to eq. (2).

The method of the syringe: piston subjected to surface tension

Let us now consider a more complex configuration, illustrated in fig. 2, in which a single component spherical liquid drop is formed from the bulk liquid at the end of a syringe whose hollow needle tapers to an infinitely fine point. The set up is in thermal equilibrium with the surroundings at temperature T in absence of any external field. Through application of pressure by means of the piston, a spherical drop can be formed at the end of the needle. Since the process is reversible, the pressure of the vapor phase surrounding the drop and the syringe is always the vapor pressure of the drop.

At the beginning, in absence of the drop, the piston only subjects the bulk liquid to pressure p_β , but in order to form a drop of small radius it is necessary for the piston to apply a slightly higher pressure in excess, p_α . If we assume that the liquid is incompressible and that no motion takes place until p_α is reached, no work is performed while the pressure is being increased. Once the piston begins to move, the reversible work may be computed as follows. The work performed by the piston on the liquid is $-p_\alpha dV_\alpha$, where dV_α is the increment in the volume of the drop. But the drop

performs work on its environment because it displaces vapor at pressure p_β . This work is $-p_\beta dV_\beta$. Thus, the total work performed on the liquid is

$$\delta W = -p_\alpha dV_\alpha - p_\beta dV_\beta . \quad (4)$$

For an incompressible liquid $dV_\beta = -dV_\alpha$, and thus, from eq. (4),

$$\delta W = -(p_\alpha - p_\beta) dV_\alpha . \quad (5)$$

Evidently, this work is employed to increase the surface area of the drop, keeping constant the temperature and the volume of the whole system. Therefore, this work can be written as in eq. (1), and then eq. (5) becomes

$$p_\alpha - p_\beta = \gamma \frac{d\Sigma}{dV_\alpha} . \quad (6)$$

Unfortunately, the above conditions are not considered in some texts (Pippard 1964, Adkins 1968).

The connection between Σ and V_α is purely geometric. Since

$$\Sigma = 4\pi r^2 \quad (7)$$

and

$$V_\alpha = \frac{4}{3} \pi r^3 , \quad (8)$$

by introducing eqs. (7-8) into eq. (6) we get eq. (2). Some authors (Becker 1967) develop this method following a very simplistic approach, which leads to lack of accuracy in the demonstration.

The method of cylinder: piston not subjected to surface tension

In fig. 3 we have a single component spherical liquid drop in equilibrium with its vapor at temperature T . The whole system is enclosed in a cylinder and may exchange work with the environment through the action of the piston. The pressure in the drop is denoted by p_α and that of the vapor by p_β . Notice that the piston makes contact with the system only

through the vapor, i. e., the piston is not subjected directly to the surface tension. Thus, in this configuration any work exchanged between the system and its environment will be volume work performed at the pressure p_β . Therefore,

$$\delta W = p_\beta dV , \quad (9)$$

where

$$dV = dV_\alpha + dV_\beta \neq 0 , \quad (10)$$

being V_α the drop volume, V_β the vapor volume and V the total volume of the system.

Since the molar volume of a component in the vapor phase is larger than its molar volume in the liquid phase, the decrease in total volume due to the external work increases the amount of matter in liquid phase and therefore the drop size. If this increase in drop size takes place at constant temperature, then Kelvin's equation (Jaycock and Parfitt 1986) predicts both a decrease in p_α and p_β . As a consequence, the size of the drop increases continuously. In any case, the total work (9) can be also expressed as

$$\delta W = p_\alpha dV_\alpha + p_\beta dV_\beta - \gamma d\Sigma . \quad (11)$$

Taking into account eqs. (9) and (10), using eq. (11) and simplifying

$$(p_\alpha - p_\beta) dV_\alpha = \gamma d\Sigma , \quad (12)$$

that leads again to eq. (2).

Finally, we point out that some demonstrations based on this method (Jaycock and Parfitt 1986) are not completely rigorous.

Final thermodynamic comment

The elementary surface phenomena are also explained in terms of the Helmholtz free energy F when we use the formalism of thermodynamics in intermediate physics courses. At constant temperature, we know that the Helmholtz free energy F of an isothermal, closed system, is equal to the

work received by the system. Therefore, the change in F of the system made up of a single spherical liquid drop of radius r (phase α) immersed in its vapor (phase β) is (Pellicer *et al* 1995)

$$dF = p_{\alpha} dV_{\alpha} + p_{\beta} dV_{\beta} - \gamma d\Sigma . \quad (13)$$

Since the system is closed, the total volume remains constant and $dV_{\beta} = -dV_{\alpha}$. In order to decrease the energy of the system, the area of the interface must become smaller. This, however, causes a decrease in the volume of the liquid phase, which in turn increases the energy of the system. The size of the liquid drop is then determined by a compromise between these two tendencies, so that the overall reversible work done by the system is zero under equilibrium conditions, and dF in eq. (14) vanishes. The condition of mechanical equilibrium is then that of eq. (2).

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Figure captions

Figure 1

Imaginary hemispherical section of a spherical liquid drop. The arrows pointing radially outwards represent forces due to the pressure difference ($p_\alpha - p_\beta$). The arrows pointing to the left represent forces due to surface tension.

Figure 2

The syringe method: piston subjected to surface tension.

Figure 3

The cylinder method: piston not subjected to surface tension.





