

Shape of the Interfaces

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2.3.1 Radius of curvature

- ◆ To describe the shape of a curved surface or interface, it is necessary to know the radii of curvature. The spherical and cylindrical bodies are rather simple cases for mathematical treatment. In many interfacial phenomena, however, the shapes are more complicated.
- ◆ Consider the curve AB as shown in Fig. 2.3.1.

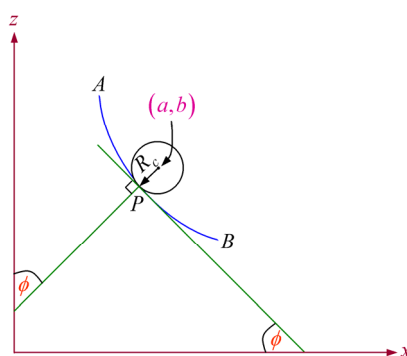


Fig. 2.3.1 Illustration of radius of curvature.

- ◆ Let P be a point on this curve. The radius of curvature of AB at P is defined as the radius of the circle which is tangent to the curve at point P (i.e., the osculating circle). If R_c is the radius of curvature at point P , the *curvature* (H) at this point is defined as,

$$H = \frac{1}{R_c} \quad (2.3.1)$$

Let (a, b) be the coordinates of the center of the tangent circle at P . The equation of the circle is,

$$(x-a)^2 + (z-b)^2 = R_c^2 \quad (2.3.2)$$

Let ϕ be the angle between the normal to the curve and the z -axis. Therefore,

$$\tan \phi = -\frac{dz}{dx} \quad (2.3.3)$$

Differentiating Eq. (2.3.2) with respect to x , we get,

$$\frac{dz}{dx} = -\left(\frac{x-a}{z-b}\right) \quad (2.3.4)$$

From Eqs. (2.3.3) and (2.3.4) we get,

$$\tan \phi = \frac{x-a}{z-b} \quad (2.3.5)$$

Therefore,

$$\cos \phi = \frac{1}{(1 + \tan^2 \phi)^{1/2}} = \frac{1}{\left[1 + \left(\frac{x-a}{z-b}\right)^2\right]^{1/2}} = \frac{z-b}{R_c} \quad (2.3.6)$$

and

$$\frac{d \cos \phi}{dz} = \frac{1}{R_c} \quad (2.3.7)$$

- ◆ The quantity $\cos \phi$ decreases with increase in z . Thus, the curvature, $H (\equiv 1/R_c)$, is negative. This is consistent with the convention that a curve which is concave outward has a negative curvature and a curve that is convex outward has a positive curvature.
- ◆ The curvature can be expressed in terms of the derivative of z with respect to x as follows.

$$\cos \phi = \frac{1}{(1 + \tan^2 \phi)^{1/2}} = \frac{1}{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{1/2}} \quad (2.3.8)$$

Therefore,

$$\frac{d \cos \phi}{dz} = \frac{d}{dz} \left[1 + \left(\frac{dz}{dx}\right)^2\right]^{-1/2} = \left(\frac{dz}{dx}\right)^{-1} \frac{d}{dx} \left[1 + \left(\frac{dz}{dx}\right)^2\right]^{-1/2} \quad (2.3.9)$$

$$\therefore \frac{d \cos \phi}{dz} = -\frac{2\left(\frac{dz}{dx}\right)\left(\frac{d^2z}{dx^2}\right)}{2\left(\frac{dz}{dx}\right)\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2}} = -\frac{d^2z/dx^2}{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2}} \quad (2.3.10)$$

$$\therefore \frac{1}{R_c} = \pm \frac{d^2 z / dx^2}{\left[1 + \left(\frac{dz}{dx} \right)^2 \right]^{3/2}} \quad (2.3.11)$$

- ◆ The $\pm$ sign has been used in the above equation to emphasize the fact that it is necessary to adjust the sign depending on the geometry. For the curve AB , the negative sign is appropriate.

2.3.1.1 Principal radii of curvature

- ◆ Let us now consider a curved surface. At each point on a given surface, two radii of curvature (which are denoted by r_1 and r_2) are required to describe the shape. If we want to determine these radii at any point (say P), the normal to the surface at this point is drawn and a plane is constructed through the surface containing the normal. This will intersect the surface in a plane curve. The radius of curvature of the curve at point P is denoted by r_1 . An infinite number of such planes can be constructed each of which intersects the surface at P . For each of these planes, a radius of curvature can be obtained.
- ◆ If we construct a second plane through the surface, containing the normal, and perpendicular to the first plane, the second line of intersection and hence the second radius of curvature at point P (i.e., r_2) is obtained. These two radii define the curvature at P completely. It can be shown that $(1/r_1 + 1/r_2)$ (called *mean curvature of the surface*) is constant, which is independent of the choice of the planes.
- ◆ An infinite set of such pairs of radii is possible. Thus, it is not a useful way to describe the shape. For standardization, the first plane is rotated around the normal until the radius of curvature in that plane reaches minimum. The other radius of curvature is therefore maximum. These are the *principal radii of curvature* (denoted by R_1 and R_2). For practical purpose, we will work with the principal radii of curvature.

2.3.1.2 Surface of revolution

- ◆ In many interfacial applications, we come across *surfaces of revolution*. A surface of revolution is a surface generated by rotating a two-dimensional curve about an axis. The resulting surface has azimuthal symmetry.
- ◆ Examples of surfaces of revolution are cone (excluding the base), cylinder (excluding the ends) and sphere. Let us consider one such surface as shown in Fig. 2.3.2.

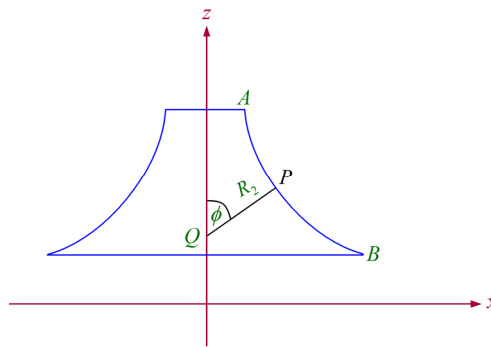


Fig. 2.3.2 Surface of revolution.

- ◆ This surface was obtained by revolving the curve AB about the z -axis. At any point P on this surface, R_1 is given by,

$$\frac{1}{R_1} = \pm \frac{d^2z/dx^2}{\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2}} \quad (2.3.12)$$

- ◆ The other principal radius of curvature is PQ , which is obtained by extending the normal to the curve AB to intersect the z -axis.

$$R_2 = PQ = \frac{x}{\sin \phi} \quad (2.3.13)$$

- ◆ We can express R_2 in terms of dz/dx as follows.

$$\sin \phi = \left[1 + \frac{1}{\tan^2 \phi}\right]^{-1/2} = \left[\frac{1 + (dz/dx)^2}{(dz/dx)^2}\right]^{-1/2} = \frac{dz/dx}{\left[1 + (dz/dx)^2\right]^{1/2}} \quad (2.3.14)$$

- ◆ From Eqs. (2.3.13) and (2.3.14) we get,

$$\frac{1}{R_2} = \pm \frac{dz/dx}{x \left[1 + (dz/dx)^2 \right]^{1/2}} \quad (2.3.15)$$

The sign needs to be chosen appropriately.

2.3.2 Young–Laplace equation

- ◆ There exists a difference in pressure across a curved surface which is a consequence of surface tension. The pressure is greater on the concave side. The Young–Laplace equation relates the pressure difference to the shape of the surface.
- ◆ This equation is of fundamental importance in the study of surfaces, and can be derived easily. Let us consider a small portion of a curved surface ($ABCD$) shown in Fig. 2.3.3.

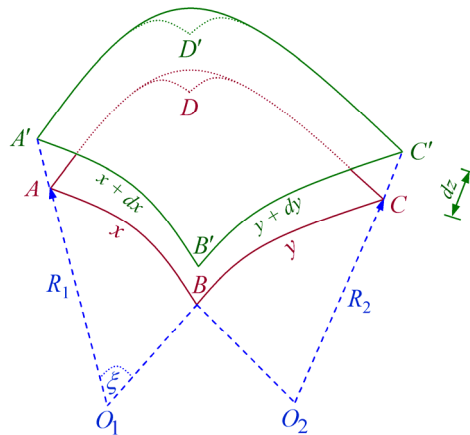


Fig. 2.3.3 Displacement of surface $ABCD$ to $A'B'C'D'$.

- ◆ The surface has been cut by two planes perpendicular to one another. Each of the planes contains a portion of the arc where it intersects the surface. The lengths of the arc are x and y . The radii of curvature are shown in the figure. The planes have been chosen in such a manner that these radii are the principal radii of curvature (viz. R_1 and R_2).

- ◆ Now, the surface is displaced outward to a new position ($A'B'C'D'$) by a small distance dz such that the arc-lengths are increased by dx and dy . Therefore, the change in area is,

$$dA = (x + dx)(y + dy) - xy = xdy + ydx + dxdy \approx xdy + ydx \quad (2.3.16)$$

The term $dxdy$ is very small since both dx and dy are small quantities. The work done to form this additional amount of surface is,

$$dW = \gamma(xdy + ydx) \quad (2.3.17)$$

- ◆ Suppose that pressure–volume work is responsible for the expansion of the surface. If the pressure difference across the surface acting on the area xy through a distance dz is Δp , then the pressure–volume work responsible for the expansion of the surface is,

$$dW = \Delta p dV = \Delta p xy dz \quad (2.3.18)$$

- ◆ From Eqs. (2.3.17) and (2.3.18), we get,

$$\gamma(xdy + ydx) = \Delta p xy dz \quad (2.3.19)$$

Now, we can observe from the figure that,

$$x = R_1 \xi \quad \text{and} \quad x + dx = (R_1 + dz) \xi \quad (2.3.20)$$

Therefore, it follows that,

$$\frac{x}{x + dx} = \frac{R_1}{R_1 + dz} \quad (2.3.21)$$

In a similar manner, it can be shown that,

$$\frac{y}{y + dy} = \frac{R_2}{R_2 + dz} \quad (2.3.22)$$

Simplifying Eqs. (2.3.21) and (2.3.22), we get,

$$\frac{dx}{x} = \frac{dz}{R_1} \quad \text{and} \quad \frac{dy}{y} = \frac{dz}{R_2} \quad (2.3.23)$$

Substituting dx and dy from Eq. (2.3.23) into Eq. (2.3.19) and simplifying, we get,

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.3.24)$$

- ◆ This is the *Young–Laplace equation* developed independently by Thomas Young (in 1804) and Pierre Laplace (in 1805).
- ◆ Substituting the expressions of R_1 and R_2 in Eq. (2.3.24), we get a differential equation. The solution of this differential equation relates the shape of an axisymmetric surface to the surface tension.
- ◆ The Young–Laplace equation, therefore, suggests the possibility of measuring surface tension from the analysis of the shape of the surface.
- ◆ The simplified forms of Eq. (2.3.24) for spherical, cylindrical and planar surfaces are given below.
 - For a spherical surface, $R_1 = R_2 = R_s$, therefore, $\Delta p = 2\gamma/R_s$.
 - For a cylindrical surface, $R_1 = R_{cy}$ and $R_2 = \infty$, therefore, $\Delta p = \gamma/R_{cy}$.
 - For a planar surface, $R_1 = R_2 = \infty$, therefore, $\Delta p = 0$.

2.3.3 Applications of Young–Laplace equation

2.3.3.1 Capillary rise or depression

The rise of water through a capillary immersed in a vessel filled with water is shown in Fig. 2.3.4. The liquid rises to an equilibrium height, h , above the air–liquid interface. The radius of the capillary is r_c .

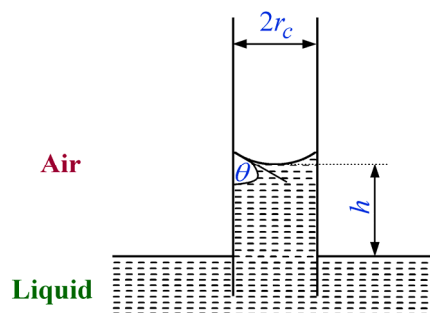


Fig. 2.3.4 Capillary rise.

- ◆ The height of the liquid column inside the capillary depends on the radius of the tube, surface tension, density of the liquid and contact angle.

- ◆ The capillary rise equation can also be derived using the Young–Laplace equation. The horizontal surface shown in the figure can be taken as the reference level at which $\Delta p = 0$. The pressure just under the meniscus in the capillary is less than the pressure on the other side of the surface due to the curvature of the surface. Therefore, the pressure in the liquid just under the curved surface is less than the pressure at the reference level. This causes the liquid in the capillary to rise until a compensating hydrostatic pressure is generated by the liquid column inside the capillary.
- ◆ Since the capillary has circular cross-section and its radius (r_c) is small, the meniscus can be approximated by a cap of a hemisphere of radius, $r_c/\cos\theta$. Therefore, $R_1 = R_2 = r_c/\cos\theta$. Thus, from Young–Laplace equation, we have,

$$\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma \cos\theta}{r_c} \quad (2.3.25)$$

- ◆ The hydrostatic pressure difference is,

$$\Delta p = h\rho g \quad (2.3.26)$$

- ◆ From Eqs. (2.3.25) and (2.3.26), we obtain,

$$h = \frac{2\gamma \cos\theta}{\rho g r_c} \quad (2.3.27)$$

- ◆ The term, $\sqrt{2\gamma/\rho g}$, is known as *capillary constant* or *capillary length*.
- ◆ Equation (2.3.27) suggests that every point on the meniscus is at the same height h from the surface of the liquid reservoir, or in other words, the meniscus is flat! A more accurate derivation should take into account the deviation of the meniscus from sphericity considering the elevation of each point above the flat surface of the liquid. This involves the solution of the general Young–Laplace equation using the expressions for R_1 and R_2 .

Example 2.3.1: Estimate the height of water inside a capillary tube of 0.75 mm radius. Take: $\gamma = 72$ mN/m and assume zero contact angle.

Solution: Since $\theta = 0$, using Eq. (2.3.27) we have,

$$h = \frac{2\gamma}{\rho g r_c} = \frac{2 \times 72 \times 10^{-3}}{1000 \times 9.8 \times 0.75 \times 10^{-3}} = 0.0196 \text{ m} = 1.96 \text{ cm}$$

Therefore, water will rise approximately 1.96 cm inside the tube.

2.3.3.2 Pendant and sessile drops

- ◆ When a drop is formed at the tip of a vertical tube (e.g., a burette), its size is mainly determined by the surface tension (or interfacial tension, if the tip is dipped inside another liquid). The drop slowly forms at the tip of the tube, grows in size and then a ‘neck’ forms. Thereafter, the drop detaches from the tip. The drop suspended from the tube is known as a *pendant drop*. A similar profile of the drop can be observed when it is suspended from a plate (e.g., droplets formed by the condensation of vapor).
- ◆ If a drop is placed on a solid surface, it rests on the surface as shown in the following figure. It is called *sessile drop*. The drop will deform from its spherical shape as it settles on the solid.
- ◆ From the profiles of pendant and sessile drops, it is possible to determine surface or interfacial tension. The sessile drop method is widely used for measuring the contact angle. The pendant and sessile drops are illustrated in Fig. 2.3.5.



(a)



(b)

Fig. 2.3.5 (a) pendant drop, and (b) sessile drops.

2.3.3.3 Bashforth–Adams equation

- ◆ Let us consider a drop sitting on a smooth solid surface inside another liquid. The same analysis will be valid if the drop sits in air. The drop is deformed by gravity.

It is assumed that no other external force acts on the drop. In absence of the gravitational force, the drop would remain spherical. The center of mass of the drop is forced to be lowered by gravity.

- ◆ However, this causes the surface area to increase (since the spherical shape occupies the least surface area), which is opposed by surface tension force. The equilibrium shape depends upon the balance of the two forces.
- ◆ Let us consider the profile of a sessile drop shown in Fig. 2.3.6.

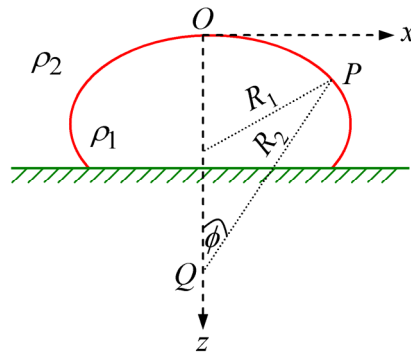


Fig. 2.3.6 Schematic of a sessile drop.

- ◆ The actual surface may be generated by rotating the profile around the axis of symmetry. The origin of the coordinate system is O , located at the apex of the surface. The two radii of curvature at point P are R_1 and R_2 . Now,

$$x = R_2 \sin \phi \quad (2.3.28)$$

At the point O , $R_1 = R_2 = R_a$. Therefore, at this point,

$$(\Delta p)_O = \frac{2\gamma}{R_a} \quad (2.3.29)$$

At the point P ,

$$(\Delta p)_P = (\Delta p)_O + \Delta \rho g z \quad (2.3.30)$$

where $\Delta \rho$ is the difference in densities of the two phases. If the drop rests in air, $\Delta \rho \approx \rho$ (where ρ is the density of the liquid). Substituting $(\Delta p)_O$ from Eq. (2.3.29) into Eq. (2.3.30) we get,

$$(\Delta p)_P = 2\gamma/R_a + \Delta \rho g z \quad (2.3.31)$$

- ◆ From Young–Laplace equation,

$$\gamma \left(\frac{\sin \phi}{x} + \frac{1}{R_1} \right) = \frac{2\gamma}{R_a} + \Delta \rho g z \quad (2.3.32)$$

- ◆ Equation (2.3.32) can be rearranged in the following form,

$$\frac{1}{R_1/R_a} + \frac{\sin \phi}{x/R_a} = 2 + \beta \frac{z}{R_a} \quad (2.3.33)$$

where β is given by,

$$\beta = \frac{\Delta \rho g R_a^2}{\gamma} \quad (2.3.34)$$

- ◆ β is a dimensionless number which is known as *Bond number*. It represents the ratio of the gravity force to the force due to surface tension. A small value (< 1) of the Bond number indicates that the drop will not deform significantly from its spherical shape whereas, a large value indicates large deformation of the drop.
- ◆ If the drop is small, interfacial tension is large, or the density difference between the two liquids is low, the Bond number would be small.
- ◆ Equation (2.3.33) is known as *Bashforth–Adams equation*. It is a differential equation which can be solved numerically.
- ◆ The solutions have been presented in tabular form by Bashforth and Adams (1883) for values of β between 0.125 and 100. The values of x/R_a and z/R_a were reported for closely-spaced values of ϕ for a given value of β .
- ◆ An illustration of the use of Bashforth–Adams table to generate the profile of the drop is given in Fig. 2.3.7 for $\beta = 25$.
- ◆ Several works have extended the work of Bashforth and Adams. The differential equation has been solved numerically using computer for more accurate results.
- ◆ The value of x/R_a is maximum at $\phi = \pi/2$ rad.

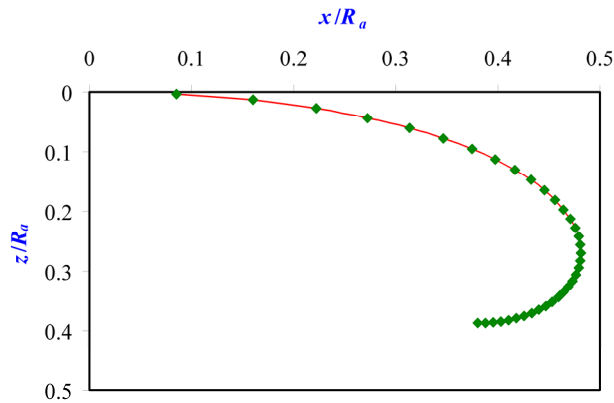


Fig. 2.3.7 Profile of drop predicted by Bashforth–Adams equation.

- ◆ If $\rho_1 > \rho_2$, β is positive and the drop is *oblate* in shape. In this case the weight of the drop flattens the surface.
- ◆ If $\rho_1 < \rho_2$, β is negative, and the shape is *prolate*. The buoyant force in this case causes the surface to elongate in the vertical direction (e.g., a sessile bubble extended into liquid).
- ◆ In a similar manner, it can be deduced that a pendant drop will be prolate and a pendant bubble will be oblate.

Example 2.3.2: Consider a soap film stretched between two parallel circular rings having equal diameter as shown in Fig. 2.3.8. Determine its shape neglecting the effects of gravity.

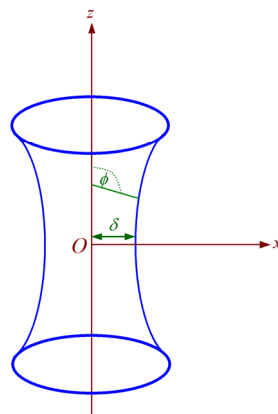


Fig. 2.3.8 Soap film formed between parallel rings.

Solution: Since the rings are open on both sides, $\Delta p = 0$. Therefore, at all points,

$$\frac{1}{R_1} + \frac{1}{R_2} = 0$$

Now,
$$\frac{1}{R_1} = \frac{d \cos \phi}{dz} = \frac{d \cos \phi}{dx} \frac{dx}{dz} = -\cot \phi \frac{d \cos \phi}{dx} = \cos \phi \frac{d \phi}{dx} = \frac{d \sin \phi}{dx}$$

$$\frac{1}{R_2} = \frac{\sin \phi}{x}$$

Therefore,
$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{d \sin \phi}{dx} + \frac{\sin \phi}{x} = \frac{1}{x} \frac{d}{dx} (x \sin \phi)$$

Thus,
$$\frac{1}{x} \frac{d}{dx} (x \sin \phi) = 0$$

$$\therefore \frac{d}{dx} (x \sin \phi) = 0$$

Integrating with respect to x , we get,

$$x \sin \phi = C$$

where C is a constant. At $z = 0$, $x = \delta$. Here the normal intersects the z -axis at right angle. Therefore, $\phi = \pi/2$ and $\sin \phi = 1$. Therefore, $C = \delta$.

$$\therefore x \sin \phi = \delta$$

$$\therefore \frac{dz}{dx} = -\tan \phi = -\frac{\sin \phi}{\cos \phi}$$

Now,
$$\sin \phi = \delta/x, \cos \phi = -\left[1 - (\delta/x)^2\right]^{1/2}, \quad \phi \geq \pi/2$$

$$\therefore \frac{dz}{dx} = \frac{\delta/x}{\left[1 - (\delta/x)^2\right]^{1/2}}$$

The above equation can be solved with the boundary condition: at $z = 0$, $x = \delta$. The solution is,

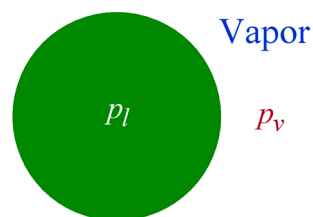
$$z = \pm \delta \ln \left[\frac{x}{\delta} + \left\{ \left(\frac{x}{\delta} \right)^2 - 1 \right\}^{1/2} \right]$$

This is the equation of the catenary. The solution can also be written as,

$$\frac{x}{\delta} = \cosh\left(\frac{z}{\delta}\right)$$

2.3.4 Kelvin equation

- ◆ The pressure difference associated with the curved surfaces has an important effect on the thermodynamic activity of substances. A very important implication of the curvature of the surface is in the vapor–liquid equilibrium.
- ◆ The Kelvin equation gives quantitative information regarding the effect of surface curvature on vapor pressure. The vapor pressure across a flat surface is p^{sat} , the saturated vapor pressure of the liquid at the given temperature. The vapor pressure across a curved surface is, however, different from the saturated vapor pressure.
- ◆ Let us consider the drop as shown in the following figure.



$$\Delta p = p_l - p_v = \frac{2\gamma}{R_d}$$

Fig. 2.3.9 Vapor–liquid equilibrium across a spherical meniscus.

- ◆ The Young–Laplace equation predicts a pressure difference across the spherical meniscus, given by,

$$\Delta p = p_l - p_v = 2\gamma/R_d \quad (2.3.35)$$

where R_d is the radius of the drop. At a constant temperature, if R_d varies, then we have,

$$dp_l - dp_v = 2\gamma d(1/R_d) \quad (2.3.36)$$

Since equilibrium is maintained during this process, the changes in the chemical potentials of the liquid and the vapor must be equal. Therefore,

$$d\mu_l = d\mu_v = \bar{v}_l dp_l = \bar{v}_v dp_v \quad (2.3.37)$$

where $\bar{v}_l$ and $\bar{v}_v$ are the molar volumes of the liquid and vapor, respectively.

- ◆ If we assume that the vapor behaves as an ideal gas and $\bar{v}_l \ll \bar{v}_v$, then from Eqs. (2.3.36) and (2.3.37) we can write,

$$\frac{RT}{\bar{v}_l} \frac{dp_v}{p_v} = 2\gamma d\left(\frac{1}{R_d}\right) \quad (2.3.38)$$

where R is the gas constant.

- ◆ Integrating Eq. (2.3.38) using the condition that the vapor pressure in the case of the flat interface (i.e., $R_d \rightarrow \infty$) is the saturated vapor pressure of the liquid (p^{sat}) we obtain,

$$\frac{p_v}{p^{\text{sat}}} = \exp\left[\frac{2\bar{v}_l\gamma}{RR_dT}\right] = \exp\left[\frac{2M\gamma H}{RT\rho_l}\right] \quad (2.3.39)$$

where M is the molecular weight, ρ_l is the density of the liquid and H is the mean curvature.

- ◆ Equation (2.3.39) is known as *Kelvin equation*. The sign of H determines whether p_v/p^{sat} would be greater or less than unity.
- ◆ For the drop shown in the figure, the liquid is on the concave side of the meniscus (the radius is measured in the liquid). Therefore, $H = 1/R_d$.
- ◆ For a bubble in a liquid, the liquid is on the convex side of the meniscus. Therefore, $H = -1/R_b$ (where R_b is the radius of the bubble).
- ◆ Therefore, the vapor pressure of a drop will be greater than the saturated vapor pressure of the liquid (i.e., $p_v/p^{\text{sat}} > 1$). On the other hand, the vapor pressure inside a bubble will be less than the saturated vapor pressure (i.e., $p_v/p^{\text{sat}} < 1$).
- ◆ The effect of curvature of the surface is pronounced for very small drops and bubbles.

2.3.4.1 Application of Kelvin equation in determining pore volume distribution

- ◆ Kelvin equation is used for determining the pore-volume distribution in porous solids. Consider a pore in the solid having radius R_p which is filled with a liquid as shown in Fig. 2.3.10.

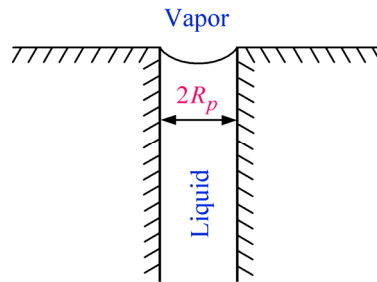


Fig. 2.3.10 Condensation of liquid in pore.

- ◆ For simplicity, let us assume that the contact angle is zero so that the liquid–vapor meniscus is a hemisphere of radius R_p . The liquid is in the convex side of the meniscus. Therefore, $H = -1/R_p$.
- ◆ From Kelvin equation, $p(R_p) = p^{\text{sat}} \exp\left[-\frac{2M\gamma}{R_p RT \rho_l}\right]$, where $p(R_p)$ is the vapor pressure of the liquid trapped inside the pore of radius R_p . The porous solid has pores of different radii. So, if we place the solid in an environment where the vapor pressure is maintained at $p(R_p)$, ideally the liquid will condense into all pores having radius R_p or less. From the mass of the liquid condensed and its density, the volume of liquid that condensed into the pores having radius less than or equal to R_p can be calculated.
- ◆ Suppose that this volume is $V(R_p)$. Since the value of $p(R_p)$ is known, R_p can be calculated from the Kelvin equation.

- ◆ If the vapor pressure is maintained at another value, the volume of liquid condensed into the pores having radii corresponding to this vapor pressure can be calculated.
- ◆ These data representing the variation of $V(R_p)$ with R_p are used to generate the cumulative pore-volume distribution.
- ◆ An example of pore-volume distribution is presented in Fig. 2.3.11.

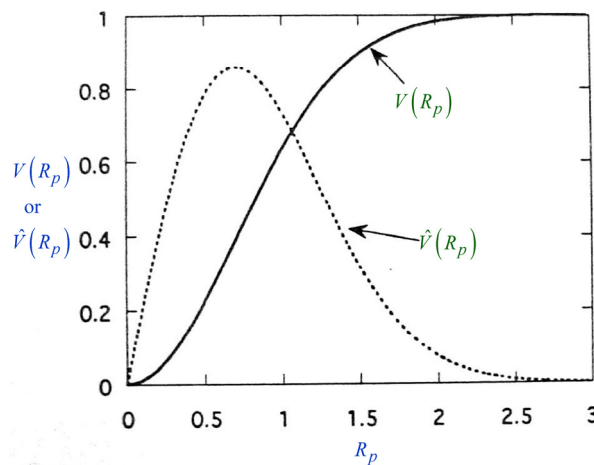


Fig. 2.3.11 Pore volume distribution.

- ◆ $\hat{V}(R_p)dR_p$ is the volume of pores in the sample having a radius between R_p and $(R_p + dR_p)$. $\hat{V}(R_p) = dV(R_p)/dR_p$.
- ◆ The pore-volume distributions have important applications in catalysis and transport through porous media.

Exercise

Exercise 2.3.1: Calculate p_v/p^{sat} from Kelvin equation for water drops at 298 K having diameters of 1 μm and 1 nm.

Exercise 2.3.2: Write a computer program to solve the Bashforth–Adams equation. Using this program, generate the profile of a sessile drop if $\beta = 10$.

Exercise 2.3.3: The pore volume distribution for a porous silica is given by,

$$\hat{V}(R) = \frac{2R}{\sigma^2} \exp(-R^2/\sigma^2)$$

where $R = 2$ nm. The saturated vapor pressure of water between 273 and 373 K can be computed from the equation,

$$\ln p = 9.0725 - 2262/T$$

where p is in kPa and T is in K. Consider water at room temperature. Plot the liquid water saturation in the pores versus the pressure of water vapor, assuming that the water completely wets the solid surface.

Exercise 2.3.4: Answer the following questions clearly.

- Define radius of curvature and curvature. Explain the principal radii of curvature.
- Explain how the variation of radius of curvature on a curved surface can be determined.
- Explain how the pressure difference across a curved surface can be related to the principal radii of curvature.
- Explain what you understand by a pendant and a sessile drop. What are the forces that act on a pendant and a sessile drop?
- What is Bond number?
- Explain the significance of Bashforth–Adams differential equation.
- Explain the shapes of sessile and pendant bubbles.

- h. What is capillary constant?
- i. What conclusions can you draw from the Kelvin equation?
- j. Explain why the vapor pressure of a drop is greater than the saturated vapor pressure of the liquid.
- k. Explain how the Kelvin equation may be used to generate the pore-volume distribution of a porous solid.
- l. Explain why nanoparticles sinter easily.

Suggested reading

Textbooks

- ◆ A. W. Adamson and A. P. Gast, *Physical Chemistry of Surfaces*, John Wiley, New York, 1997, Chapter 2.
- ◆ C. A. Miller and P. Neogi, *Interfacial Phenomena*, CRC Press, Boca Raton, 2008, Chapter 1.
- ◆ P. C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, New York, 1997, Chapter 6.
- ◆ P. Ghosh, *Colloid and Interface Science*, PHI Learning, New Delhi, 2009, Chapter 4.

Reference books

- ◆ J. C. Berg, *An Introduction to Interfaces and Colloids: The Bridge to Nanoscience*, World Scientific, Singapore, 2010, Chapter 2.
- ◆ L. L. Schramm, *Dictionary of Nanotechnology, Colloid and Interface Science*, Wiley-VCH, Weinheim, 2008 (find the topic by following the alphabetical arrangement in the book).
- ◆ R. J. Stokes and D. F. Evans, *Fundamentals of Interfacial Engineering*, Wiley-VCH, New York, 1997, Chapter 3.

Journal articles

- ◆ P. R. Pujado, C. Huh, and L. E. Scriven, *J. Colloid Interface Sci.*, **38**, 662 (1972).