

Thermodynamics of Capillary Rise: Why Is the Meniscus Curved?

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In many physical chemistry textbooks, capillary rise (or depression) is discussed in the thermodynamics chapters. Nevertheless, the phenomenon is usually treated mechanically rather than thermodynamically (1–3). Accordingly, the derivation of the standard equation for the capillary rise h of a liquid with surface tension γ and density ρ in a tube with radius r ,

$$h = \frac{2\gamma \cos \theta}{\rho g r} \quad (1)$$

where g as usual denotes the acceleration due to gravity, is straightforward and proceeds stepwise as follows (see Figure 1):

- i. The meniscus forms an angle θ , the contact angle, with the inner wall of a capillary tube with circular cross section. The contact angle is determined by the ability of the liquid to wet the inner surface of the tube.
- ii. For narrow tubes the shape of the meniscus is assumed to be spherical with radius R . The contact angle is then given geometrically by,

$$\cos \theta = \frac{r}{R} \quad (2)$$

where r is the radius of the capillary.

- iii. According to the Young–Laplace equation there is a pressure difference,

$$\Delta p = \frac{2\gamma}{R} \quad (3)$$

across the meniscus, the pressure being lower on the convex side.

- iv. This pressure difference causes the liquid to rise in the tube if $\theta < 90^\circ$ (e.g., water in a glass capillary) and to be depressed if $\theta > 90^\circ$ (e.g., mercury in a glass capillary).
- v. When the hydrostatic pressure of the liquid column in the capillary, $h\rho g$ (neglecting the density of the gas phase), balances the pressure difference Δp , mechanical equilibrium is established and the height of the liquid column is given by eq 1.

Besides the assumption of a spherical meniscus shape, a weak point in the derivation above is that the precise meaning of h is not specified. Usually, it is tacitly assumed that the mass of liquid above the midpoint of the meniscus can be neglected compared to the mass of the whole liquid column. However, it will be shown later on in this article (see

eq 20) that eq 1 holds generally if h is defined as the height of a cylinder with the same volume as the actual liquid column. Although the derivation presented above gives the correct equation, eq 1, for the capillary rise, and can be extended to generate a differential equation for a general meniscus shape (4–6), see eq 14 below, it does not provide any clear-cut clues as to the true thermodynamic driving force actually causing the liquid column to rise in the capillary, nor as to why the meniscus is curved.

In more specialized textbooks, for example, ref 7, the driving force is properly identified as the free energy gained when the liquid wets the wall, which is counterbalanced by the work needed to lift the liquid column in the gravitational field. Since, for an incompressible liquid, this is a process occurring at constant volume, the equilibrium condition is that the Helmholtz free energy A is at minimum. Increasing the column height at constant temperature from h to $h + dh$ in a tube with circular cross section without changing the shape of the meniscus causes a change in the Helmholtz free energy of the system by

$$dA = -\Delta\gamma^s 2\pi r dh + \Delta\rho g \pi r^2 h dh \quad (4)$$

where the first term is the gain in free energy as a result of the wetting and the second term is the work it takes to raise the column in the gravitational field. $\Delta\gamma^s = \gamma^{sg} - \gamma^{sl}$ is the difference in surface free energy between the solid–gas interface and the solid–liquid interface and $\Delta\rho = \rho^l - \rho^g$. In inte-

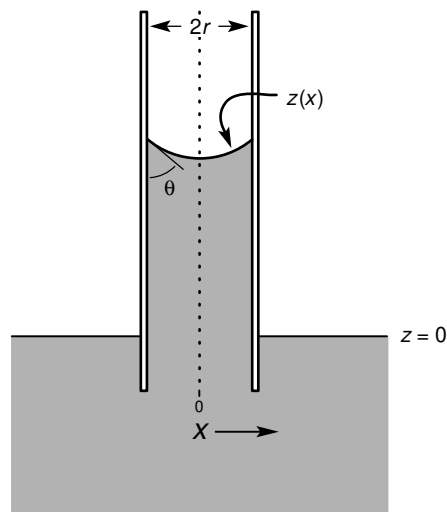


Figure 1. Capillary rise of a liquid in a capillary tube with circular cross section.

grated form we thus get:

$$A = -\Delta\gamma^s 2\pi r h + \frac{\Delta\rho g \pi r^2 h^2}{2} \quad (5)$$

The function $A(h)$, which is displayed in Figure 2 for water in a glass capillary with $r = 1$ mm, has a minimum (the second derivative is always positive) when,

$$\Delta\gamma^s = \frac{h g \Delta\rho r}{2} \quad (6)$$

which is the equilibrium condition. It is thus evident that it is the surface free energy difference, $\Delta\gamma^s$, that is the thermodynamic driving force causing the liquid column to rise if $\Delta\gamma^s > 0$, that is, if it is favorable for the liquid to wet the solid wall. Physically, γ^{sg} and γ^{sl} correspond to the reversible work per unit area of cleaving the solid in contact with the gas and the liquid, respectively. However, under constant chemical potential conditions they also manifest themselves as mechanical tensions (8).

It is noteworthy that the resulting equilibrium condition, eq 6, does not involve the curvature of the meniscus or the surface tension of the liquid $\gamma = \gamma^{lg}$. In other words, following this thermodynamic route, the question as to why and how the meniscus is curved has not been addressed. To come to grips with these matters as well as the precise meaning of h in eqs 1 and 6, it is necessary to consider the detailed meniscus shape $z = z(x)$ as defined in Figure 1.

Why Is the Meniscus Curved?

The answer to this question furnished by thermodynamics is that the existence of a curved meniscus is a consequence of the universal condition that the chemical potential μ of the liquid must be the same everywhere in the system at physicochemical equilibrium. As a result of gravity, the potential energy increases with the height in the liquid column, which per se increases the chemical potential. In order for

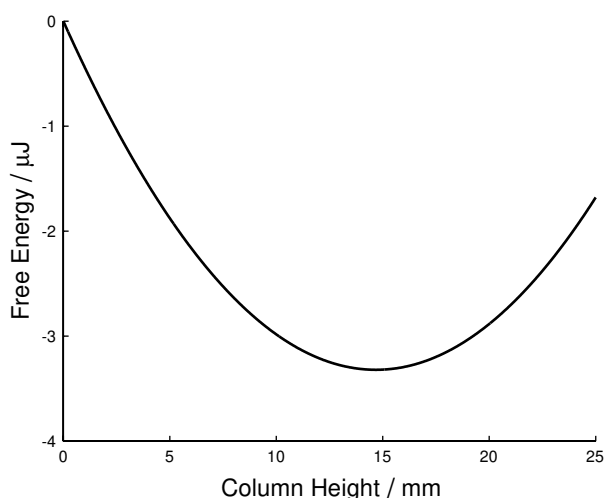


Figure 2. The Helmholtz free energy A according to eq 5 for water ($\Delta\gamma^s = 72 \times 10^{-3}$ N/m, $\Delta\rho = 10^3$ kg/m³) in a capillary with radius 1 mm as a function of the height of the liquid column. $-dA/dh$ is the net force acting on the liquid column.

the chemical potential to remain constant, this increase is counterbalanced by lowering the pressure, which is achieved by curving the meniscus, thus creating a pressure drop Δp across the meniscus and a pressure gradient along the column. Seen this way, it is the increase in chemical potential in the liquid column owing to the gravitational field that causes the meniscus to curve to maintain physicochemical equilibrium.

From height h to height $h + dh$ in the column the chemical potential changes by,

$$d\mu = -S_m dT + V_m dp + Mgdh \quad (7)$$

where M is the molar mass, S_m and V_m the molar entropy and volume respectively. At equilibrium $d\mu = 0$ and thus, at constant temperature,

$$Mgdh = -V_m dp \quad (8)$$

as was derived by Gibbs (9). Integration between $p = p_0$ at $h = 0$ and $p = p_0 - \Delta p$ at $h = z$ yields, for an incompressible liquid, the physicochemical equilibrium condition in the form,

$$\Delta p = \rho^l gz \quad (9)$$

where Δp , as before, is the pressure drop across the meniscus and z is the height of the meniscus above the bulk liquid (see Figure 1). To be strict, ρ^l in eq 9 should be replaced by $\Delta\rho = \rho^l - \rho^g$ as an increase in height of the liquid column causes a slight decrease in the potential energy of the gaseous component.

How Is the Meniscus Curved?

Equation 9 is the general equilibrium condition. When combined with the Young–Laplace equation for the pressure drop over a curved surface it gives a differential equation for the meniscus shape $z = z(x)$. At a point on the meniscus at distance x from the center the Young–Laplace equation gives,

$$\Delta p(x) = 2\gamma H(x) \quad (10)$$

where $H(x)$ is the mean curvature that can be expressed as,

$$H = \frac{1}{2} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (11)$$

where R_1 and R_2 are the two principal radii of curvature. $H(x)$ adjusts so that the equilibrium condition, eq 9, is fulfilled for every point on the meniscus:

$$\Delta\rho gz(x) = 2\gamma H(x) \quad (12)$$

Since $z(x)$ increases towards the wall, the curvature of the meniscus will also increase, and the meniscus is therefore never strictly spherical in shape.

For a surface with axial symmetry, like the meniscus in a tube with circular cross section, the mean curvature $H(x)$ at any point is given by (4–6),

$$2H(x) = \frac{z''}{(1 + z'^2)^{3/2}} + \frac{z'}{x(1 + z'^2)^{1/2}} \quad (13)$$

where z' and z'' are the first and second derivatives of the

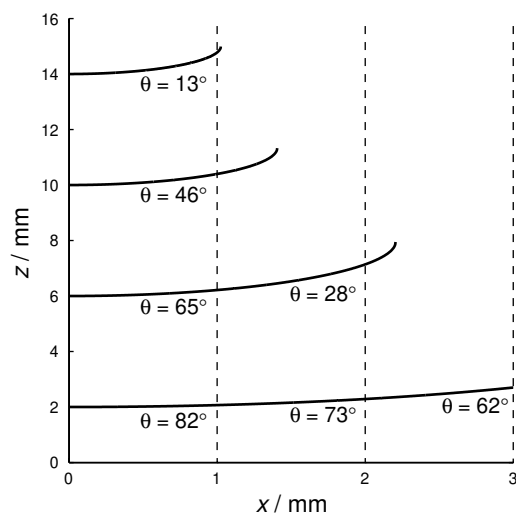


Figure 3. Calculated meniscus shapes for water ($\gamma = 72 \times 10^{-3}$ N/m, $\Delta\rho = 10^3$ kg/m³) for different values of z_0 , the height of the liquid column at the center of the tube.

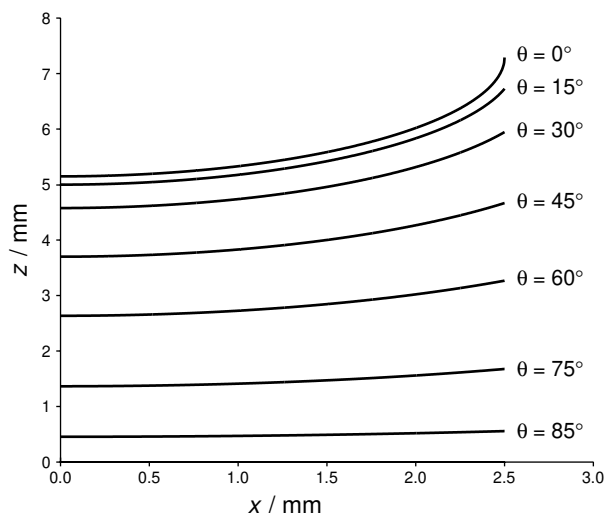


Figure 4. Calculated meniscus shapes for water ($\gamma = 72 \times 10^{-3}$ N/m, $\Delta\rho = 10^3$ kg/m³) for different contact angles θ in a tube with radius 2.5 mm.

function $z(x)$. The equilibrium condition eq 12 gives:

$$z(x) = \frac{2\gamma}{\Delta\rho g} H(x) = \frac{\gamma}{\Delta\rho g} \left[\frac{z''}{(1 + z'^2)^{3/2}} + \frac{z'}{x(1 + z'^2)^{1/2}} \right] \quad (14)$$

A complete treatment of this topic is given, for example, in ref 6 where eq 14 is derived by minimizing the excess free energy of the meniscus at constant chemical potential in the gravitational field.

To calculate the meniscus shape, the differential eq 14 has to be solved numerically with the boundary conditions,

$$z'(0) = 0 \quad (15)$$

$$z'(r) = \cot\theta \quad (16)$$

where the contact angle θ is a parameter. The easiest way to solve eq 14 is, however, to use the height of the liquid column in the center of the tube, z_0 , as a parameter rather than the contact angle, and to solve it numerically with the initial conditions:

$$z(0) = z_0 \quad (17)$$

$$z'(0) = 0 \quad (18)$$

When the numerical solution $z = z(x)$ is available for a certain z_0 value, the corresponding contact angle θ can be calculated from the slope at $x = r$. The smaller z_0 is chosen, the closer to 90° will the contact angle be. $z_0 = 0$ gives $z(x) = 0$, that is, a flat surface with no capillary rise corresponding to $\theta = 90^\circ$.

Equation 14 was solved by numerical integration in 1883

by Bashforth and Adams (10) who published tables that have been used by several workers in the field (4, 5, 11). Today it can be readily solved with commercially available software. Figures 3–6 show some meniscus shapes $z = z(x)$ for water calculated numerically by the Runge–Kutta method using the Matlab ode45 routine. For a certain liquid (surface tension γ and density ρ), a set of curves with the single parameter z_0 is obtained (see Figure 3). Note that a certain z_0 value represents different combinations of contact angle θ and tube radius r . For example, the curve for $z_0 = 6$ mm in Figure 3 represents the meniscus for $\theta = 28^\circ$ in a tube with $r = 2$ mm and the meniscus for $\theta = 65^\circ$ in a tube with $r = 1$ mm; that is, these two combinations (and several others) give the same capillary rise and meniscus shape.

It is evident from the lower curve in Figure 5 that for wide tubes and small contact angles the curvature increases rapidly close to the wall while the main part of the meniscus is practically flat as expected. Moreover, it is interesting to note that a lower value for g , the acceleration due to gravity, as on the surface of the moon, gives rise to a meniscus that deviates considerably less from spherical shape (upper curve in Figure 5).

As seen from Figures 6 and 7 the deviation from spherical shape is small for narrow capillaries. For a spherical meniscus with $\theta = 0^\circ$, the meniscus height $z_m = z(r) - z(0)$ is equal to the tube radius r . For water at 25°C , the numerically calculated meniscus heights deviate less than 1% from r for radii < 0.5 mm while the deviation is larger than 10% for radii > 2 mm.

Definition of the Capillary Rise

The total volume of the liquid column in the capillary can be calculated from eq 14 (5):

$$V = 2\pi \int_0^r xz dx = \frac{2\pi\gamma}{\Delta\rho g} r \cos\theta \quad (19)$$

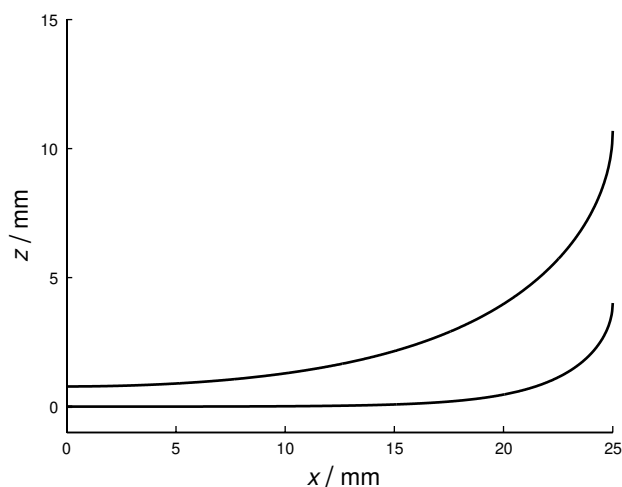


Figure 5. Calculated meniscus shapes for water ($\gamma = 72 \times 10^{-3}$ N/m, $\Delta\rho = 10^3$ kg/m³) in a tube with radius 25 mm and contact angle $\theta = 0^\circ$. Lower curve: $g = 9.81$ m/s² and the height at the center of the tube is $z_0 = 1.94$ μ m. Upper curve: $g = 1.62$ m/s² as on the surface of the moon and the height at the center of the tube is $z_0 = 0.78$ mm.

Defining the capillary rise h as the height of a cylinder with the same volume as the actual liquid column,

$$V = \pi r^2 h = \frac{2\pi\gamma}{\Delta\rho g} r \cos\theta \quad (20)$$

the standard expression for the capillary rise, eq 1, is obtained immediately. Evidently, assumption (ii), which states that the meniscus is spherical, is *not* a necessary condition for eq 1 to be valid. With h defined in this way, eq 1 holds for a general meniscus shape characterized by eq 14, which in turn derives from the physicochemical equilibrium condition that the chemical potential of the liquid is the same everywhere in the system.

The Contact Angle Condition

A comparison between eqs 20 and 6 shows that the Young equation,

$$\Delta\gamma^s = \gamma \cos\theta \quad (21)$$

is fulfilled as is obviously required in view of the mechanical significance of γ^g and γ^l as interfacial tensions (12). As was clarified by Gibbs (13), at physicochemical equilibrium, the surface free energy difference $\Delta\gamma^s = \gamma^g - \gamma^l$ equals a mechanical tension, the “adhesion tension”, acting on the three-phase contact line. In other words, eq 21 is valid both energy-wise as well as tension-wise and may also be considered as the thermodynamic definition of the equilibrium contact angle θ .

The contact angle θ appearing in eqs 1 and 20 is, however, not necessarily equal to the equilibrium contact angle but may well correspond to a metastable state, that is, to a local minimum in the A versus h function with a free energy slightly above the lowest minimum value corresponding to the true equilibrium contact angle. All that matters in the end is

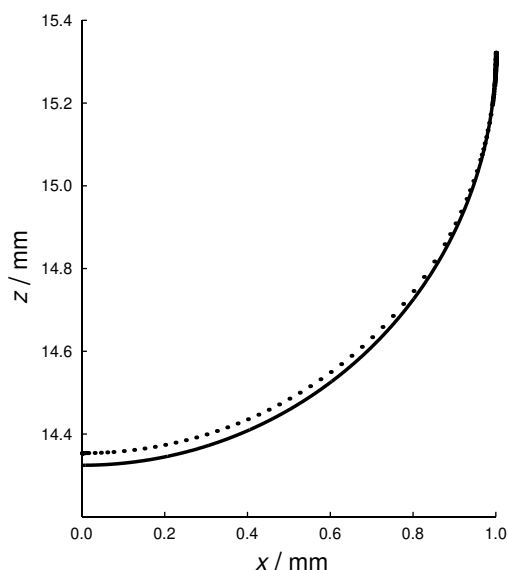


Figure 6. Calculated meniscus shapes for water ($\gamma = 72 \times 10^{-3}$ N/m, $\Delta\rho = 10^3$ kg/m³) in a tube with radius 1 mm and contact angle $\theta = 0^\circ$ (dotted curve) compared with a spherical meniscus (solid curve) with the same curvature as the meniscus at the wall.

that the three-phase junction can give rise to a tension component that balances the meniscus tension component $\gamma \cos\theta$. In this way one can account for the notorious difficulties, encountered more often than not, to actually realize hysteresis-free contact angle equilibrium. Hence, eq 1 holds true irrespective of whether θ is the equilibrium contact angle or not. Yet, it is worth keeping in mind that $\Delta\gamma^s > 0$ always provides the thermodynamic driving force for capillary rise even if the true equilibrium contact angle may be beyond reach for kinetic reasons.

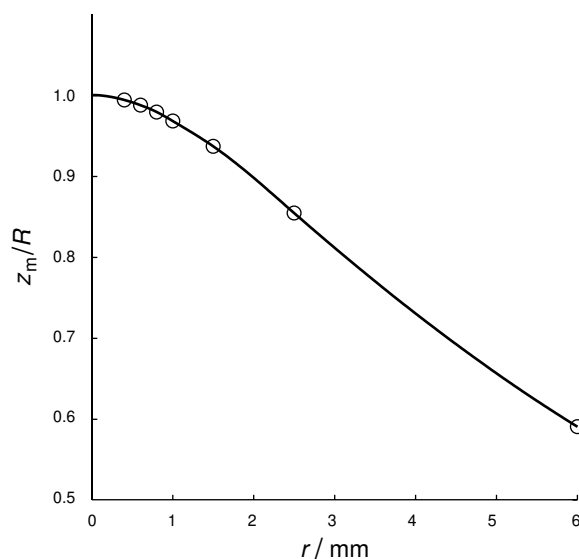


Figure 7. z_m/r , where $z_m = z(r) - z(0)$ is the meniscus height, as a function of the tube radius r for water and $\theta = 0^\circ$. For spherical menisci $z_m/r = 1$.

The Vapor Pressure above the Meniscus

It should also be noted that although the pressure just under the meniscus may be considerably lower than the surrounding pressure, the chemical potential of the liquid component is always the same throughout the system. Hence, the vapor pressure at the height h is obtained by applying eq 8 for the pure vapor phase resulting in the barometer formula where the factor $\exp(-Mgh/RT)$ accounts for the h dependence. Accordingly, the vapor pressure of water at $h = 1$ m is $\approx 99.993\%$ of the value at $h = 0$. In other words, the vapor pressure above the meniscus is for all practical purposes the same as over the bulk liquid.

Conversely, for the case of capillary condensation in the absence of the effect of gravity, for example, for water in a horizontal glass capillary, the formation of a curved meniscus results in a lowering of the pressure and, hence, of the chemical potential of the liquid, which in turn manifests itself as a reduction of the equilibrium vapor pressure.

Summary

The thermodynamic approach presented in this article gives the following picture of capillary rise:

- i. The lifting of the entire column of liquid in the gravitational field is caused by the favorable contact between the liquid and the solid wall.
- ii. Establishing physicochemical equilibrium throughout the liquid column in the gravitational field results in a curved meniscus with increasing curvature from the center of the tube towards the wall.
- iii. Although the meniscus is never strictly spherical in shape, the standard equation for capillary rise, eq 1, still holds generally if the capillary rise h is defined as the height of a cylinder with the same volume as the actual liquid column irrespective of whether θ is the true equilibrium contact angle or not.

To properly point out the most essential physical features of the capillary rise phenomenon to students it is advisable to

focus on the full equilibrium case and to dwell mainly on point i above while referring to the readily accepted Young equation, eq 21, as a result that either follows from points i and ii, or from the condition for mechanical equilibrium at the three-phase contact line. In this way the standard equation for capillary rise, eq 1, can be derived without introducing any ad hoc assumption about the shape of the meniscus. Treating the subject matter along these lines should leave the reflecting student neither with the impression that capillary rise is basically caused by the pressure drop at the curved interface, nor with an erroneous belief that the standard equation for capillary rise holds merely for spherical menisci.

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