

Unsaturated Zone Hydrology for Scientists and Engineers

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Potential and Thermodynamics of Soil Water

INTRODUCTION

Water that has entered a soil but has not drained deep into the soil profile will be retained within pores or on the surface of individual soil particles. In the unsaturated zone, soil particles are typically surrounded by thin water films that are bound to solid surfaces within the medium by the molecular forces of adhesion and cohesion. Because of this, a simple measurement of water content is not sufficient to enumerate the complete status of water in a soil. An example of this may be observed in two different field or laboratory soils that have been treated in the same manner: though the same amount of water has been applied to each, they will have different water contents and varying abilities to contain water, due to individual physical and chemical properties. As a result, defining water content alone will not give any indication of chemical, osmotic, or other potentials involving water.

While the quantity of water present in soil is very important (affecting such processes as diffusion, gas exchange with the atmosphere, soil temperature, and so on), the potential or affinity with which water is retained within the soil matrix is perhaps more important. This potential may be defined as the amount of work done or potential energy stored, per unit volume, in moving that mass, m , from the reference state (typically chosen as pure free water). In this manner, one may think of matric potential as potential energy per unit volume, E (J m^{-3}). Energy is work with units N (Newton) per distance ($\text{N} \cdot \text{m}$). Consequently, $\text{J m}^{-3} = \text{N} \cdot \text{m m}^{-3}$, or N m^{-2} , which is also expressed as a Pascal (Pa). A Pascal is a force per unit area or pressure, which explains the use of the term “pressure potential,” and is the reason why some unsaturated zone hydrologists refer to matric potential as “soil pressure.”

This chapter will discuss the concepts of potential and thermodynamics (chemical potential) of soil water, beginning with the structure of water and the properties of adsorbed water and following with discussions of capillary water and various components of soil-water potential, including the thermodynamics of soil water. Hysteresis will also be addressed.

4.1 THE STRUCTURE OF WATER

Molecules are polarized when a separation exists between the “center of gravity” of the negative and the positive charges in the molecule. With molecules like water, such a condition is always present. The water molecule is arranged so that the oxygen atom is bonded to the hydrogen atoms with an angle of 105° between two bonds (figure 4.1). The center of the negative charge is near the oxygen atom while the center of the positive charge is at a point midway between the hydrogen atoms (represented by x in the figure). Materials composed of molecules

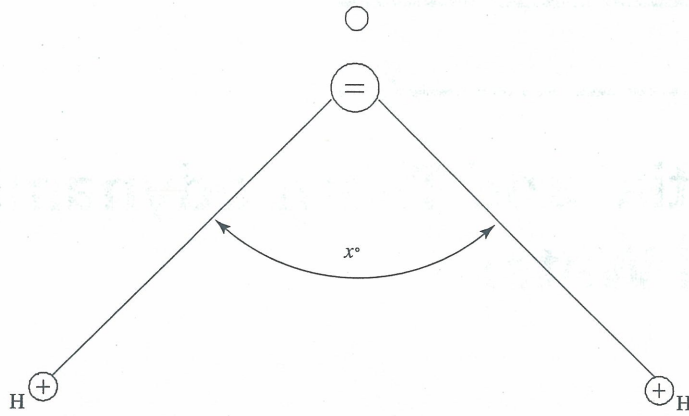


Figure 4.1 The positive charge of the hydrogen atom produces a polarized water molecule (H_2O) that appears bent

that are permanently polarized in this way usually have large dielectric constants. As an example, the dielectric constant (D , unitless) of water is 80.4, compared to 2.24 for carbon tetrachloride (both measured at 20°C). A symmetrical molecule might have no permanent polarity; however, polarity can be induced by an external electric field. For example, if a linear molecule lies along the x axis, an external electric field in the positive direction of x would cause the center of the positive charge to shift to the right from its initial position; the center of the negative charge would thus shift to the left.

The electric charge structure of an individual water molecule has a basic tetrahedral shape in which the oxygen atom is near the center (figure 4.2). Two corners of this structure are positively charged, due to the partially screened protons of the hydrogen atoms. The remaining two corners of the tetrahedral structure are negatively charged, due to two pairs of lone-pair electrons. Such an arrangement makes the water molecule a dipole; that is, one end of the water molecule tends to be positive while the other end tends to be negatively charged. We can determine the potential energy of an electric dipole as a function of its orientation with respect to an external electric field. To accomplish this, we must recognize that work must be done by an external agent to rotate the dipole through a given angle, θ , in the electric field. The work done is stored as potential energy in the system (i.e., the dipole and the external field), U . The work, dW , required to rotate the dipole through an angle $d\theta$ is given by $dW = \tau d\theta$, where $\tau = pU \sin \theta$ (p is a vector).

The electric dipole, using the water molecule as an example, consists of two equal and opposite charges separated by a distance $2a$. The electric dipole moment of the water molecule has a vector p whose magnitude is $2aq$; that is, the separation $2a$ multiplied by the associated charge q . Because the work is transformed into potential energy E , for a rotation from θ_0 to θ , the change in potential energy is

$$E - E_0 = \int_{\theta_0}^{\theta} \tau d\theta = \int_{\theta_0}^{\theta} pU \sin \theta d\theta = pU \int_{\theta_0}^{\theta} \sin \theta d\theta \quad (4.1)$$

and

$$E - E_0 = pU[-\cos \theta]_{\theta_0}^{\theta} = pU(\cos \theta_0 - \cos \theta) \quad (4.2)$$

The term involving $\cos \theta_0$ is a constant that depends on the initial orientation of the dipole. For convenience, we choose $\theta_0 = 90^\circ$, so that $\cos \theta_0 = \cos 90^\circ = 0$. Additionally, we choose $E_0 = 0$ at $\theta_0 = 90^\circ$ as our reference of potential energy. As a result, we may express E as

$$E = -pU \cos \theta \quad (4.3)$$

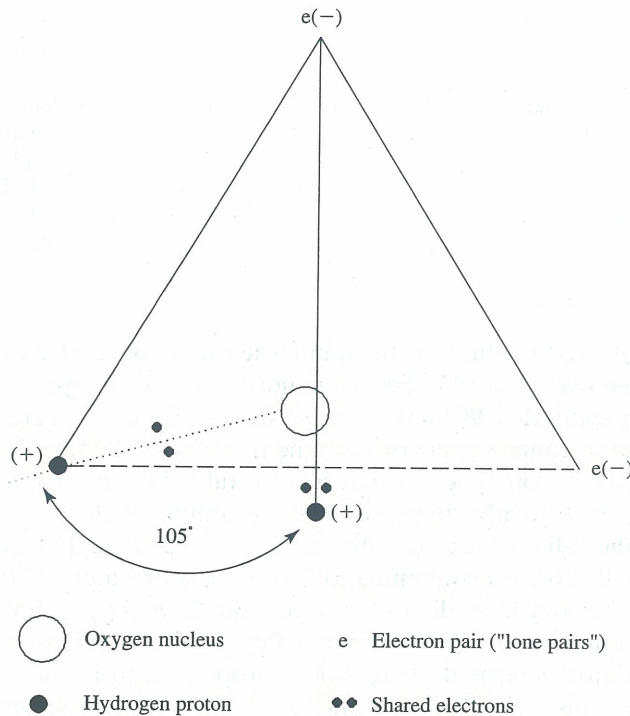


Figure 4.2 Tetrahedral charge structure of a water molecule

Equation 4.3 can also be written as the dot product of vectors p and U : $E = -p \cdot U$.

QUESTION 4.1

The water molecule has a dipole moment of $6.3 \times 10^{-30} \text{ C} \cdot \text{m}$. A sample contains 10^{21} molecules. The dipole moments of all these molecules are oriented in the direction of an electric field of $2.75 \times 10^5 \text{ N C}^{-1}$. How much work is required to rotate the dipoles from $\theta = 0^\circ$ to $\theta = 90^\circ$ (i.e., where all the moments are perpendicular to the field)?

4.2 AIR–WATER INTERFACE: CONTACT ANGLE

When a water droplet is formed or placed on a clean surface, like a freshly waxed automobile, the size of the droplet will depend on the attractive forces associated with the air–liquid, solid–liquid, and solid–air interfaces (figure 4.3). Forces, for bulk water, consist primarily of London–van der Waals forces and hydrogen bonding; one-third London–van der Waals and two-thirds hydrogen bonding (Stumm 1992). Molecules at an air–water interface are not subjected to attractive forces from without, but are attracted inward to the bulk phase. This attraction tends to reduce the number of molecules on the surface region of the droplet due to an increase in intermolecular distance. For the area of the interface to be enlarged, energy must be expended. For water at 20°C , this force, per unit of new area, may be expressed as a force per unit length that has the value 73 mN m^{-1} .

As can be seen in figure 4.3, the curvature of the liquid surface is dependent on the contact angle. The angle that the tangent to the fluid surface makes at the point of contact with the solid surface (inside the fluid) is known as the contact angle, and is generally represented

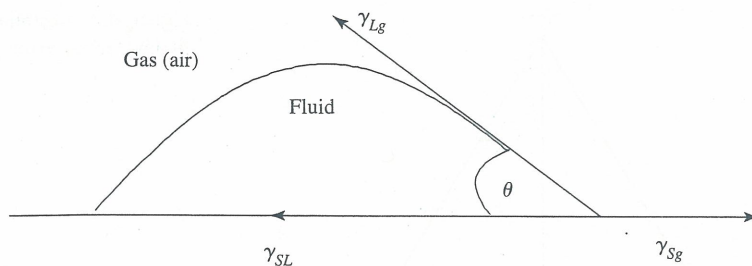


Figure 4.3 Interfacial tension components for the equilibrium of a droplet of fluid on a smooth surface in contact with air. The subscripts *S*, *L*, and *g* refer to solid, liquid, and gas. The contact angle is shown by angle θ .

by the symbol θ (not to be confused with volumetric water content). Normally, this angle is curved, but can range from 0 to 180°. For the majority of fluids on glass it is less than 90°. If the contact angle is greater than 90°, $\cos \theta$ is negative. For example, if a glass tube is immersed in mercury, which has a contact angle of 140°, the mercury in the tube is pressed below the mercury level directly surrounding and outside the tube. For this same tube immersed in water, the water will rise slightly along the tube: the contact angle, the angle tangent to the water surface and the tube immersed in the water, will be acute. For pure water on clean glass, the contact angle is 0°; any contamination of the glass or water will increase the contact angle. For example, the contact angle for tap water and clean glass is about 15–18°. For practical purposes, when the contact angle is greater than 90°, the liquid does not wet the solid. For water, this condition is termed hydrophobic; drops tend to move about easily, but not enter capillary pores. This is a well known phenomena in organic soils throughout the world and also on golf course greens in the southeastern United States.

The change in surface free energy, ΔG^s , that accompanies a small displacement of the fluid per change of solid area (ΔA) covered, is

$$\Delta G^s = \Delta A(\gamma_{SL} - \gamma_{Sg}) + \Delta A \gamma_{Lg} \cos (\theta - \Delta \theta) \quad (4.4)$$

and

$$\gamma_{Lg} \cos \theta = \gamma_{Sg} - \gamma_{SL} \quad (4.5)$$

where γ is the interfacial tension (J m^{-2} or N m^{-1}), the subscripts *L*, *g*, and *S* refer to liquid, gas, and solid, and $\Delta \theta$ is the change in contact angle with change in solid area wetted. Equation 4.5, known as the Young equation, implies that various surface forces can be represented by surface tensions acting in the direction of the surface of the fluid.

4.3 CAPILLARITY

Capillarity, also referred to as surface tension (force per unit length), is related to stretched surfaces in tension. Capillarity concerns interfaces that are mobile and can assume an equilibrium shape. Common examples are water droplets formed in air, drops formed by liquids in liquids, thin films, menisci, and so on. Capillarity deals with both the macroscopic and statistical behavior of interfaces, rather than their molecular structure. This phenomenon is extremely important in soil water retention. Surface tension occurs at the molecular level and involves two types of molecular forces: adhesive forces, which are the attractive forces of molecules of dissimilar substances (the force varies depending on the substance), and cohesive forces, which are the attractions between molecules in like substances. Cohesive forces decrease rapidly with distance, and are strongest in the order solids, liquids, gases.

Surface tension is normally expressed by the symbol γ . Because γ is work per unit area, the customary units are ergs cm^{-2} or dynes cm^{-1} . In the SI unit system, γ is J m^{-2} or N m^{-1} ;

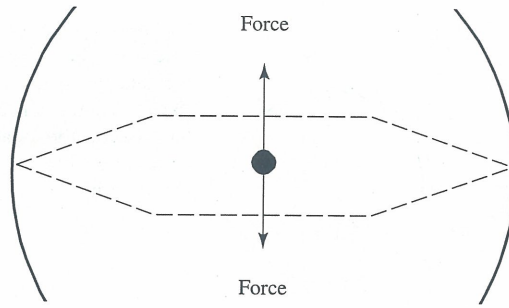


Figure 4.4 Forces inside a soap bubble

surface tensions reported as dynes cm^{-1} and 10^{-3} N m^{-1} have the same numerical value. Surface tension is highly dependent on temperature, decreasing almost linearly as temperature increases. Simply stated, cohesive forces at the surface and inside the fluid phase decrease with thermal expansion; this is generally accompanied by an increase in vapor pressure.

Examination of a simple soap bubble illustrates the significance of surface tension. For a soap bubble to form, a pressure difference must exist between the inside of the bubble and the atmosphere outside the bubble. As one would suspect, the pressure inside the bubble is greater than the pressure outside the bubble. Without this inside pressure, the bubble would collapse as a result of surface tension. Figure 4.4 shows an imaginary central plane inside a soap bubble that separates it into two hemispheres. Letting P (J m^{-3}) represent the excess pressure inside the bubble, there is a tendency for the two hemispheres to be driven apart by a force F . This force is equal to a product of both the pressure and area of the plane where the two hemispheres meet (indicated by the dashed line in the figure), where the area $A = \pi r^2$. As a result, this force can be obtained by calculating $F = PA$. The force is counteracted by the surface tension γ of the bubble, acting along the plane between the two hemispheres, which has a tendency to draw the two hemispheres together and can be represented as $2\pi r\gamma$. Because at equilibrium the two forces must be equal, by equating the two quantities we have

$$P = \frac{2\gamma}{r} \quad (4.6)$$

The larger the radius of the bubble, the smaller the difference in pressure (i.e., the inside pressure is inversely related to the bubble radius). The radius of curvature of the liquid surface plays an important role in soil water retention for various soil types. For nonspherical bubbles, we may write

$$P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (4.7)$$

where R_1 and R_2 are the radii of curvature for a specific point on the bubble interface. This curvature of the liquid surface is related to the contact angle.

As water rises in a cylindrical tube (figure 4.5), the meniscus is spherical in shape and concave upward. By letting r equal the tube radius, the excess pressure above the meniscus compared to the pressure directly below it can be described by $2\gamma/r$; that is, the pressure in the liquid below the meniscus will be less than the atmospheric pressure above the meniscus by this amount. In the laboratory, the pressure on the water surface outside the capillary tube will be atmospheric. This will force the fluid up the tube until the hydrostatic pressure of the fluid column within the tube equals the excess pressure of $2\gamma/r$. Because the circumference of the tube is $2\pi r$, the total force (upward) on the fluid is $2\pi r\gamma \cos \theta$. This force supports the

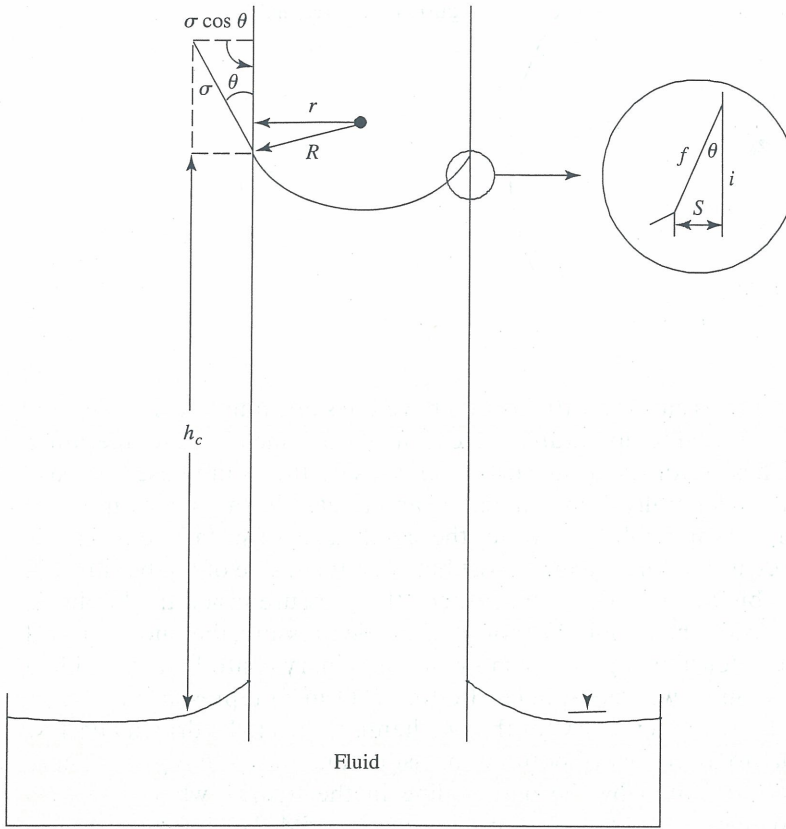


Figure 4.5 Capillary rise in a cylindrical tube, where θ is the contact angle, r is the tube radius, R is radius of curve of the gas-liquid interface, γ is the surface tension, and h_c is the height of capillary rise; i is the area of the solid-water interface associated with the tringular volume, and f is the air-water interface

weight of the fluid column to the height h_c . The total weight of fluid in the tube can be determined by

$$\rho_l g (\pi r^2 h_c + V) \quad (4.8)$$

where ρ_l is liquid density (kg m^{-3}), V is the volume of water in the meniscus (m^3), and all other parameters are as previously defined.

At equilibrium, both the force on the fluid and the weight of the fluid must be balanced, thus

$$2\pi r \gamma \cos \theta = \rho_l g (\pi r^2 h_c + V) \quad (4.9)$$

However, in very small capillaries (such as those found in soils), V is negligible, and the height of capillary rise can be given as

$$h_c = \frac{2\gamma \cos \theta}{\rho_l g r} \quad (4.10)$$

The radius of curvature, R , of the capillary meniscus in figure 4.5 can be determined by $R = r / \cos \theta$. It should also be noted that for a contact angle of zero, $r = R$. An approximation of the height of capillary rise is $h_c = 0.15/r$, which assumes a pure water state at 20°C and its corresponding parameters for surface tension and density, and a contact angle of zero. Equation 4.10 can be used to calculate the height of water rise in a specific soil for which the

largest effective pore size is known, and also to calculate the diameter of the largest effective pore (assuming one knows h_c). These equations are exact for capillary tubes; however, because soils do not behave as a single capillary such as a glass tube, these equations are at best approximations of water behavior in soils.

From the equation of capillary rise (4.10), one can observe that it is both adhesive and cohesive forces that bind water in soil capillaries. Both adhesion and repulsion of water by solid soil surfaces are characterized by the potential energy of water molecules near that surface, divided by the area of the solid-water interface. A positive γ indicates that the energy of water molecules near the soil surface is greater than the energy of molecules in bulk solution. When this situation occurs, water will not adhere to the solid surface and the condition is known as hydrophobic. Solid surfaces with a negative value for γ will readily attract water, because the energy near the soil surface is lower than the energy in the bulk solution. This condition, termed hydrophilic, is typical of field situations for most soils.

Cohesive forces can be described similarly. Within a bulk solution, a molecule is attracted in all directions equally. However, at an air-water interface, molecules are attracted only inwardly because no water molecules exist, in a liquid state, on the air side of the interface. As a result, the energy within molecules at the interface is greater than that in bulk solution, and this energy difference is characterized by the surface tension. Because the potential of water molecules in bulk solution is zero, γ is positive, which means that water in contact with air will attempt to reduce its surface area. This is easily seen in the fact that water droplets (rainfall, spray irrigation, and so on) are spherical in shape.

Considering that all three phases (air, water, and solid) are present in a capillary, the interfacial shape, which is characterized by the contact angle, θ , is dependent on whether or not γ is positive, negative, or zero, and upon the magnitude of γ with respect to σ (surface energy per unit area of fluid-gas interface in J m^{-2}). The inset in figure 4.5 illustrates this more clearly. The triangular volume that is horizontal to the tube has a maximum distance, s , to the solid surface of the tube. This distance is arbitrary, except that it will (or should) be large compared to the distance at which both the cohesive and adhesive forces are active, but should be small in comparison to the radius of curvature of the meniscus, R . The area of the air-water interface associated with the triangular volume is represented by f , while the area for the solid-water interface is represented by i . The total energy associated with both interfaces can be represented by

$$E = \sigma f + \gamma i = \frac{\sigma s}{\sin \theta} + \frac{\gamma s}{\tan \theta} \quad (4.11)$$

The contact angle, θ , will adjust itself until the interfacial energy is at a minimum, which can be given as

$$\frac{dE}{d\theta} = -\frac{\sigma s \cos \theta}{\sin^2 \theta} - \frac{\gamma s}{\sin^2 \theta} = 0 \quad \cos \theta = -\frac{\gamma}{\sigma} \quad (4.12)$$

As a result, we can see that $\theta = 180^\circ$ when $\gamma = \sigma$; $\theta = 0^\circ$ when $\gamma = -\sigma$; and $\theta = 90^\circ$ when $\gamma = 0$, where $\theta = 180^\circ$ and $\theta = 0$ are the physical limits (i.e., $\theta = 0$ for $\gamma \leq -\sigma$ and $\theta = 180^\circ$ for $\gamma \geq \sigma$). For exact solutions to the capillary rise problem and methods of measuring capillary rise, the reader is referred to Adamson (1990).

QUESTION 4.2

Determine the height of capillary rise of a fluid in a clean glass tube of $85 \mu\text{m}$ inner diameter; assume surface tension is 0.05 N/m .

4.4 CAPILLARY POTENTIAL

Figure 4.6 illustrates capillary potential on the basis of weight, volume, and mass (note bottom scale in figure). As can be seen, the pressure potential of the water in the capillary tube, ψ_p , decreases with height to offset the increasing gravitational potential, ψ_g (both potential components are discussed in section 4.5). As a result, the pressure of the water within the capillary tube is less than atmospheric pressure (which is pressing down on the water in the tray), creating a pressure difference on both sides of the meniscus. Thus, it can be seen that the pressure potential in the air above the concave portion of the meniscus in the tube is 0. Because $R = r/\cos \theta$ (which can be rearranged to $r = R \cos \theta$), a general relation for the pressure difference across the meniscus interface with radius of curvature R is $\Delta p = 2\sigma/R$. It should be noted here that the highest pressure is on the concave side of the meniscus. This results in the pressure difference across the interface being inversely proportional to R , which is why reference points for pressure potential are not chosen at the meniscus, but at the water surface, thus avoiding the influence of a solid surface.

Capillary potential relates directly to the air entry value of porous ceramics, because the porosity of such ceramics mimics that found in soils of similar pore geometry. For example, the capillary tube in figure 4.6 has a meniscus height or capillary rise, h_c , of 0.6 m. If this tube is immersed in a container of water and then slowly raised, R is gradually decreased, but the capillary tube remains filled with water until its top reaches a height above the water level of the container that equals the maximum height of capillary rise (0.6 m, in this case). If

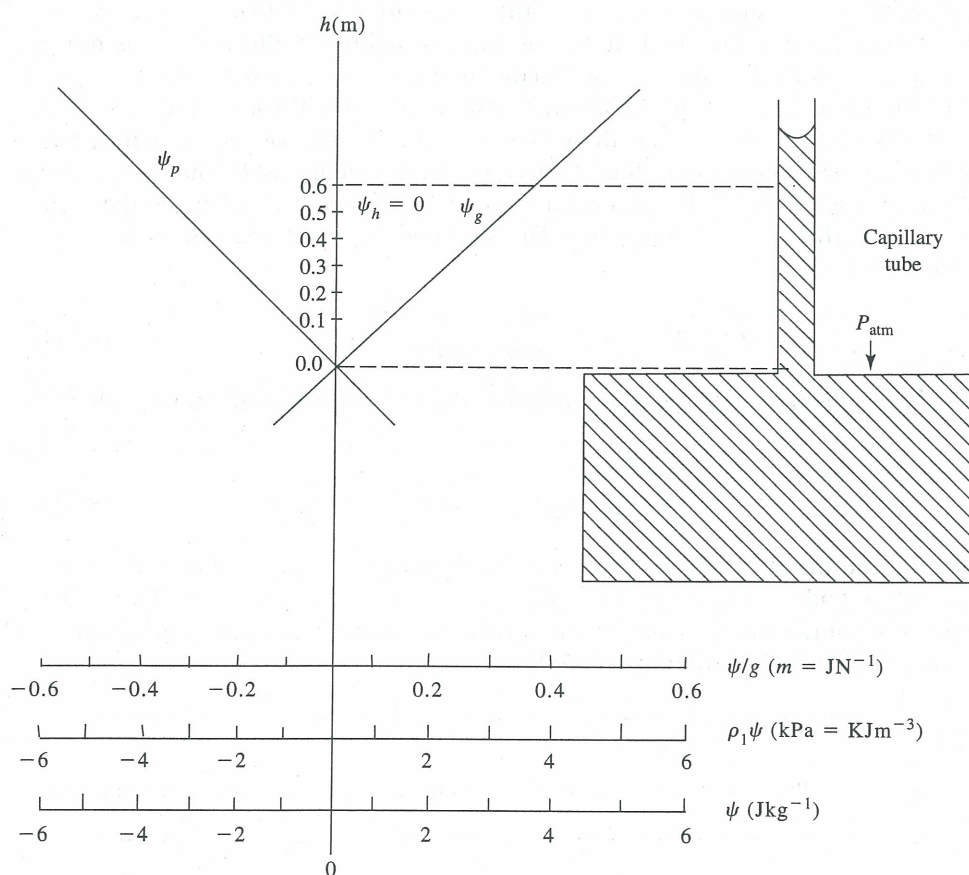


Figure 4.6 Diagram of potential in a capillary tube, where ψ_p is the pressure potential, ψ_h is head potential, ψ_g is gravitational potential, and h is head in meters

the tube is raised further, air enters from the top so that the water column remains at a height of 0.6 m. This is the reason why the pressure equivalent ($-\rho_l g h_c$) of the h_c is termed the air entry value. If water is expelled from a capillary by a positive gas pressure, that pressure is termed the bubbling pressure. Because h_c is the pressure head at the air-water interface of the meniscus, this concept can be extended to soil pores. For example, if the pressure potential in a soil pore is lower than the air entry value, both cohesive and adhesive forces cannot hold the water any longer. This will result in water draining from the pore until the pressure potential at the air-water interface is equal to that of the air entry value. Because soils are of many irregularly shaped “capillaries,” and not a clean glass tube, the concepts discussed here can only be applied qualitatively to capillary water in soils.

QUESTION 4.3

Considering equation 4.10, what is a suitable expression for the pressure potential, volume basis (kPa), of water at the meniscus in figure 4.6?

QUESTION 4.4

In a typically irrigated, completely wetted soil, the noncylindrical capillaries have an air entry value of -20 kPa. Calculate the height of capillary rise and the capillary diameter.

QUESTION 4.5

A capillary has a diameter of $18 \mu\text{m}$. Assuming complete wetting, what is the air entry value for this capillary?

4.5 COMPONENTS OF SOIL WATER POTENTIAL

The total potential of soil water has been defined as “the amount of work that must be done per unit quantity of pure water in order to transport reversibly and isothermally an infinitesimal quantity of water from a pool of pure water at a specified elevation at atmospheric pressure to the soil water at the point of consideration” (Bolt 1976). This transformation of pure water from the reference state to the soil-water state is actually broken into a series of steps. These steps are generally reversible and isothermal. Because of this, the total potential is actually a sum of each sequential step. These steps have been referred to as force fields (Hillel 1982), but are actually various components constituting the total potential that we shall discuss.

Consider a mass, m , that moves due to an external force acting in the opposite direction. The force applied is termed a static force, F^s . Any force applied must be only infinitesimally larger than the present force for movement to occur. The energy gained or lost in this process is the difference in potential energy of the mass between the starting and ending positions.

If we divide the potential energy difference by mass, we obtain the potential difference, $\Delta\psi$, which can be described by

$$\Delta\psi = -\frac{F^s}{m} \Delta s \quad (4.13)$$

where s is distance. The minus sign arises because potential decreases as the mass moves in the direction of the force. Since potential is potential energy divided by mass, it is expressed in J kg^{-1} .

Equation 4.13 is only valid when F^s is constant over the change in distance, Δs . However, in unsaturated zone studies with soil water, this is not normally true. If Δs is confined to a minute distance over which the force F^s can be assumed constant, equation 4.13 can be expressed as

$$\frac{F^s}{m} = -\lim_{\Delta s \rightarrow 0} \frac{\Delta \psi}{\Delta s} = -\frac{d\psi}{ds} \quad \text{or} \quad d\psi = -\frac{F^s}{m} ds \quad (4.14)$$

If we choose a reference point s_0 such that $\psi = 0$, then the potential for any point s_p can be obtained by integrating the right-hand equation in 4.14, yielding

$$\psi = -\int_{s_0}^{s_p} \frac{F^s}{m} ds \quad (4.15)$$

Because we are generally concerned only with differences in potential between two points, absolute values are neglected and we can assign an arbitrary value to the potential at s_0 , usually zero.

For a combination of directions of F^s and ds , equation 4.15 can be expressed as

$$\psi = -\int_{s_0}^{s_p} \frac{F^s}{m} \cdot ds = -\int_{s_0}^{s_p} \frac{F^s}{m} \cos \theta ds \quad (4.16)$$

where θ is the angle of direction of movement. Because more than one force field or component is generally present in a soil system, each component will contribute its own potential. This can be called a partial potential ψ_i , where the subscript is the i th component. Thus, the total potential, ψ_t , is the sum of all i th potentials. This is written as

$$\psi_t = \sum_i \psi_i = \sum_i -\int \frac{F_i^s}{m} \cdot ds = -\int \frac{\sum_i F_i^s}{m} \cdot ds \quad (4.17)$$

Assuming $\sum F_i^s = 0$ (static equilibrium), then

$$\psi_t = -\int \frac{F_i^s}{m} \cdot ds = -\int 0 ds = c \quad (4.18)$$

where c is the constant of integration.

As an example of two of the components, we can examine hydrostatics, the study of pressures or potentials in liquids at hydrostatic equilibrium. In hydrostatics (and in the hydraulic flow of a soil solution), the gravitational potential, ψ_g , and hydrostatic pressure potential, ψ_h , are generally the only two components of total potential that need to be accounted for. The sum of these two potentials is termed the hydraulic potential, and is expressed

$$\psi_h = \psi_g + \psi_p \quad (4.19)$$

However, additional components sometimes need to be measured. The following is a complete list of the potential components: gravitational potential (ψ_g), osmotic potential (sometimes referred to as solute potential) ψ_o , vapor potential (ψ_a), matric potential (ψ_m), hydrostatic pressure (submergence) potential (ψ_p), and overburden pressure potential (ψ_b). A discussion of each component follows.

Gravitational Potential (ψ_g)

All objects on the earth are attracted downward due to gravitational force. This force is equal to the weight of an object, which is a product of mass and gravitational acceleration. Gravitational potential is the energy of water (on a unit volume basis) that is required to

move a specific amount of pure, free water from an arbitrary reference point to the soil-water elevation. If the soil water elevation is above the reference point, z is positive (+); if the soil water elevation is below the reference, z is negative (−), where z is the vertical distance from the reference point to the point of interest. This means that the gravitational potential is independent of soil properties, and is solely dependent on the vertical distance between the arbitrary reference point and the soil-water elevation or elevation in question. Gravitational potential has the value

$$\psi_g = \rho_l g z \quad (4.20)$$

Here, ψ_g has the units of J m^{-3} and is assumed to be positive upward. Suppose one has chosen two soil-water elevation points in a soil column (for example, points 1 and 2 in figure 4.7). What would $\Delta\psi_g$ between the two points be? Because ψ_g is dependent on vertical distance (and not chemical, pressure, or other potentials), the answer is a simple one; it would merely be

$$\psi_g = \rho_l g(z_1 - z_2) = \rho_l g(0.25 - (-0.40)) = \rho_l g(0.65) \quad (4.21)$$

Often, the soil surface is chosen as the reference point. In such cases, the distance, $z(\text{m})$ to each point of interest below the surface is negative by convention.

Osmotic Potential (ψ_o)

The primary effect of salts in soil water is that of lowering the vapor pressure. However, this does not directly affect the mass flow of water in the soil, except in the presence of a membrane barrier of some type and in the case of vapor diffusion. Plants usually make up

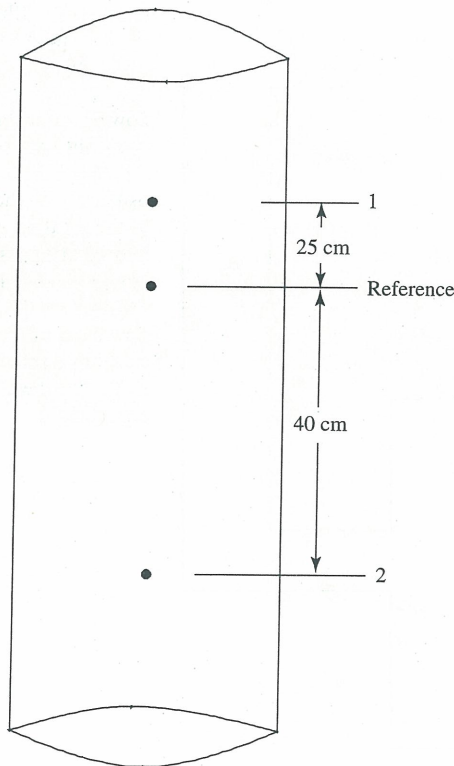


Figure 4.7 Soil column showing two points of soil water elevation in respect to an arbitrary reference

part of a dynamic soil-water-plant system, and their roots are often affected by the presence of salts in the soil solution. The membranes of plant roots transmit water more readily than salts, and are influenced by osmotic forces.

Osmotic potential may be thought of more as a suction than a pressure. This is illustrated in figure 4.8. In the presence of a selective permeable membrane (as found in plant roots), the pressure or energy potential (a suction) on the solution side is less than that of pure, free water, and the water first will pass through the membrane to the solution side. This will cause an initial rise in the solution level in the column (figure 4.8), and a fall in the fluid level on the pure water side. As equilibrium is established, both the concentration and fluid level will be constant on each side of the membrane. One can prevent flow across the membrane and maintain static equilibrium by exerting gas pressure, P , on the soil solution side of the container in excess of atmospheric pressure. This will result in the total potential at the surface of the solution, ψ_t , being

$$\psi_t = \frac{1}{\rho_w} P + \psi_g + \psi_o \quad (4.22)$$

where P is the air pressure (Pa) in excess of atmospheric. The term $1/\rho_w$ is included due to the small difference between the density of the solution and that of pure water, and is expressed in units of J kg^{-1} . However, in practice, it is often neglected, and the simple term P is used (in which case the units are expressed in J m^{-3}). At the surface of the pure water, the total potential is

$$\psi_t = \psi_g + \psi_m + \psi_o = \psi_g + 0 + 0 = \psi_g \quad (4.23)$$

Because the solution is pure water, we can ignore the matric potential, ψ_m , and osmotic

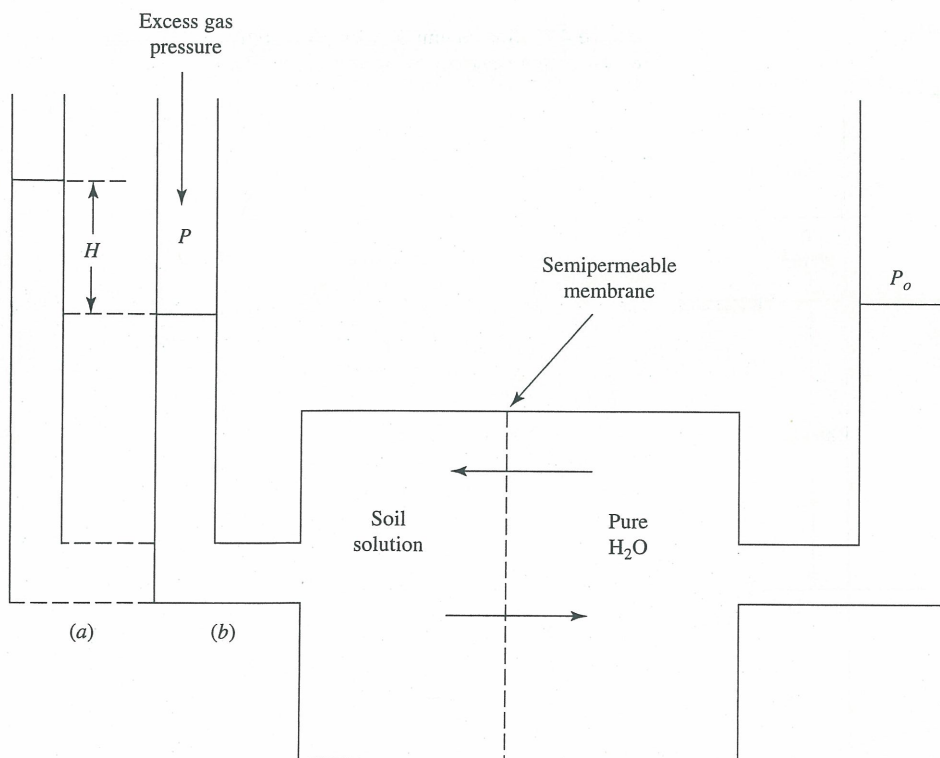


Figure 4.8 Illustration of osmosis in relation to osmotic potential/suction across a permeable membrane. (a) illustrates that the flow of water through the membrane into the solution is greater than from solution to water (i.e., osmosis); (b) the osmotic pressure of the solution is equal to the hydrostatic pressure that must be applied on the solution side, a (+) pressure on the P_o side, to equalize flow from the solution to the water side, or (-) suction on the P side. Both must be equal to obtain equilibrium.

potential, ψ_o . At static equilibrium, $\psi_t = \psi_g$. Consequently, expressed in J m^{-3} ,

$$P + \psi_o = 0 \quad (4.24)$$

To maintain equilibrium, the excess air pressure needed must be equal to what is commonly referred to as the osmotic pressure, Π , of the solution, resulting in an expression for osmotic potential of

$$\psi_o = -\frac{\Pi}{\rho_w} \quad (4.25)$$

If we assumed the presence of soil and water, equation 4.25 (in J/kg) could be expanded to include the total potential of soil water components, and written as

$$\psi_t = \frac{(\Pi - \psi_m)}{\rho_w} + gz \quad (4.26)$$

Because soil is porous, it acts as a semipermeable barrier for salt solutions. As the reader may recall from chapter 3, each individual particle has an electric field that causes a decrease in concentration of the soil solution near the particle surface. This results in an increased cross sectional area for water transport compared to the area available for transport of dissolved salts, and causes water to move, due to osmotic differences. The amount of flow depends on the particle size of the media and the gradient of osmotic pressure. For example, in a coarse, saturated sand, soil pores are relatively large in comparison to those in clays. Consequently, the thickness of the fluid layer with decreased salt concentration is small when compared to the total area available for transport. As a result, the semipermeability will be small, and the transport of soil solution due to osmotic potential is negligible. In clays, the opposite is true. With many more pores, the solutes in soil solution can be completely repelled from the soil and restricted from flow. In such soils, water movement in response to an osmotic pressure gradient is as significant as when a hydraulic pressure gradient of equal size is applied. Hence, osmotic and hydraulic pressure gradients have equivalent effects on water movement. This can be proven by a modification of Darcy's law, such that $q = -K[dH/dz - (1/\rho g)(d\Pi/dz)]$.

Vapor Potential (ψ_a)

A combination of matric and osmotic forces determines the equilibrium vapor pressure for soil vapor diffusion. Since water vapor consists of pure water, both the osmotic and matric potentials are 0. The total potential in the vapor phase (the soil vapor pressure and the position of the gravitational field) can be determined such that

$$\psi_t(\text{vapor}) = \int \frac{1}{\rho_{\text{vapor}}} dP + gz \quad (4.27)$$

where the denominator is the density of the vapor. However, we can make substitutions to obtain the total potential of the water vapor as

$$\psi_t = \int \frac{RT}{PM} dP + gz = \frac{RT}{M} \ln P + gz + C \quad (4.28)$$

where R is the gas constant (8.314 J/mol K), T is temperature (K), P is vapor pressure (Pa), M is the molar mass of water (18.013 g), and C is an integration constant.

If we assume the gas-liquid interface, gz , is identical for both the liquid and the water vapor, then it can be expressed as

$$\psi_t(\text{liquid}) = gz = \psi_t(\text{vapor}) = \frac{RT}{M} \ln P_0 + C + gz \quad (4.29)$$

and

$$C = -\frac{RT}{M} \ln P_0 \quad (4.30)$$

By substituting equation 4.30 into equation 4.28, we obtain the total potential of water vapor at a vapor pressure, P :

$$\psi_t(\text{vapor}) = \frac{RT}{M} \ln \frac{P}{P_0} + gz \quad (4.31)$$

where p_0 is the vapor pressure at a free surface of pure water under atmospheric conditions (see figure 4.8). By convention, at static equilibrium, the total potential in the soil solution must be equal to the total potential of water vapor in the soil air; thus,

$$(\Pi - \psi_m) \frac{1}{\rho_l} = \frac{RT}{M} \ln \frac{P}{P_0} \quad (4.32)$$

Assuming standard unit values for pure water density, R , T , and M at 25 °C, equation 4.32 may be rewritten as

$$\ln \frac{P}{P_0} = (\Pi - \psi_m) 7.5 \times 10^{-9} \text{ Pa}^{-1} \quad (4.33)$$

Thus, one can see that the relative vapor pressure, P/P_0 , at the interface of the soil water and soil air is determined by both the osmotic potential and the matric potential of the soil. The matric potential is sometimes referred to as tensiometer pressure and denoted as p_r . In field studies, it is generally assumed that soil air is at atmospheric pressure and, as such, can be expressed as

$$\ln \frac{P}{P_0} = (\Pi - p_m) 7.5 \times 10^{-9} \text{ Pa}^{-1} \quad (4.34)$$

where p_m is the pressure (Pa) equal to the matric potential of the soil. The relative vapor pressure may also be expressed in head equivalent form; that is, $\rho_l g$ (approximately 10^4 N m^{-3}) as

$$\ln \frac{P}{P_0} + (h_m + h_o) 7.5 \times 10^{-5} \text{ m}^{-1}; \quad h_o = \frac{\Pi}{\rho_l g} \quad (4.35)$$

where h_m is the matric head of soil water (m) and h_o is the osmotic pressure head of the soil water. As a note, the reader should remember that $\Pi = MRT$, where M in this case is the molar concentration of the solution; R and T are as previously defined.

QUESTION 4.6

Why is the total potential of soil water at the water surface $\psi_t = gz$ (see equation 4.26)?

QUESTION 4.7

If the relative vapor pressure in a laboratory is kept at 50%, what is the head value of air measured by a tensiometer in the laboratory?

Matric Potential (ψ_m)

The matric potential of a soil results primarily from both the adsorptive (see van der Waals-London forces in chapter 3) and capillary forces due to soil matrix properties and is, thus, a dynamic soil property. The matric potential is often referred to as capillary or pressure potential, and is usually expressed with a negative sign. By convention, pressure is generally expressed in positive terms. Suppose one had a standing soil column one meter in height with a water table at a depth of 0.80 m (figure 4.9). The matric potential above the water table would be negative, the potential at the water table would be zero, and the potential below the water table would be positive in sign. By convention, ψ_m , the matric potential, becomes ψ_p below the water table, the pressure potential, and is sometimes referred to as the submergence potential. Below the water table, the pressure potential is equivalent to ρgh , where h is distance below the water table. It should be noted that an unsaturated medium has no pressure potential, but only a matric potential with negative units.

The term matric potential works well for rigid, self-supporting soils. In these soil types, the weight of the solid portion of the soil above the specific point of measurement is sustained by the soil matrix. External forces will not influence the matric potential in this case, as it is characterized by the amount of soil water present. However, in swelling soils, solid particles are not in complete contact with each other. Consequently, part of the weight overlying the soil matrix may be exerted on any element of soil water. Also, with a change in water content, a reorientation of solid particles may occur that can influence the interfacial

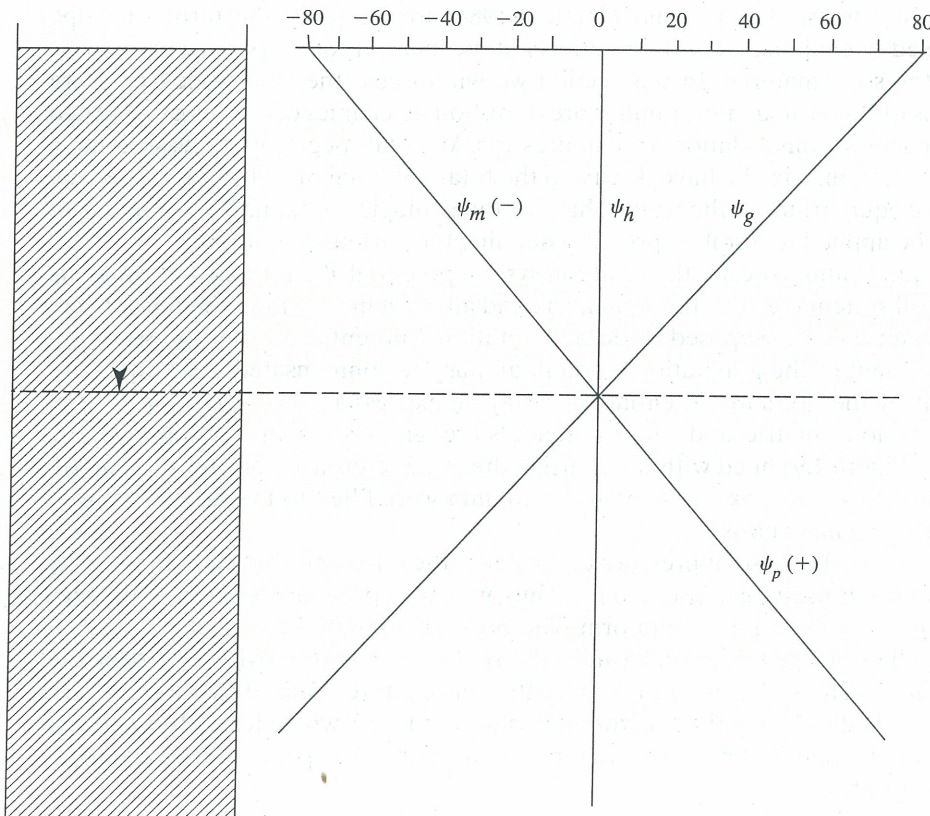


Figure 4.9 Soil column with water table at 80 cm, illustrating relation between soil component potentials

curvature of water in the soil. Variation in the pneumatic potential may also cause reorientation of solid particles. As a result, the matric potential typically is separated into two additional components for swelling soils. These components are: the effects of mechanical forces exerted by the pressure of the solid material (this is generally referred to as the overburden pressure, ψ_b , and is described in a subsequent section); and the effect of soil geometry, such as interfacial curvature and adsorptive forces. The latter component can be adequately described by the wetness potential, ψ_w , which is the value of the matric potential when both the soil stress, P_e , and external air pressure are 0.

Hydrostatic Pressure Potential (ψ_p)

The term pressure potential usually implies that soil water is at a hydrostatic pressure greater than atmospheric pressure and, thus, has a positive sign. Observation of the column in figure 4.9 indicates that the water beneath the free surface (water beneath 80 cm) has a positive pressure potential. Water at the surface—at 80 cm in the column—has a pressure potential of 0. The pressure potential for any point beneath the water table can be written as

$$\psi_p = \rho_l gh \quad (4.36)$$

where h is the distance below the water table. It is sometimes expressed as $z_{wt} - z_{soil}$ where the subscripts “wt” and “soil” refer to the water table and to a specific point within the soil.

Overburden Pressure Potential (ψ_b)

In many soil physics texts, Marshall and Holmes (1988) for example, the term envelope pressure, P_e , is used in conjunction with the effects of mechanical forces (stress) exerted by the pressure of the solid material. In this section we will discuss the overburden pressure potential, which is often termed intergranular pressure. Soil mechanics describes overburden in terms of compaction, consolidation, or compression. We shall begin by discussing static equilibrium for the soil matrix. We have discussed the total potential of soils, and applied the condition of static equilibrium to the water phase of the geologic medium. These same conditions may also be applied to a soil by properly defining the various potentials.

For static equilibrium to occur, the total soil system potential, ψ_t , must also be uniform. In this case, the soil system includes the soil matrix and all substances within the pore spaces of the matrix. Because ψ_t is composed of both gravitational potential, ψ_g , and pressure potential, ψ_p , the gradient of the gravitational potential must be compensated at an equal but opposite gradient by the pressure potential. This may be expressed as $\psi_t = \psi_g + \psi_p = \text{uniform}$, where the osmotic, matric, and vapor potentials are ignored. As an example, suppose one had a column (figure 4.9) filled with water; using the same reference points for ψ_p and ψ_g , the potential diagram would look the same if the column were filled to the same level with soil (for potentials on a mass basis).

For a volume basis, because of pressure equivalents, the difference between the density of the soil and soil water must be accounted for. Thus, we can express the total potential on a volume basis as $\rho_b \psi_t = \rho_b \psi_g + \rho_b \psi_p = \text{uniform}$. The pressure potential on a volume basis is generally termed the soil stress, σ_s , which can be expressed as $\sigma_s = \rho_b \psi_p$, where ρ_b is the dry bulk density (kg m^{-3}). The soil pressure is simply the vertical force caused by the weight of the overlying material divided by the horizontal surface area over which it lies. It is actually the normal component; that is, that component perpendicular to the plane of interest of the stress at a specific location.

Intergranular Pressure (σ_g)

Intergranular pressure, σ_g , written in terms of stress, is the contact force between individual particles divided by the area. In water-saturated soil, the weight of the overlying medium is supported by both the contact force between particles and also the contact force in the water itself, which may be expressed simply as $\sigma_s = \sigma_g + \psi_p$, where ψ_p is the water pressure (which can also be defined as $\psi_p = p - p_{\text{atm}}$). Here, ψ_p is the tensiometer pressure potential of soil water, and p is the absolute pressure potential. In a dry soil, the vertical intergranular pressure will be equal to the soil pressure, σ_s , because the weight of overlying material will be supported solely by the contact forces between individual particles. For a rigid soil, this may be expressed as $\sigma_s = \sigma_g$.

Due to friction between individual particles, soils resist motion of the particles relative to each other that might result from differential loading. Examples of soil movement due to differential loading include compaction of soils due to construction practices, operation of heavy equipment on soils, and agricultural activities such as tillage. The resistance of the soil to each of these activities is determined by friction caused by intergranular pressure.

For a rigid unsaturated medium, ψ_p is negative, simply because this negative pressure is supported by the soil particles pressed against each other with a force that exceeds the weight of the overlying soil. Thus, the ψ_p is active only within water-filled pores. As a result, the soil pressure for an unsaturated rigid soil may be expressed as

$$\sigma_s = \sigma_g + \frac{\theta}{\phi} \psi_p \quad (4.37)$$

Remembering that the volumetric water content, θ , cannot exceed the porosity, ϕ , this coefficient for the water pressure will vary from 0 at air dryness to 1 at full saturation. It should be noted that the second term on the right hand side of equation 4.37 has been termed the wet bulk density (Bolt 1976), and often appears as the term ρ_{wb} . Assuming an absence of load at the soil surface (such as machinery or structure), the overburden pressure at a chosen depth is due to the load of soil above that depth and can be expressed by

$$\psi_b = \sigma_g + \int_z^0 \frac{\theta}{\phi} \psi_p dz \quad (4.38)$$

Intergranular pressure decreases due to upward water transport. This causes a reduction in the bearing capacity of the soil, which is dependent on frictional forces between individual particles. In certain cases of strong upward flux the intergranular pressure may completely disappear; an example of this is quicksand.

In contrast to rigid soils, clay soils have unique properties, especially in regards to the propensity of some clays to swell. The intergranular or overburden pressure in these soils is not supported solely by the grain to grain contact as in rigid soils, but includes the pore water, which forms continuous vertical columns between the grains. In these soils, consolidation plays a major role in the ability of the soil to conduct water, which affects the hydraulic properties because of subsequent reduction in void space with time. Thus, with depth, the pressure or stress of the overlying material increases, reducing the gradient in hydraulic potential (Philip 1971).

The hydraulic potential, $\psi_h = \psi_{mL} + \rho gz$ (where ψ_{mL} is the matric potential of the loaded sample), of a swelling soil can be expressed as

$$\psi_h = \psi_{mu} + \beta \psi_b + \rho gz \quad (4.39)$$

where ψ_{mu} is the matric potential of the unloaded sample, ρ is the density of water, z is depth relative to soil surface (where $z = 0$), and β is the compressibility factor, often termed in soil

mechanics the pore compression coefficient. The pressure potential, $\beta\psi_b$, due to overburden pressure expressed in equation 4.39, on a per unit volume of water basis, can be expressed as

$$\beta\psi_b = -\beta g p_{wb} z \quad (4.40)$$

where ρ_{wb} is wet bulk density. To obtain the hydraulic potential, equations 4.39 and 4.40 can be combined such that

$$\psi_h = \psi_{uL} + \rho g \left(\frac{1 - \beta \rho_{wb}}{\rho} \right) z \quad (4.41)$$

where ψ_{uL} is the hydraulic potential of the unloaded sample. Equation 4.41 indicates a reduction in the gravitational component due to overburden pressure.

The β term, or pore compression coefficient, may be expressed as the instantaneous increase in pore-water pressure divided by the increase in total stress of the overburden: $\beta = P_w/\psi_b$. The compressibility of pore water is negligible in fully saturated soils if we assume that the compressibility of the solid particles is 0. In this case, $\beta = 1$. For partially saturated soils, the compressibility of pore fluid is high and $\beta < 1$. As soil water content decreases, β also decreases. Talsma (1977) measured field samples of $\beta < 0.25$ for several swelling clay soils, whereas Croney, Coleman, and Black (1958) reported values of 1, 0.3, and 0.02, for a clay, silty clay, and sand, respectively, which had unloaded suctions of < 40 cm. While the degree of saturation will vary for each soil type, a typical variation of β with degree of saturation is shown in figure 4.10. The value for β is typically measured in a triaxial test as cell pressure is increased. Note: “loaded samples” refers to samples that have been placed in the triaxial cell, brought to a certain water content, and a pressure then applied. “Unloaded samples” refers to soils extracted from the field, in which the pore pressure is then measured.

For most soils, three cases of soil-water equilibrium can occur. First, if a soil system contains a selective or semipermeable barrier that allows movement of water but not solutes, an

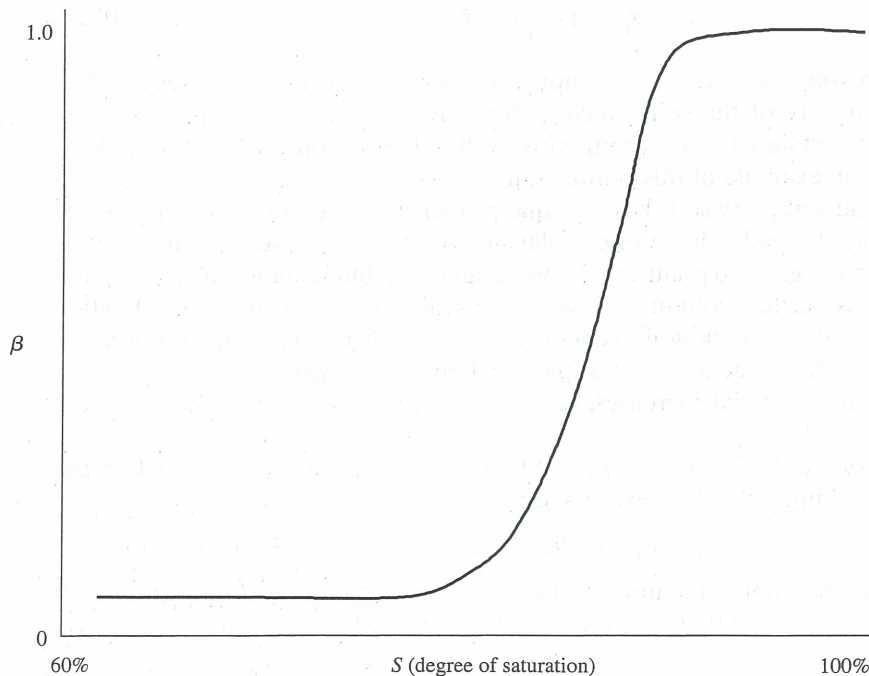


Figure 4.10 The pore pressure coefficient, β , versus degree of saturation

equilibrium will be obtained only if the total potential is uniform; that is, if $\psi_t = \psi_m + \psi_g + \psi_o$. This case would be most likely in dry soils where water is in thin films, small pores, or electrical double layers and movement occurs through the gas phase. Second, solutes and dissolved salts can generally move freely through sandy soils. In this case, if the hydraulic potential is uniform (hydraulic potential is defined as the sum of the pressure potential, ψ_p , and the gravitational potential, ψ_g ; $\psi_h = \psi_p + \psi_g$), an equilibrium of the soil solution will occur if $\psi_h = \psi_m + \psi_g$. This assumes that the hydraulic potential does not vary with position. Third, in the case of moist clay soils, salt transport is difficult, especially in fine, clayey soils, because soil water is normally present in thin films on individual particles. Moist clay soils have barriers that obstruct the transport of salts or solutes without completely preventing it. As water diffuses in the direction of the solute, small quantities of solute are transported. Before equilibrium occurs, the difference in hydraulic potential in the water and solute balances the difference in osmotic potential. However, because the solute concentration is still different on both sides (i.e., the water next to the soil particle and that within the bulk solution), total equilibrium will exist only if $\psi_h = \text{uniform}$ and $\psi_o = \text{uniform}$. At some time, $\psi_t = \text{uniform}$ (i.e., equilibrium is reached). Because of the effects of the electrical double layer, anions are repelled by the electrostatic charge (see chapter 3).

QUESTION 4.8

An experiment is conducted on a dry sandy soil with a bulk density of 1500 kg m^{-3} . Assuming the soil is at static equilibrium, what is the soil pressure 1 m below the surface?

4.6 CHEMICAL POTENTIAL OF SOIL WATER

Prior to reading this section, the reader may wish to review the basic laws and relations of thermodynamics, and the correlation with enthalpy, entropy, and free energy, by consulting a standard physical chemistry text such as Alberty (1987). The increase in internal (or stored) energy of a system must be equivalent to the quantity of heat energy, Q_h , absorbed by the system from its surroundings, less the energy lost by the system to the surroundings as a result of work, W , done by the system due to the absorption of heat. This change of free energy at constant temperature and pressure in an open system is associated with the transfer of mass from one phase to another (i.e., a change in mass from one chemical combination to another, such as condensation, evaporation, and inflow and outflow from a given section). Differentially, the equation for chemical potential, μ_i , of the i th component can be written as

$$d\mu_i = -S_i dT + V_i dP + \sum_j \left(\frac{d\mu_i}{dM_i} \right)_{T,P,m_j} dM_i \quad (4.42)$$

where S , T , V , and P refer to entropy, temperature, volume, and pressure, respectively; m_i is the mass or number of moles of the various constituents in the system; and M_i is the mole fraction of the i th constituent. However, equation 4.42 describes the thermodynamics of the system involving T , P , and M_i only as variables. The description of water in soil will also require at least one external force field as an additional variable. That force field and variable is gravity. A generalized equation for the internal energy of the system, E , with the new variable, x_n , can be expressed as

$$dE = T dS - P dV + \sum_i \mu_i dm_i + \sum_n \left(\frac{\partial E}{\partial x_n} \right)_{S,V,m_i,x_n} dx_n \quad (4.43)$$

The new intensive property X_n can be defined as

$$X_n = \left(\frac{\partial E}{\partial x_n} \right)_{S,V,m_i,x_n} \quad (4.44)$$

This allows equation 4.43 to be rewritten as

$$dE = T dS - P dV + \sum_i \mu_i dm_i + \sum_n X_n dx_n \quad (4.45)$$

We can specify X_n using only gravity as the external force field. For example, if a mass of soil water, m , is at a height in the soil, z , in a gravitational field above a specific reference point, we can express the potential energy, E_p , associated with this soil water as $E_p = mgz$. This implies the gravitational potential, $\psi_g = E_p/m = gz$. In this case, the gravitational potential is an intensive property which will allow X_n to be specified as $X_n = \psi_g = gz$ (on a mass basis; expressed on a volume basis it is $X_n = \psi_g = \rho gz$), and

$$dX_n = \sum_i M_i dm_i \quad (4.46)$$

By substituting these relations into equation 4.45, we obtain

$$dE = T dS - P dV + \sum_i (\mu_i + M_i \psi_g) dm_i \quad (4.47)$$

and

$$\left(\frac{\partial E}{\partial m_i} \right)_{S,T,m_i} = \mu_i + M_i \psi_g \quad (4.48)$$

Because the intensive properties of substances are not affected by the presence of a gravitational field, and because ψ_g is independent of mass, equations developed for chemical potential in the absence of a gravitational field are also valid if a field is present. Consequently, at constant entropy, volume, and mass and with $\psi_g = 0$, we may write

$$\mu_i = \left(\frac{\partial E}{\partial m_i} \right)_{S,V,M_i,(\psi_g=0)} \quad (4.49)$$

Recalling the relation of the ideal gas law and Raoult's law for an ideal solution, and because the activity of a pure solid or liquid at a chosen reference state at each selected temperature and pressure is unity, the chemical potential for various conditions for the i th component of a soil water system can be expressed as:

$$(\mu_w - \mu_w^0) + RT \ln \left(\frac{P_w}{P_w^0} \right) = RT \ln \left(\frac{e}{e^0} \right) \quad (4.50)$$

$$(\mu_w - \mu_w^0) = RT \ln M_w \quad (4.51)$$

and

$$(\mu_w - \mu_w^0) = RT \ln a_w \quad (4.52)$$

where the subscript w is the soil water component; the superscript 0 indicates the component of pure free water at the same temperature and atmospheric pressure; P indicates pressure, and a is activity; e is the soil water vapor pressure, and e^0 saturated water vapor pressure.

The partial molal free energy, F , of soil water is expressed as

$$\left(\frac{\partial F}{\partial m_w} \right)_{T,P,m_i} = F_w = \mu_w + M_w \psi_g \quad (4.53)$$

However, it should be noted that F_w is under the influence of forces associated with fluid-air and solid-fluid interfaces within the soil matrix. By ignoring gravity, the effect of volumetric water content can be factored into any change in chemical potential of soil water. This can be expressed as

$$d\mu_w = -S_w dT + V_w dP + \sum_j \left(\frac{\partial \mu_w}{\partial m_i} \right)_{m_j, T, P} dm_i + \left(\frac{\partial \mu_w}{\partial \theta} \right)_{m_w, T, P} d\theta \quad (4.54)$$

where P is the pressure in the gaseous phase at the fluid-solid interface, V_w is the partial molal volume of soil water, and $\partial \mu_w / \partial \theta$ is the change in chemical potential with respect to the change in volumetric water content. The summation is for all chemical species, but for those for which the mole number does not change, the contribution is 0. Examination of equation 4.54 indicates that under isothermal conditions, the first term on the right-hand side will disappear, and for unsaturated zone conditions, the second term can be ignored as well, because the pressure difference between the soil surface layers up to the active biological zone and the atmosphere generally is small. That leaves the third and fourth terms to obtain.

The pressure in soil water is less than that of pure water due to the presence of solutes; the soil water is brought to equilibrium by applying external gas pressure, P (as described in figure 4.8), to raise the chemical potential of the soil water so that it is in equilibrium with that of pure water. This can be expressed mathematically by

$$\int_{\mu_w(m_i)}^{\mu_w^0} d\mu_w = \int_P^{P_{\text{ext}}} V_w dP \quad (4.55)$$

where μ_w^0 is the chemical potential of pure water, $\mu_w(m_i)$ is the chemical potential of soil water, and P_{ext} is the external pressure required to bring the soil-water chemical potential to that of pure water. Because the net volume is constant at equilibrium, one may integrate equation 4.55 to obtain

$$[\mu_w(m_i) - \mu_w^0] = -V_w(P_{\text{ext}} - P) = -V_w \Pi = V_w \psi_o \quad (4.56)$$

To determine the fourth term on the right hand side of equation 4.56, one may use the analogy of a porous cup tensiometer. In unsaturated soils, the porous cup of a tensiometer is permeable to both the soil water and other chemical constituents of the fluid present in the system. When an equilibrium within the porous cup and the soil solution has been attained, the water in the cup will have the same composition as that in the surrounding soil matrix. However, in this case, equilibrium is attained by decreasing the pressure of water in the porous cup from P_o to P . The chemical potential is also correspondingly lowered from μ_w^0 to μ_w . As a result, we may obtain the fourth term from

$$\int_{\mu_w(\theta)^{(B)}}^{\mu_w^{0(A)}} d\mu_w^{0(A)} = \int_{P_o}^P V_w^{(A)} dP \quad (4.57)$$

where A and B refer to solution in tensiometer and soil (see figure 4.11). Because $V_w^{(A)}$ is constant at equilibrium, we obtain

$$[\mu_w(\theta) - \mu_w^0] = V_w^A(P - P_o) = V_w \psi_m \quad (4.58)$$

This allows us to write equation 4.54, due to isothermal conditions, as

$$d\mu_w = V_w dP + V_w d\psi_o + V_w d\psi_m \quad (4.59)$$

As a result, the chemical potential of soil water, compared to pure free water, may be expressed as

$$\frac{\mu_w - \mu_w^0}{V_w} = P + \psi_o + \psi_m \quad (4.60)$$

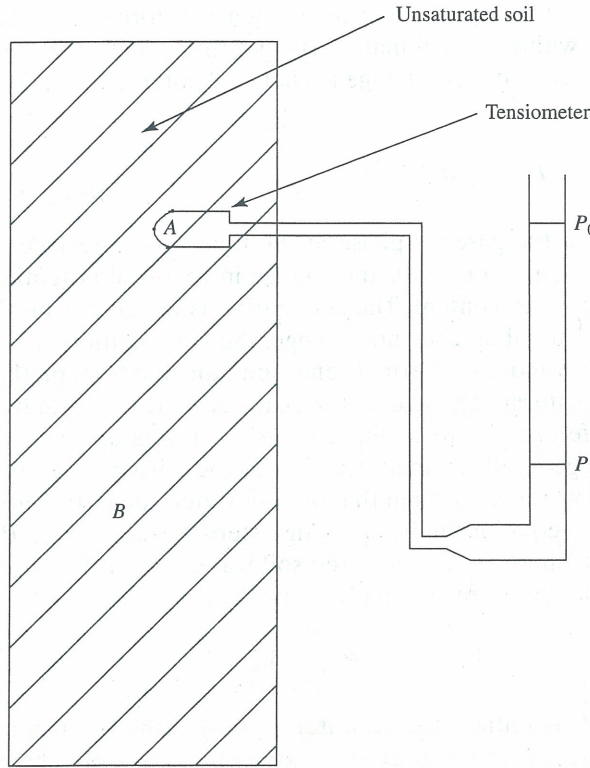


Figure 4.11 Chemical potential measurements in tensiometer, A, and unsaturated soil, B, in conjunction with equation 4.57

These equations assume a uniform geometry of particles in the soil matrix. For swelling soils, a geometric term would have to be added to equation 4.54 to obtain the chemical potential. Equation 4.54 would be rewritten as

$$d\mu_w = -S_w dT + V_w dP + \sum \left(\frac{\partial \mu_w}{\partial m_i} \right)_{m_w, T, P, v} dm_i + \left(\frac{\partial \mu_w}{\partial \theta} \right)_{m_w, T, P, v} d\theta + \left(\frac{\partial \mu_w}{\partial v} \right)_{m_i, T, P, m_v} dv \quad (4.61)$$

where v is the geometric term and can be expressed in volume units as

$$\left(\frac{\partial \mu_w}{\partial v} \right)_{m_i, T, P, m_v} dv = \left(\frac{\partial \mu_w}{\partial V} \right)_{m_i, T, P, m_v} dV \quad (4.62)$$

Pursuant to this discussion we may say that the energy status of the soil can be expressed in both mechanistic and thermodynamic terms. The mechanistic view represents the microscopic viewpoint and isothermal conditions (no change in temperature), where a volume element of water is used to describe the force fields which act upon soil water, but are external to the unit volume of water. (These force fields arise primarily because of solutes, gravity, matrix properties, etc.) The thermodynamic view considers measurable variables such as external pressure, temperature, volume, ions, water, soil particles, and so on. Thermodynamically, the derivation of Gibbs function (equation 4.54) and the chemical potential (i.e., consistent with the first and second laws of thermodynamics), includes temperature and entropy, which allows broader applicability in a description of the soil-water energy status than a mechanistic (microscopic) viewpoint.

The term “free energy” has been widely accepted as the best to use in describing the energy status of soil solutions. This term includes all types of energies: kinetic, chemical,

potential, heat, electrical, and so on. Rather than the absolute value of free energy, differences in free energy between two different states are typically determined. By knowing the difference, the direction of a spontaneous energy change between the two states can be obtained. A number of measurements are necessary to characterize the different components of soil water. Once taken, they must be integrated to obtain the difference of free energy between soil water and a reference water. Perhaps the best method of measuring chemical potential is the vapor pressure method (Ghildyal and Tripathi 1987) which, although concise, is also complicated.

4.7 HYSTERESIS

A typical soil-moisture characteristic curve for an initially saturated soil is shown in figure 4.12. As matric potential decreases, that is, becomes more negative (increased suction), the volumetric water content decreases. Generally, these types of curves are obtained to relate soil moisture to matric potential. The moisture curve shown in figure 4.12 is termed a “desorption” curve. However, in typical field situations, not only will there be a drying or drainage cycle as illustrated in the figure, but there will also be a sorption cycle as the soil profile is rewetted through natural or artificial means. The sorption curve is obtained by wetting an initially dry soil while measuring the soil matric potential. Two curves can be obtained, a desorption and a sorption curve, which are illustrated in figure 4.13. The primary curves from saturation to dryness and vice versa are known as main branches. Due to the wetting and drying history of a soil, especially in the field, these two curves normally will not be the same, although they will typically be smooth in shape. One may see that during equilibrium, at any point along the curve, the moisture content for the desorption curve is always greater than for the sorption curve (figure 4.13). The dependence of soil-water

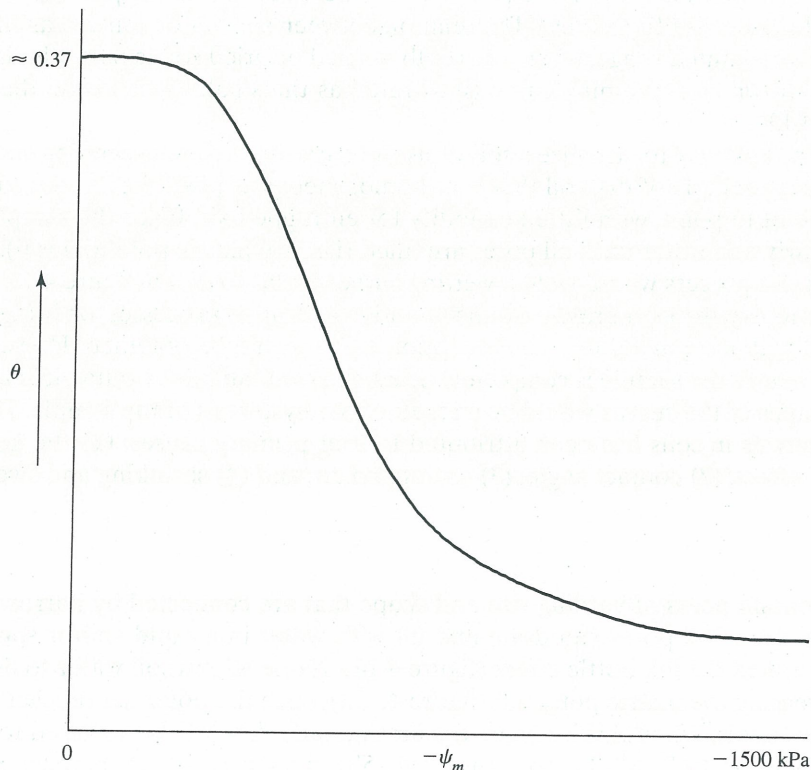


Figure 4.12 Soil-moisture characteristic curve

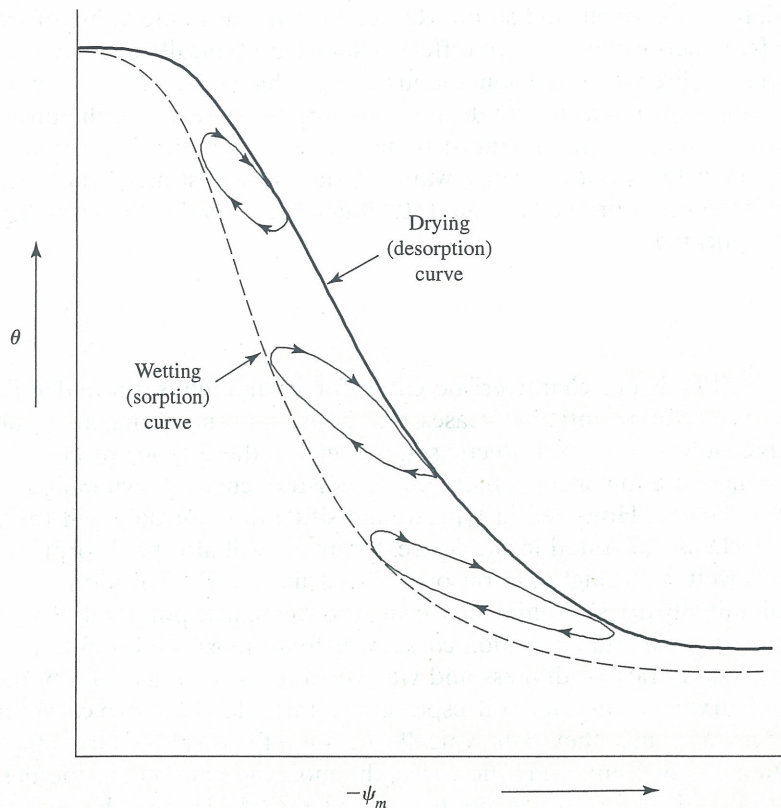


Figure 4.13 Sorption and desorption curves, illustrating effects of hysteresis

equilibrium content and matric potential on the direction of the process leading up to it is termed hysteresis (Topp 1969). The relation between soil-water content and matric potential over a very limited range, when a partially wetted or dried soil is partially drained or rewetted, is known as a scanning curve (illustrated as the small loops inside the main curves in figure 4.13).

The best way to visualize a soil-moisture curve and related scanning curves is to assume you have a sample of dry soil that is as homogeneous as possible; i.e., the soil does not vary from point to point, with little possibility for entrapped air. Place the sample in a container and slowly add water until all pores are filled (i.e., the matric potential is 0). Plotting the results of this process would yield a wetting curve similar to that in figure 4.13. By allowing the sample to dry through gravity drainage and evaporative processes, or bringing the soil into contact with a dry medium, the desorption curve would be obtained. However, if rewetting occurs before the sample is completely dried, the resultant plot would yield a scanning curve. The shapes of the curves would be a result of the hysteresis of the sample. The phenomenon of hysteresis in soils has been attributed to four primary causes: (1) the geometric or “ink bottle” effect; (2) contact angle; (3) entrapped air; and (4) shrinking and swelling.

Ink Bottle Effect

Soils contain pores of varying size and shape that are connected by narrow passageways of various sizes. Soil pores can drain and fill with water in a rapid and/or sporadic manner, a result termed the ink bottle effect (figure 4.14). If one allows soil water to drain from a pore by increasing the matric potential (figure 4.15a), once the potential reaches ψ_r , the pore will drain suddenly. When this happens, the air-fluid interface will be lowered to a critical radius of the pore neck. To fill the pore (figure 4.15b), the matric potential must increase to ψ_R , in

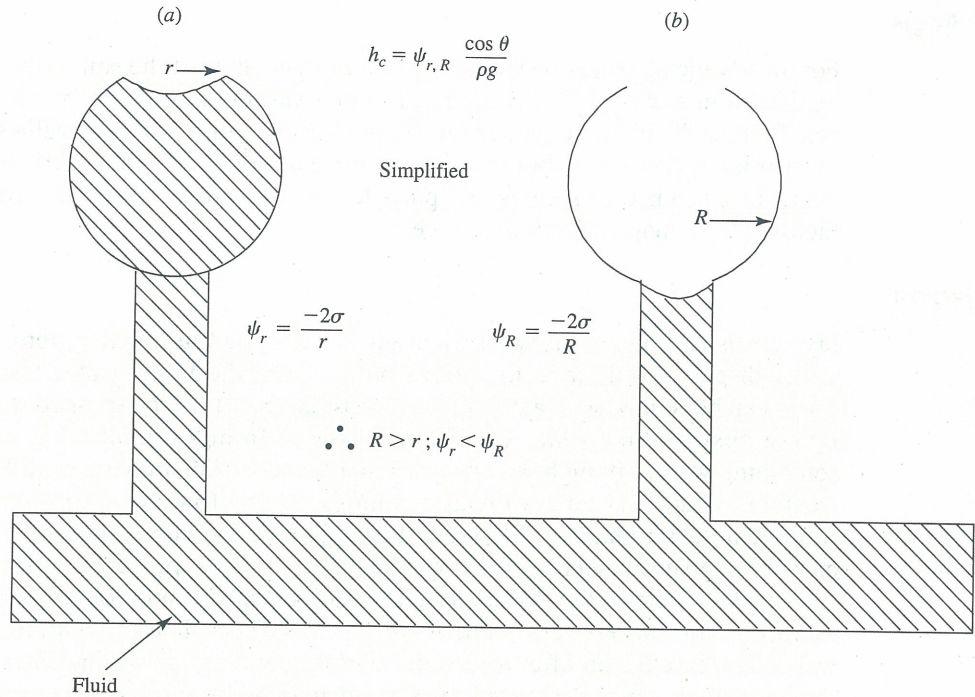


Figure 4.14 The “ink bottle” effect determines the equilibrium height of soil water in a nonuniform width pore. (a) desorption and (b) sorption (data from Hillel 1982)

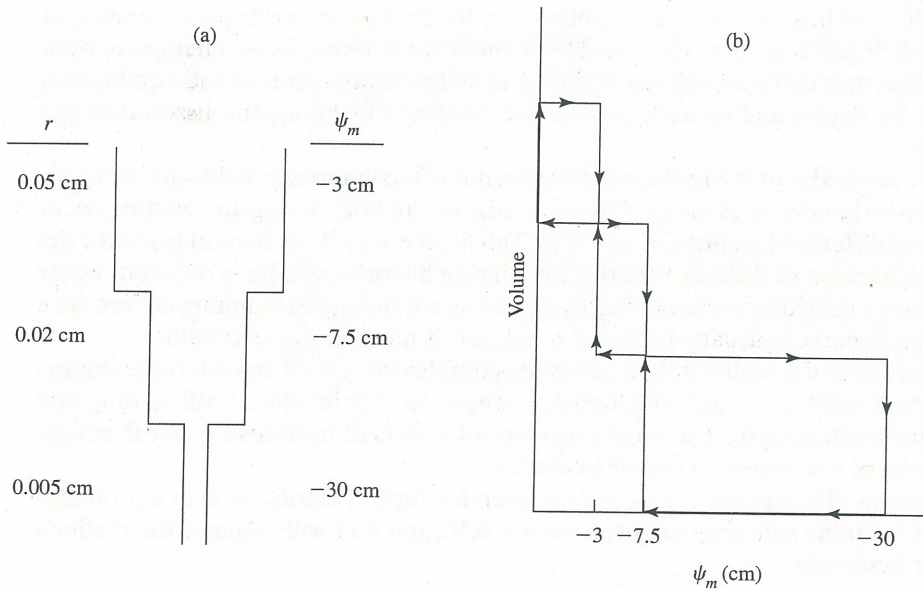


Figure 4.15 Matric potential associated with soil pore radius and hysteresis

which case the pore will fill abruptly. These sudden changes in pore water content are termed Haines jumps. At this point, $\psi_r > \psi_R$. Consequently, we see that the desorption process is dependent upon the smallest radius of the neck or connecting channels, while the sorption process is dependent on the largest diameter of the larger pores. Because of this, as is easily seen in figure 4.13, the equilibrium water content at any matric potential will depend on whether the soil system is draining or wetting.

Contact Angle

For an advancing (sorption) meniscus, the contact angle of the soil water on the pore wall (as explained in section 4.2) and the radius of curvature are greater than for a receding meniscus. This results in the tendency for the suction or matric potential values to be higher in the desorption process than in the sorption process for a given volumetric water content. However, the presence of solutes, the particle and pore size, the surface roughness, and other factors play a major role in the process.

Entrapped Air

Hysteresis can be accentuated when air is entrapped in a soil system. During infiltration, water displaces soil air from various pores. Once the initial water front redistributes, soil pores can be refilled with air from the atmosphere that will be trapped and moved downward by the next wetting front. Also, O_2 will exsolve from the infiltrating water and enrich the remaining soil air. It might be expected that the rewetting process would renew or replace all existing soil air, especially with large rainfall events. However, a considerable amount of entrapped air can remain in the system because of dead-end and occluded pores. (Further discussion is given in section 10.13 and chapter 11.) The presence of entrapped air initially lessens the ability of the system to reach equilibrium, because of greater pressure within the entrapped air pockets versus surrounding pores. This will lessen with time, especially in very wet soils where the air effervesces into the surrounding soil water. Entrapped air will reduce the volumetric water content of the system, making hysteresis more pronounced.

Shrinking and Swelling

Alternate drying and rewetting of soils can cause both shrinking and swelling (see chapter 3). This can cause changes in soil structure, accompanied by changes in pore space, dependent on the wetting and drying history of the soil (Hillel and Mottes 1966). These changes in pore size and distribution may cause significant variation in soil moisture content and equilibrium processes during the drying and rewetting processes, because of subsequent dissolution and release of soil air.

Due to the complexity of the hysteresis process, it is often ignored in field studies. However, it is known to be important in many soils, especially where both drying and wetting occur at the same time at different locations in a profile. The profile may have several layers of the same texture that, because of different wetting and drying histories, will have different water contents. The primary difficulty in simulating hysteresis is obtaining the scanning curves. As a result, the desorption curve is usually reported because it is much easier to obtain.

While hysteresis is not well studied due to its complexity, it is of considerable importance in evaporation, infiltration, and in coupled processes in soils in which both wetting and drying may occur simultaneously. The most pronounced effects of hysteresis occur in coarse soils (usually sands) at low values of matric potential.

The phenomena of hysteresis can be represented for further clarification in a problem-solving manner. Obtaining solutions to questions 4.9, 4.10, and 4.11 will enhance the reader's understanding of hysteresis.

QUESTION 4.9

Figure 4.16 illustrates a "soil pore" with a cylindrical shape, encased in a walled cylinder—that is, like an intact core sample with a smaller radius neck at each end; the respective diameter and height are listed. Since one can calculate both the volume of the inner pore and the total volume of the sample (i.e., the encasement cylinder), what is the total porosity of the soil pore?

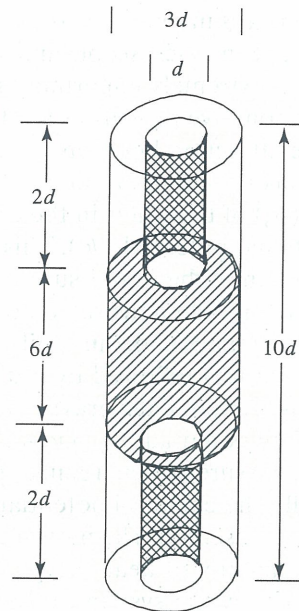


Figure 4.16 Diagram of soil pore in an encasement

QUESTION 4.10

Assume that you completely saturate the sample in question 4.9. **(a)** What is the volumetric water content? **(b)** Sketch a desorption curve of the sample assuming that you are applying a gradual pressure to the bottom end of the sample (assume $\sigma = 7 \times 10^{-2} \text{ N/m}$ and $d = 15 \mu\text{m}$). *Hint:* ignore gravitational potential due to pore size.

QUESTION 4.11

Draw a sorption curve (on the same graph as you created for question 4.10), assuming that you gradually increase the pressure again—back to 0. Having performed the steps in questions 4.10 and 4.11, you have illustrated the effects of hysteresis on the soil pore!

SUMMARY

In this chapter we have discussed various concepts of soil water potential. Within the unsaturated zone, soil particles are typically surrounded by thin water films that are bound to the solid surfaces of the medium by the molecular forces of adhesion and cohesion. A simple definition of water content is not sufficient to enumerate the complete status of water in a porous medium. We have presented the definition of matric potential, the force with which water is held to individual particles in the soil, which may be defined as the amount of work done or potential energy stored, per unit volume, in moving that volume, m , from the reference state (typically chosen as pure free water). We have also discussed the structure of water: how materials composed of molecules that are permanently polarized, as is water, usually have large dielectric constants. Included was a discussion of the formation of water droplets and the attractive forces associated with the air-liquid, solid-liquid, and solid-air interfaces. Forces for bulk water consist primarily of van der Waals-London forces and hydrogen bonding. Molecules at an air-water interface are not subjected to attractive forces from without, but are attracted inward to the bulk phase.

Capillarity and how it relates to surfaces in tension was explained, and common examples illustrated. Because capillarity deals with macroscopic and statistical behavior of interfaces rather than molecular structure, it is extremely important in soil water retention and in unsaturated zone studies. Adhesive and cohesive properties are the attractive forces of molecules of dissimilar substances, and the attraction between molecules in like substances. A detailed description of capillary potential on a weight, volume, and mass basis was presented, illustrating that the pressure potential (ψ_p) of the water in the capillary tube decreases with height to offset the increasing gravitational potential (ψ_g). This causes the pressure of the water in a capillary tube to be less than atmospheric pressure, and in certain circumstances this is analogous to soil-water systems. We also demonstrated how capillary potential relates directly to the air-entry value of porous ceramics and, thus, soil pores.

The discussion of capillary potential was followed by a discussion of total soil water potential and its definition and various components: gravitational potential (ψ_g), osmotic potential (sometimes referred to as solute potential) ψ_o , pneumatic (air or vapor) potential (ψ_a), matric potential (ψ_m), hydrostatic pressure (submergence) potential (ψ_p), and overburden pressure potential (ψ_b). Additionally, the chemical potential of soil water, which is very complex and often overlooked, was also presented. The increase in internal (stored) energy of a system must be equivalent to the quantity of heat energy, Q_h , absorbed by the system from its surroundings less the energy lost by the system to the surroundings as a result of work, W , done by the system due to the absorption of heat. The change of free energy at constant temperature and pressure in an open system is associated with a transfer of mass from one phase to another, or a change in mass from one chemical combination to another (i.e., chemical potential). Examples of a change in free energy include condensation, evaporation, and inflow and outflow from a section of soil.

Additionally, soil moisture characteristic curves and the relation to hysteresis were discussed, as were the primary curves from saturation to dryness and vice versa (known as the main branches of soil-moisture characteristic curves). The four primary causes of hysteresis were elaborated: (1) the geometric or 'ink bottle' effect; (2) contact angle; (3) entrapped air; and (4) shrinking and swelling. While hysteresis is very important, it is often dismissed due to its complexity and an inability to effectually measure its effects on a soil system.

ANSWERS TO QUESTIONS

- 4.1. The work required to rotate one molecule by 90° is equal to the difference in potential energy between the 90° orientation and the 0° orientation. By using equation 4.3, $W = E_{90} - E_0 = (-pU \cdot \cos 90^\circ) - (-pU \cos 0^\circ) = pU = (6.3 \times 10^{-30} \text{ C} \cdot \text{m})(2.75 \times 10^5 \text{ N/C}) = 1.73 \times 10^{-24} \text{ N} \cdot \text{m}$ or $1.73 \times 10^{-24} \text{ J} \times 10^{20} \text{ molecules} = 1.7 \times 10^{-3} \text{ J}$.
- 4.2. Remembering that the contact angle for clean glass is 0 and $r = 42.5 \mu\text{m}$, we may use equation 4.10, substituting the necessary conversion factors. Thus,

$$h_c = \frac{2(0.05 \text{ N m}^{-1})}{(1000 \text{ kg m}^{-3})(9.81 \text{ N kg}^{-1})(42.5 \mu\text{m})(10^{-6} \text{ m } \mu\text{m}^{-1})} = 0.24 \text{ m}$$

- 4.3. Assuming that the reference point is taken at the flat water surface, then for every location where $\psi_h = 0$ and $\psi_p = -\psi_g$, the volume basis pressure potential at the meniscus will be

$$\rho_l \psi_p = -\rho_l \psi_g = -\rho_l g h_c = -\frac{2\sigma \cos \theta}{r}$$

- 4.4. Noncylindrical capillaries have the same height of rise as cylindrical ones. The air entry value, -20 kPa , is converted to meters, yielding 2.0 m ; this value is the air-entry value and also the height of capillary rise. Substitute 2.0 m into equation 4.10, and solve for the radius of the capillary tube. You will find that $r = 7 \mu\text{m}$, thus the diameter of the capillary tube is $14 \mu\text{m}$.

- 4.5. Assuming complete wetting, a contact angle of 0° , and a surface tension of 0.07 N/m , we may use equation 4.10 to obtain

$$h_c = \frac{2\sigma \cos \theta}{\rho_l g r} = \frac{(2)(0.07 \text{ N/m})(1)}{(1000 \text{ kg m}^{-3})(9.81 \text{ N/kg})(9 \mu\text{m})(10^{-6} \text{ m}/\mu\text{m})} = 1.53 \text{ m}$$

Thus, the air entry value is 1.53 m or $-\rho_l g h_c$, which is -15.3 kPa .

- 4.6. The reason for this is quite simple: $\Pi = 0$ in pure water, and under atmospheric pressure at the “free” water surface, $\psi_m = 0$. As a result, $\psi_t = gz$.
- 4.7. First, we assume that $h_o = 0$ (no salt in the atmosphere); then, using equation 4.28 (rearranged), we have

$$h_m + 0 = \frac{\ln 0.50}{7.5 \times 10^{-5} \text{ m}^{-1}} = -9.24 \times 10^3 \text{ m}$$

As one can see, this is a large negative value. A tensiometer can only read about -1.0 m . As a result, the water in the tensiometer will evaporate through the porous cup, the entire tensiometer will fill with air, and no reading will be obtained.

- 4.8. The soil pressure is easily calculated by $\sigma_s = -\rho_b g z = -1500 \text{ kg m}^{-3} \times 9.81 \text{ N kg}^{-1} \times (-1 \text{ m}) = 14,715 \text{ N m}^{-2}$ or 14.715 kPa . Remember that an N m^{-2} is equal to a Pascal unit of pressure.
- 4.9. The porosity is determined as the volume of the soil pore divided by the volume of sample. Thus, $(2 \times 1/4\pi d^2 \times 2d) + (1.5^2\pi d^2 \times 6d) = \pi d^3 + 13.5\pi d^3 = 14.5\pi d^3$ = the pore volume. The volume of the sample = $2.25\pi d^2 \times 10d = 22.5\pi d^3$. Hence, the porosity, ϕ , is

$$\phi = \frac{14.5\pi d^3}{22.5\pi d^3} = 0.644$$

- 4.10. (a) The volumetric water content, $\theta = \phi = 0.644$ at $\psi_m = 0$. (b) To draw the desorption curve one must calculate the capillary rise potential thus,

$$h_c > \frac{-2\sigma}{\rho_l g r} = \frac{-2(7 \times 10^{-2} \text{ N/m})}{1000 \text{ kg/m}^3 \times 9.81 \text{ N/kg} \times (7.5 \times 10^{-6} \text{ m})} = -1.90 \text{ m}$$

The desorption curve is shown in figure 4.17. Essentially, the soil pore is full as the pressure is

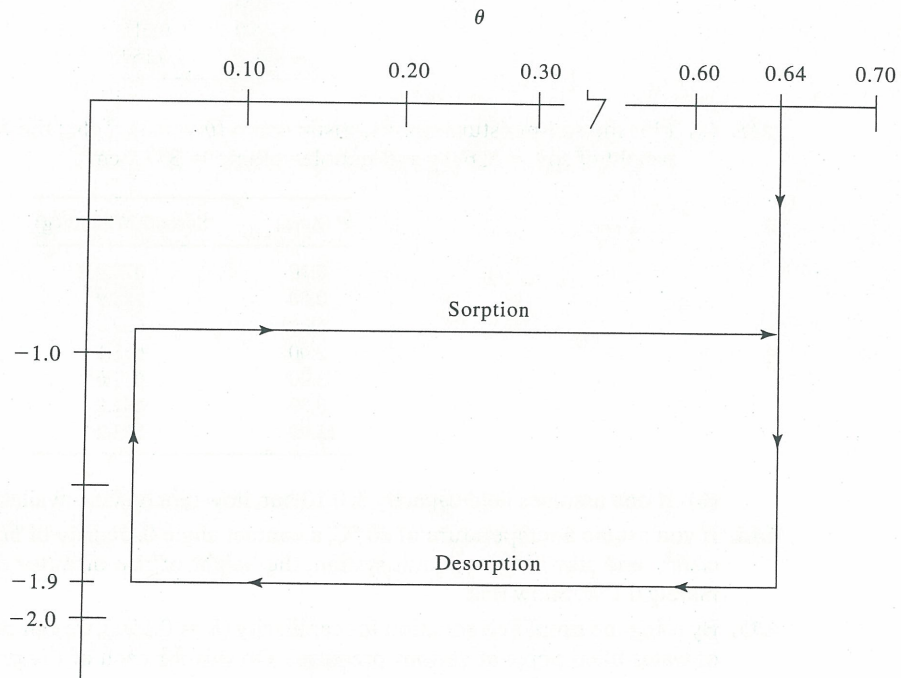


Figure 4.17 Hysteretic effects on soil pore

increased from 0 to -1.90 m. However, there will be a slight decrease in θ due to a change in the shape of the meniscus from flat to concave (hemispherical); but when the pressure reaches -1.90 m, the pore will empty completely.

- 4.11.** To draw the sorption curve, one must consider that the small neck at the bottom of the soil pore will refill with water when the pressure is larger than the pore's air-entry value (-1.87 m), and the main body of the soil pore will fill when

$$h_c > \frac{-2\sigma}{\rho_l g r} = \frac{-2(7 \times 10^{-2} \text{ N/m})}{1000 \text{ kg/m}^3 \times 9.81 \text{ N/kg} \times (15 \times 10^{-6} \text{ m})} = -0.95 \text{ m}$$

When the pore is filled, $\theta = 0.444$, but when only the lower neck is filled,

$$\theta = \frac{1/4\pi d^2 \times 2d}{22.5\pi d^3} = 0.02$$

The corresponding sorption curve is shown in figure 4.15b. Thus, one can see the effects of drying and wetting of a soil; in other words, hysteresis.

ADDITIONAL QUESTIONS

- 4.12.** Calculate the total potential (ψ_m , ignoring osmotic effects) of soil water on a volume basis at a depth of 63 cm, where the relative humidity (RH) of air in a soil pore is 98.9% (temperature = 25°C).
- 4.13.** Explain how a pressure plate apparatus works. Why is the air pressure equal to the negative of the ψ_m of the sample of soil water?
- 4.14.** Calculate the percent pore volume in each of five size categories (pore diameter in microns) for the following.

ψ_m	θ
0	0.495
-60	0.393
-200	0.304
-1000	0.215
-10000	0.159

- 4.15. (a)** Plot the soil-moisture characteristic curve (θ versus P) for the following soil, given that dry weight of soil = 556.0 g and sample volume = 347.5 cm^3 .

P (bars)	Sample Weight (g)
0.10	674.4
0.50	658.9
1.00	639.9
2.00	631.1
3.00	617.6
8.00	601.0
15.00	573.2

- (b)** If one assumes field capacity is 0.10 bar, how much plant-available water is in this soil?
- 4.16.** If you assume a temperature of 20°C , a contact angle 0, density of $\text{H}_2\text{O} = 1\text{g/cm}^3$, and $g = 978.05 \text{ cm/s}^2$, and stay in the cgs unit system, the height of rise of water due to capillarity is approximately $0.15/r$. Show this.
- 4.17.** By using the simplified equation for capillarity ($h = 0.15/r$), we can calculate the maximum radius of water-filled pores at various pressures. Do this for each of the pressures in problem 4.15 (a). Express the size of the pore diameter in μm . Remember, the simplified equation requires that h and r be in cm (1 bar = 1022 cm of water).

- 4.18. In figure 4.18, the vertical distance from the surface of the mercury reservoir to the center of the ceramic cup is 20 cm and the value of z_{Hg} is 14.2 cm. What is ψ_m ?

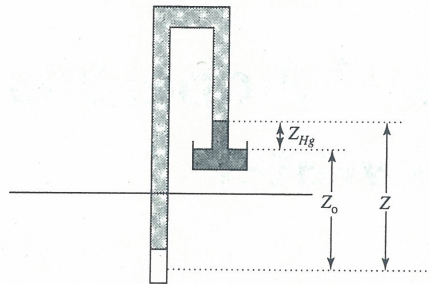


Figure 4.18

- 4.19. A uniformly-packed (homogeneous), U-shaped soil column has one end suspended in a container of water (see figure 4.19). The water level in the container has been kept constant and sealed against evaporative losses so that the soil column has reached equilibrium. As a result, there is no net water flow in the column. Calculate ψ_h (weight hydraulic potential) and its components (ψ_p , ψ_m , and ψ_z) for points A through F in the soil column.

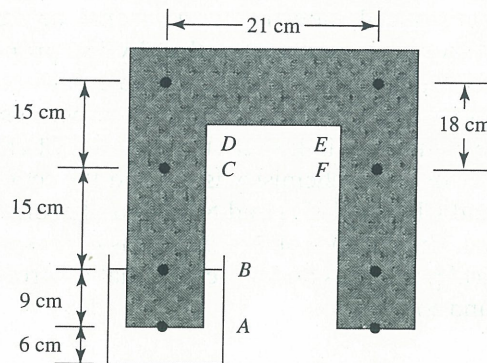


Figure 4.19 Data from Hanks and Ashcroft (1980)

- 4.20. Given a soil in which the liquid water is in equilibrium with a water table at -70 cm, and the reference level is at soil surface, find the values of ψ_m , ψ_z , ψ_p , and ψ_h throughout the soil profile to -110 cm.
- 4.21. Water is evaporating at a soil surface; find values of ψ_z , ψ_p , and ψ_h throughout the soil profile to -60 cm. In order to find ψ_h , measured or estimated values of ψ_m must be available. Make estimates of ψ_m for the conditions specified. *Note:* there may be variations in the gradient $\Delta\psi_h/\Delta z$ with depth; but for upward flow, the sign must always be negative.
- 4.22. This is a revisitation of material discussed in section 4.5. Relative humidity is the ratio of saturated vapor pressure to total vapor pressure. Calculate the relative humidity (in percent) at 25°C for matric suctions of (a) -0.1 , (b) -2.0 , (c) -15.0 , (d) -100.0 , and (e) -1000.0 bars.