
SETTING THE STAGE

1.1 INTRODUCTION

The purpose of this text is to introduce the fundamental concepts that underlie the physics of multiphase flow and transport through porous media. This first chapter introduces some of the qualitative physical characteristics of porous media. Parameters are introduced that provide quantitative measures of the characteristics that arise in modeling fluid flow and chemical transport in the system of interest. Some simple elementary equations are employed that are helpful in initiating the translation of a qualitative understanding to a quantitative description. In the second chapter, the equations of conservation of mass are developed. In Chapter 3 appropriate constitutive relationships¹ are introduced that provide information needed to complete the mathematical definition of the physical systems involving fluid flow. Chapter 4 is dedicated to developing the equations that describe mass transport. Finally, in the fifth chapter, example physical problems involving multiphase flow and transport through porous media are detailed.

The approach of this presentation is to progress from observations of system behavior and characteristics to a mathematical description of those observations. This approach involves three steps: (i) description of experiments that reveal various phenomena; (ii) development and presentation of the governing equations; and (iii) application of the resulting equations to physical systems of interest.

¹ Constitutive, or closure, relationships are typically correlations between fluxes and physical variables. The correlations are motivated by experimental observations or from simplified theoretical considerations. They are not universal principles but are appropriate for some systems under certain operating conditions. Constitutive relations provide specific information that makes it possible to apply conservation equations to problems.

1.2 PHASES AND POROUS MEDIA

A *phase* is a liquid, solid, or gas that is separated from another solid, liquid, or gas by an identifiable boundary. An example is an oil bubble or oil globule submerged in water, where the oil and the water are each phases and the physical demarcation between the two liquid phases is an interface. Some transfer of material, momentum, and energy may occur between phases; a phase need not have a homogeneous composition or temperature. Thus, although gradients of properties may exist within a phase, sharp discontinuities in composition at an identifiable boundary are considered to be interfaces between phases. A second example of a two-phase system is raindrops falling through air. A raindrop is a liquid phase while the air is a gas phase, and transfer of water to the air may occur by evaporation across the boundary of the raindrop. Because of evaporation, gradients in humidity may exist in the gas. An important attribute of this system is that the gas phase is continuous in that every point in the gas phase may be reached by a physical path without entering into the liquid phase. On the other hand, the liquid phase, comprised of raindrops, is an assemblage in which the properties of each drop may be distinctly different from those of a nearby drop. Modeling of a discontinuous phase as a unit requires some approximations or simplifications that are not needed when describing a continuous phase. As a third example, dry sand is actually a mixture of solid sand grains and air. The behavior of this two-phase mixture will be very different when air is pumped through a packed column of essentially immobile sand from when the air entrains the sand grains, imparting momentum and energy to them and causing them to move at significant velocity in a cloud. Thus identification of the components of a system is not sufficient for determining how to model it. Multiphase models must be formulated to account for the modes of transfer of chemical constituents, momentum, and energy within each phase and across the phase interfaces.

Porous media are considered herein to exhibit a specific set of physical attributes that distinguish them from general multiphase systems. The most notable of these are the requirements that more than one phase exist within a specified control volume, that one of these be a relatively immobile solid, and that at least one of these phases be fluid (either a liquid or a gas). Furthermore, the definition of a mixture of phases as a porous medium requires that the solid phase contain multiply-connected spaces that are accessible to the fluid.

Although the definition of a porous medium requires that the solid be “relatively” immobile, a precise specification of the degree of solid mobility or deformation that is allowable by this definition is not possible. At one extreme, an immobile solid, such as well-consolidated sand or a block of granite, may form the solid phase of a porous medium. At the other extreme, a solid such as sand scoured from the bottom of the ocean and carried in the waves or grain flowing out of a grain elevator is a solid phase mixed with fluid in a system that is not a porous medium. For a porous medium, the velocity of the solid phase with respect to the boundary of the system is much less than the velocity of the fluid that can flow within the porous system.

In natural porous media systems, some consolidation of the solid phase may occur as flow moves through the pore space. This can be accounted for under the theoretical framework of porous media flow. Infiltration of rainwater into a soil and movement of subsurface water through a geologic formation are examples where porous

medium considerations apply. Situations where the withdrawal of water from the subsurface causes the ground to subside over a period of years may also be analyzed within a porous medium framework because the movement of the solid is very slow in comparison to the water movement. A system composed of snow, air, and melt-water may be studied as a porous medium consisting of a solid and two fluids if the rate of melting is small enough that the snow particles respond as a unit, are relatively immobile, and are not carried off as solid particles within the flowing water. The precise specification of the conditions under which a fluid-solid system cannot be studied in a meaningful way as a porous medium is elusive. The study of flow of water in a sponge is another system that may or may not fall under the umbrella of traditional porous media studies depending on the degree of deformation of the solid structure for the conditions of interest.

Despite the fact that it is not possible to define precisely a porous medium, we will persevere and identify additional attributes of porous systems under study here. To be amenable to porous media flow modeling, the pore space within the solid must, in general, be continuous. For example, Styrofoam is composed of a solid phase in which air bubbles are encapsulated and separated. These air pockets are disconnected, and thus the behavior of the air in the Styrofoam cannot be studied under the guise of porous media analysis. At a larger scale, Swiss cheese is composed of both gas and solid phases. However, the gas phase is contained in isolated, generally disconnected void spaces within the cheese. Gas in one void space cannot readily travel to another void space. Although the absence of a connected void space precludes the scientific study of Swiss cheese as a porous medium, experimental sampling of this system remains a highly rewarding and widely practiced endeavor.

In porous media to be studied here, the individual fluid phases must, under suitable conditions, have the potential to be continuous. That is, the possibility must exist for fluid to flow from one location to another within the porous medium. Thus the structure of the pore space within the solid must be such that pathways exist that connect the regions of the system. For a single fluid phase in such a system, the fluid region will certainly be connected. However, when more than one fluid is present in the connected pore space, one of the fluids may divide into a number of separate disconnected elements. Systems in which a phase becomes disconnected are very difficult to model as the physics of each disconnected region of fluid must be accounted for.

The study of porous media typically assumes that the solid phase is connected. However, the definition of "connection" for the solid is imprecise and the discussion can disintegrate to what it means for grains of sand to be "touching." Nevertheless, we can make the somewhat satisfying observation that for the solid in a porous medium to possess the necessary degree of immobility, any individual grains must be in contact with other grains with points of mechanical interaction between grains changing very slowly relative to the rate of change of fluid molecules that interact with a particular point on a grain. This observation does not preclude the possibility that grains will reorganize or deform in response to various stresses placed on the solid system, although it does suggest that treatment of consolidated media, in which the grains are essentially cemented together, may be somewhat more straightforward. Cases where the solid deforms more quickly and chaotically, as in grain flow or an avalanche, cannot be modeled as porous media.

As an illustration that reveals some of the fundamental concepts that arise in porous media, consider the following simple experiment. Into a graduated cylinder of 2.0 cm diameter and a height of 30 cm pour sand until the top of the sand is located at the 10.0 cm mark (see Figure 1.1). The sand-air mixture in the graduated cylinder constitutes a porous medium because the air phase that is intermixed with the sand is continuous, identifiable interfaces exist between the air and sand phases, and the sand is essentially immobile relative to the bounding walls of the cylinder. Of course, shaking the cylinder can mobilize the sand and invalidate the porous medium assumption, but this will not be the situation in this example.

The portion of the sample that is not sand is called the *pore space*. In the present case, the pore space is occupied completely by air, and the air-sand mixture constitutes a porous medium.

From a device capable of measuring the amount of fluid dispensed, add water to the graduated cylinder until the water level is located at the 15.0 cm mark, 5.0 cm above the top of the sand surface. Assume that the experimental technique employed is such that the sand in the cylinder is not disturbed by the addition of water and that all of the pore space in the sand is filled with water with no air being trapped. Under these conditions, the porous medium is said to be saturated with water. We note that achievement of saturation is difficult as air tends to become trapped in the system. Nevertheless, taking advantage of the fact that this is an illustrative example, we happily discount this experimental complication. Assume the water dispenser indicates that the total volume of water added to the graduated cylinder, V_T^w , is 25.0 cubic centimeters (cm^3). The cylinder is now occupied by a sand-water mixture that is a porous medium, and this porous medium is overlain by a water phase that is connected to the water in the medium.

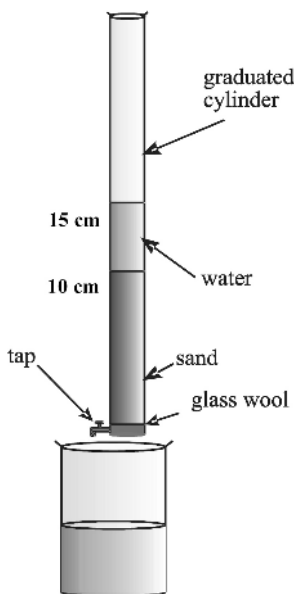


Figure 1.1: Diagrammatic presentation of experiment to show concepts of phase and porous media.

The fraction of the porous medium that is pore space can be determined by analyzing this experiment. First, determine the total volume of the porous medium consisting of the fluid and solid mixture. Based on the equation for the volume of a cylinder of radius r and height h , the volume of the porous medium in the cylinder with radius of 1.0 cm and a height of 10.0 cm is:

$$V = V^s + V^w = \pi r^2 h = \pi \times (1.0 \text{ cm})^2 \times 10.0 \text{ cm} = 31.4 \text{ cm}^3 \quad (1.1)$$

where V is the total volume of the porous medium composed of sand and water, V^s is the volume of sand in the porous medium, and V^w is the volume of water in the porous medium. In this case, where water completely fills the pore space, V^w is also the volume of pore space. Although we have calculated the total volume of porous medium, the distribution of this volume between sand and pore space is not yet known. Consideration of the total amount of water dispensed will lead to this information.

The 25.0 cm³ dispensed into the cylinder fills the pore space and the volume that extends 5.0 cm above the sand. The water volume in this 5-cm region within the cylinder, V_C^w , is easily calculated from the equation for a cylinder as:

$$V_C^w = \pi r^2 h = \pi \times (1.0 \text{ cm})^2 \times 5.0 \text{ cm} = 15.7 \text{ cm}^3 \quad (1.2)$$

Thus the volume of water in the pore space of the sample is:

$$V^w = V_T^w - V_C^w = 25.0 \text{ cm}^3 - 15.7 \text{ cm}^3 = 9.3 \text{ cm}^3 \quad (1.3)$$

Combination of equations (1.1) and (1.3) also provides the volume of sand in the system:

$$V^s = V - V^w = 31.4 \text{ cm}^3 - 9.3 \text{ cm}^3 = 22.1 \text{ cm}^3 \quad (1.4)$$

The fraction of the porous medium that is pore space, ε , is thus obtained as:

$$\varepsilon = \frac{V^w}{V^s + V^w} = \frac{9.3 \text{ cm}^3}{31.4 \text{ cm}^3} = 0.30 \quad (1.5)$$

This fraction ε is called the *porosity* or *void fraction* of the sample. In general, for a sample of porous medium of size V , the porosity is defined in terms of the size of the volume sample and the volume of solid in the sample as:

$$\varepsilon = 1 - \left(\frac{1}{V} \int_{V^s} dV \right) \quad (1.6)$$

Realize that the porosity calculated in this experiment provides a value that is characteristic of the entire sample. It provides no information as to how the pore volume is distributed within the sample. If half the sand were removed from cylinder, the value of porosity obtained from the remainder of the sample could be different from that for the entire sample. Certainly if one removes sand such that there

are only a few grains left in the cylinder, the porosity for that sample could be quite different from that for the full sample, or even meaningless as a quantity intended to characterize the system. These observations introduce the notion that when one is studying porous media, the length scale at which observations are made can be an important factor that influences the values of variables measured.

Furthermore, although the total volume of pore space within a sample can be measured, in general the geometry and volume of individual pores cannot be measured. Some specific information at this small scale can be obtained for samples of size on the order of 1 cm^3 using advanced imaging techniques, but, at best, only statistical distributions of the pore sizes of larger samples can be determined. Despite the fact that no single accepted physical measure of the size of a single pore exists, the concept of pore size is widely used. Each naturally occurring pore will have a variable cross section, and *grain size* is commonly used as a surrogate for the size of the pore. Methods for describing the distribution of grain sizes and pore sizes are discussed in the next section.

1.3 GRAIN AND PORE SIZE DISTRIBUTIONS

While the volume of a pore does depend upon the size of the grains in some sense, the relationship can be complex because of the influence of *grain packing*. For example, the packing of spherical grains of uniform size in Figure 1.2 is referred to as *cubic* and the porosity is 0.48. On the other hand the packing of the same grains in Figure 1.3 is *rhombohedral* and has a porosity of 0.26. The pore space is fully connected in both cases, and the pore space can be identified as the region between adjacent spheres. Although the precise specification of what constitutes a pore is not obvious, the pore space does illustrate the channels of fluid flow. If any consistent measure of a pore is selected in both figures, the volume and pore diameter of an individual pore in Figure 1.2 is larger than that in Figure 1.3. A random *packing* of uniform spheres will result in different values of porosity depending on the looseness and organization of the spheres. A loose random packing of spheres will generally generate porosities from 0.32 to 0.35 [8]. Addition to this mix of solid spherical particles with a range of sizes and of nonspherical, arbitrarily shaped grains adds complexity to the identification of “pore size” and to the range of porosities that

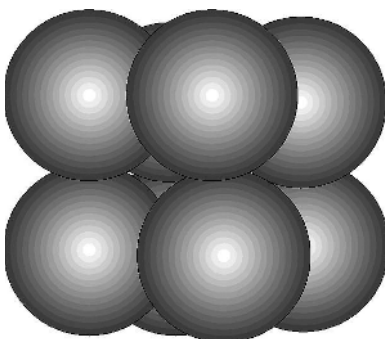


Figure 1.2: Cubic packing of spheres generates a porosity of 0.48 [6].

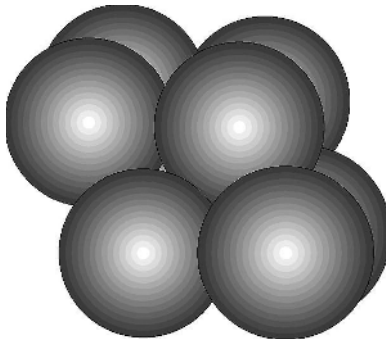


Figure 1.3: Rhombohedral packing of spheres generates a porosity of 0.26 [6].

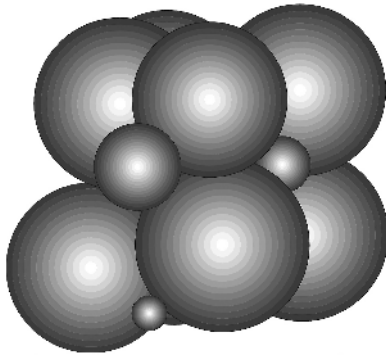


Figure 1.4: Small grains tend to occupy spaces left between larger grains to yield smaller porosities.

can be achieved. In nature one is not likely to find spheres of the same size or, for that matter, spherical particles at all. Normally one will find a variety of grain sizes with the smaller grains occupying the spaces between the larger grains as conceptualized in Figure 1.4.

Because of the difficulty in characterizing pore space, the grain size distribution is used as a surrogate. For unconsolidated media, grain size is easily measured through the use of *sieves*. A classical sieve is composed of a metal cylinder approximately 5 cm in length and approximately 20 cm in diameter. It is open at one end and contains a metal screen at the other. Sieves are normally stacked with the sieve with the smallest screen size opening, or *mesh size*, at the base of the stack. Below the last sieve is a pan to collect those grains smaller than the smallest screen size (see Figure 1.5).

Sieve sizes are designated in two principal ways. Some sieves provide the sieve diameter in inches or millimeters. Others designate the sieve by a standard number that is not directly related to the mesh size but indicates the number of openings per inch. For example, a number 20 sieve has 20 openings per inch, or 400 openings per square inch. Typical sieve sizes are shown in Table 1.1.

To sieve a sample of soil, a known weight of the soil is placed in the uppermost sieve. This sieve is covered and a shaking apparatus is used to vibrate the column

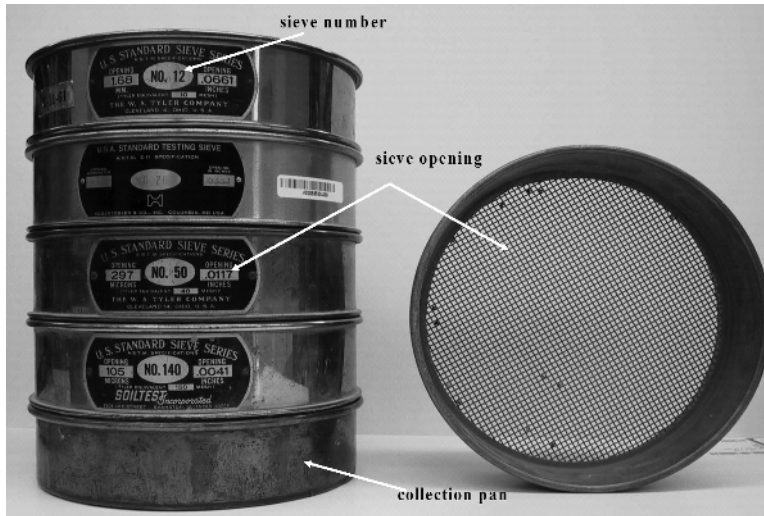


Figure 1.5: Screens are stacked sequentially from the finest mesh at the bottom to the coarsest at the top.

Table 1.1: Typical sieve sizes

U.S. Standard Test Sieves (ASTM) [1]			
Sieve Designation		Nominal Sieve Opening	
Standard	Alternative	Inches	Millimeters
25.0 mm	1 in	1	25.7
11.2 mm	7/16 in	0.438	11.2
4.75 mm	No. 4	0.187	4.76
1.70 mm	No. 12	0.0661	1.68
0.075 mm	No. 200	0.0029	0.063

of sieves while it remains approximately vertical. The grains smaller than the opening in the top sieve eventually pass to the next lower sieve. This sieve, in turn, retains those grains with a diameter larger than its mesh size and smaller than the mesh size of the upper sieve. This process continues until the grains retained in the container at the bottom of the column are smaller than the diameter of the sieve with the smallest mesh. Each soil fraction is then weighed and the results plotted as weight vs. sieve size.

Soils are classified as coarse-grained when they are composed of sand and gravel. Typically, less than 50% of coarse-grained material will pass through the No. 200 mesh. Fine-grained soils are composed of silt and clay. Fifty percent or more of a fine-grained soil will pass the No. 200 mesh.

Normally, solid material with components smaller than those captured by the No. 200 mesh screen is very difficult to screen further and is therefore analyzed via a “wet” method that exploits the dependence of the settling rate of a small particle in a quiescent fluid on its size. Wet methods make use of Stokes’ law, which states

that the diameter of a spherical particle falling through a fluid is related to the velocity according to²:

$$D = \sqrt{\frac{18\mu v}{g(\rho_s - \rho_f)}} \quad (1.7)$$

where D is the particle diameter, μ is the dynamic viscosity, v is the settling velocity, g is gravity, ρ_s is the solid particle density, and ρ_f is the density of the fluid. In the analysis, ρ_s is assumed to be a constant independent of particle size, and the velocity, v , is considered to be reached as soon as settling begins. The general idea in employing a wet method is to begin with a mixture of particles uniformly distributed in a fluid consisting of water and a dispersing agent, such as hexametaphosphate, added to the mixture to ensure that the particles do not aggregate. The maximum size particle will be the largest size that passes through a number 200 sieve, D_{200} , approximately $70\ \mu\text{m}$ based on Table 1.1. Then measurement of the evolution of the density profile of the mixture due to the different settling rates of the particles provides information concerning the distribution of particle sizes. Two principal *wet methods* are employed. One is the *pipette method* while the second is the *hydrometer method*.

The pipette method involves collection of samples of the solid-fluid mixture in a cylinder at various times and depths. Initially, the distribution of particles in the fluid is uniform with a mass per volume of m_0 . If the solution is dilute enough so that collisions between particles are not significant, at a depth L at time t , all particles with diameter greater than that given by equation (1.7) with v replaced by L/t will have settled to a depth below L . Suppose a small sample of the mixture collected at this time and location using a pipette has a mass of sediment per volume of $m(L, t)$. Then $1 - m/m_0$ is the mass fraction of particles with diameter, D , in the range:

$$\sqrt{\frac{18\mu L}{g(\rho_s - \rho_f)t}} < D < D_{200} \quad (1.8)$$

Collection of samples at various times and depths in the mixture allows the distribution of particle diameters to be constructed.

The hydrometer method also exploits the differential settling characteristics of a dilute mixture of particles. By this approach, a hydrometer is inserted into the settling solution at various times and the depth of flotation as well as the density of the mixture associated with that flotation are recorded. If the density of the solid fluid mixture as would be measured by the hydrometer is initially ρ_{h0} and the density reading obtained at some later time is $\rho_h(L, t)$, then:

$$\frac{m(L, t)}{m_0} = \left(\frac{\rho_h - \rho_f}{\rho_{h0} - \rho_f} \right) \quad (1.9)$$

²An important assumption that is made in Stokes' law is that the grains are spherical. While this may be appropriate for sand particles, clay particles tend to be platelike and some calibration of the procedure may be necessary.

Table 1.2: Experimental results from a wet method experiment for determining fine grain size distribution

Grain Size D (mm)	Weight with Diameter $< D$ (g)	Mass Ratio m/m_0
0.070	150.0	1.00
0.040	147.0	0.98
0.010	127.5	0.85
0.005	91.5	0.61
0.002	42.2	0.28
0.001	22.5	0.15

where m/m_0 is the mass fraction of particles with diameter less than D calculated using equation (1.7). The distribution of particle sizes may be constructed using this data collected at a sequence of times.

Although the methods outlined above are conceptually very simple, they are complicated by the need to compensate for temperature effects, for the time intervals for insertion of the pipette into the solution, the initial concentration of particles in the solution, the method of obtaining the initial uniform particle distribution in the fluid, and other protocols. Details of implementation of these methods have been standardized, for example in [1] and [5]. For purposes of subsequent discussion here, an example of a set of data that could be obtained from the pipette or hydrometer method is provided in Table 1.2.

The information gained from sieve and wet method analyses reveals more than just the range of grain sizes. It can help to classify the soil as to its type, e.g., sand, silt, silty sand, etc. Particle sizes smaller than 0.002 mm are considered to be clay or clay-sized fractions. In addition the data reveal the degree of sorting of the soil. A course-grained soil for which all the grains are approximately the same size is called well sorted (or poorly graded). A soil that exhibits a wide range of grain sizes is designated as poorly sorted (or well graded). The shape of the resulting *grain size distribution curve* can also reveal information regarding the history of the soil.³

The grain size distribution curves for two soil samples are plotted in Figure 1.6. Along the horizontal axis is plotted the grain size. On the vertical axis is plotted the percent weight finer than the indicated grain size. For example, the percent by weight of grains with diameter smaller than 0.01 mm in the clayey sandy-silt sample is approximately 40%. Similarly, in the case of the silty fine-sand sample, approximately 25% of the grains have diameters smaller than 0.1 mm. It should be kept in mind that the process of sieving measures the smallest cross-sectional diameter of the grain. A needle-shaped grain will be categorized as having a size equal to its width rather than its length, assuming of course it does not get lodged crosswise in the sieve. Thus only spherical particles that have the same measure of size regardless of orientation are uniquely identified by sieving. Nevertheless sieving is applied widely to soils containing grains of all shapes.

Figure 1.6 demonstrates that the clayey sandy-silt sample is finer grained than the silty fine-sand sample. In fact, by referring to the soil classification found beneath the distribution curve, it is evident how these samples received their classification.

³ We will consider this in more detail in the next chapter.

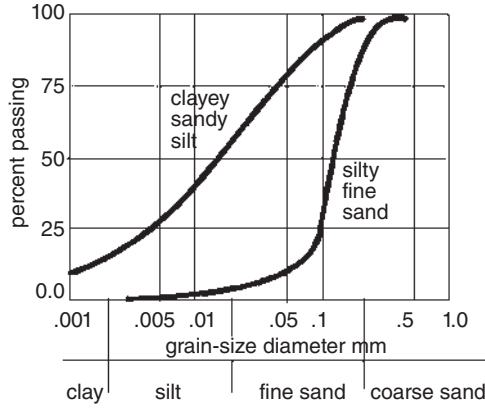


Figure 1.6: The grain size distribution indicates the soil classification of a sample and its degree of gradation.

Additional information may be obtained from the shape of the distribution curves. Note that the largest slope of the silty fine-sand curve is much steeper than that of the clayey sandy-silt curve. This indicates that the silty fine sand has a more uniform size distribution. In other words, the silty fine sand is considered to be better *sorted* or more poorly *graded* than the clayey sandy silt.

Two measures have been developed to describe the range in grain sizes of a soil sample. One is called the *coefficient of uniformity* and is defined as:

$$C_u = \frac{D_{60}}{D_{10}} \quad (1.10)$$

where D_n refers to the grain size greater than or equal to $n\%$ of the grains by weight. For example, 60% of the grains by weight are smaller than D_{60} . The denominator designated as D_{10} is also known as the *effective grain size*. The second measure is the *coefficient of curvature* calculated as:

$$C_c = \frac{D_{50}^2}{D_{10}D_{60}} \quad (1.11)$$

A well-graded soil has a coefficient of curvature between 1.0 and 3.0. Additionally, the coefficient of uniformity is greater than 4.0 for a well-graded gravel and greater than 6.0 for sands. A soil whose coefficient of uniformity is less than 2.0 is a *uniform soil*. A poorly graded soil violates at least one of these criteria, and a soil is said to be uniform if its coefficient of uniformity is less than or equal to 2.0 [7]. For the data of Figure 1.6, the coefficients of uniformity and curvature of the clayey sandy-silt sample are, respectively:

$$C_u = \frac{D_{60}}{D_{10}} = \frac{0.02 \text{ mm}}{0.001 \text{ mm}} = 20.0 \quad (1.12)$$

$$C_c = \frac{D_{30}^2}{D_{10}D_{60}} = \frac{(0.008 \text{ mm})^2}{(0.001 \text{ mm})(0.02 \text{ mm})} = 3.2 \quad (1.13)$$

For the silty fine sand, these coefficients are calculated as:

$$C_u = \frac{D_{60}}{D_{10}} = \frac{0.15 \text{ mm}}{0.05 \text{ mm}} = 3.0 \quad (1.14)$$

$$C_c = \frac{D_{30}^2}{D_{10}D_{60}} = \frac{(0.1 \text{ mm})^2}{(0.05 \text{ mm})(0.15 \text{ mm})} = 1.3 \quad (1.15)$$

The fact that C_u for clayey sandy silt is greater than C_u for silty fine sand confirms the previous observation that the clayey sandy silt is a better graded, or less uniform, soil⁴

1.4 THE CONCEPT OF SATURATION

Consider again the experimental apparatus consisting of a graduated cylinder containing 10 cm of a porous medium composed of sand and water covered by 5 cm of water. Suppose that a tap at the base of the graduated cylinder covered by a piece of glass wool is opened to allow the water to drain out while preventing the sand from escaping. The water that drains out is collected in a glass beaker. When the water has drained sufficiently such that no water remains above the porous medium, what remains in the bottom 10 cm of the graduated cylinder is a mixture of air, water, and sand. This is a three-phase porous media system. The fraction of pore space occupied by the water phase is called the *saturation*. Mathematically, the water saturation is defined as:

$$s^w = \frac{1}{V^v} \int_{V^w} dV = \frac{V^w}{V^v} \quad (1.16)$$

where V^v is the pore volume within the sample volume of porous medium, V , and is defined as:

$$V^v = V - V^s \quad (1.17)$$

Notice that in equation (1.16) the size of the sample is important. For example, if the entire porous medium is used, a single average value of saturation is obtained for the medium at any time. If smaller subvolumes within the porous system are considered, one may produce a spatially variable saturation field that characterizes the system at any instant. If the sample size is too small, the value of s^w calculated will change with small changes in the sample size. The saturation can take on values ranging from 0, when no water is present in the sample such that the void space is

⁴See the Earth Manual [3] for more information regarding grain size distributions and soil classification.

occupied completely by air, to 1, when the water occupies all of the void space and no air phase is present in the porous medium sample. From equation (1.15), the porosity is the pore volume divided by the total volume occupied by the porous medium such that $\varepsilon = V^v/V$. Substitution of this expression into equation (1.16) to eliminate V^v and multiplication by the porosity yields:

$$\varepsilon s^w = \frac{1}{V} \int_{V^w} dV = \frac{V^w}{V} \quad (1.18)$$

This relation motivates definition of the *water content* as the ratio of the volume of water to the total volume denoted by θ , such that:

$$\theta = \varepsilon s^w = \frac{V^w}{V} \quad (1.19)$$

After a sufficiently long period of time (where the definition of “sufficiently” is itself an interesting question usually answered as being somewhere from minutes to several hours), the drainage from the sand will stop, although some water will remain held in the sand. This water is called the *residual saturation*, and it exists as isolated droplets, is immobile, and will not normally drain.

While the concept of residual saturation is useful in theory, it is actually an imprecise quantity that is difficult to define unambiguously either physically or mathematically. In fact, if the graduated cylinder with the sample is kept in a low humidity environment for a number of days after residual saturation has been reached, the sand will continue to dry out gradually, and the saturation will decrease below residual. The reason for this is that the water will evaporate into the air in the pore space and then move out of the sand, primarily by vapor diffusion. The transfer of vapor from the liquid water phase to the vapor phase is a *phase transformation*. Water changes from liquid to gas as it moves across the interface from the liquid to the gas phase. Residual saturation will be encountered again when the topic of constitutive relationships is explored.

Consider, again, the drainage of the sand saturated with water. Suppose that while the drainage is occurring, some olive oil is poured onto the sand such that it seeps into some of the space between the grains. For this scenario, four phases comprise the porous medium: solid grains, water, the vapor, and oil. Although identifiable interfaces exist between each pair of phases, some material will transfer across the interfaces. Over time, some of the oil will dissolve into the water, and some of the water will dissolve into the oil. This transfer of molecules between phases is an example of *interphase transfer* or *interfacial transport* between two liquid phases across their interface. Despite this interphase transfer, the distinct interface remains as a location where material properties undergo a sharp transformation.

1.5 THE CONCEPT OF PRESSURE

Pressure, by its definition, is the magnitude of a force acting normal to a surface per unit area. It is also a measure of energy per unit volume. The concept is most easily

understood for a static system. Consider the simple case of a graduated cylinder filled to the point where the water depth is 15 cm as shown in Figure 1.7. As a reference define the pressure at the top of the water column to be zero, and define a coordinate axis z that is positive downward and also equal to zero at the top of the water column. For this small system, the water density can be considered constant throughout the column. The force due to water acting downward at any cross section of the cylinder is equal to the weight of water above the cross section. This weight, W , is equal to the density of water times the gravitational acceleration times the volume. Thus, at a distance z from the top of the water column, the downward force exerted by the water is:

$$W = \rho_w g V = \rho_w g \pi r^2 z \quad (1.20)$$

where ρ_w is the density of water and r is the radius of the cylinder. Pressure is the force per unit area; thus division of equation (1.20) by the cross-sectional area, πr^2 , gives the water pressure, p_w , as:

$$p_w = \frac{W}{A} = \rho_w g z \quad (1.21)$$

The pressure is independent of the size or shape of the cross section of the cylinder; it depends only on the distance from the water surface. At the bottom of the cylinder, under 15 cm of water, the pressure is:

$$p_w = \rho_w g z_{\text{bot}} = 1.0 \frac{\text{g}}{\text{cm}^3} \times 980 \frac{\text{cm}}{\text{sec}^2} \times 15 \text{ cm} = 1.47 \times 10^4 \frac{\text{dynes}}{\text{cm}^2} \quad (1.22)$$

Pressure is also energy per volume. Thus the energy in the cylinder due to water, E_p , can be calculated by integrating the pressure over the cylinder of fluid. Since the cross-sectional area is constant, this integral is:

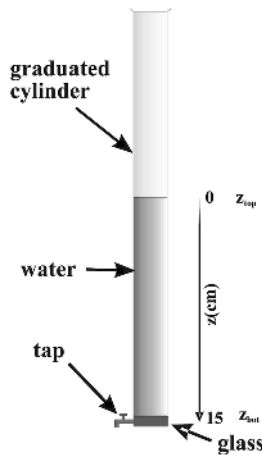


Figure 1.7: Definition sketch for discussion of pressure. Note that the axis is positive downwards with a value of zero at the top of the water column.

$$E_p = \int_{z_{\text{top}}}^{z_{\text{bot}}} \pi r^2 p_w dz = \int_{z_{\text{top}}}^{z_{\text{bot}}} \pi r^2 \rho_w g z dz = \pi r^2 \rho_w g \frac{z_{\text{bot}}^2 - z_{\text{top}}^2}{2} \quad (1.23)$$

where z_{bot} is the coordinate of the bottom of the cylinder (15 cm in the present example) and z_{top} is the coordinate of the top of the cylinder (0 cm in the present example). Since the volume of the fluid in the cylinder is $\pi r^2(z_{\text{bot}} - z_{\text{top}})$, the energy per volume is a pressure denoted as p_w such that:

$$\frac{E_p}{V} = p_w = \rho_w g \frac{z_{\text{bot}} + z_{\text{top}}}{2} \quad (1.24)$$

Thus p_w , the pressure obtained as energy per volume is equal to the pressure calculated as force per area using equation (1.21) if the area is located at the mid-height of the water column, the centroid.

The quantity p_w is also seen to be a volume-averaged pressure for the region of interest. For the cylindrical geometry considered here, the pressure obtained by averaging over the cylindrical volume of water can easily be shown to be equal to the pressure obtained by averaging the pressure over the surface of the cylinder. For an arbitrarily shaped region, and even for a cylinder whose axis is not aligned with the direction of gravity, this is not the case. This observation introduces the important concept that even if the point values of a quantity are well-described, average values of the quantity can be different depending on the averaging procedure used.

The preceding discussion of pressure is relatively transparent because the water is static and the geometry is simple. Most important, one can measure pressure in a fluid, p_w , based on the above concepts whenever a static column of water (or any other liquid of known density) can be created and placed in contact with a location where it is desired to measure the pressure. To demonstrate this fact and to provide a foundation for a subsequent presentation of constitutive theory, another experiment is discussed next based on the design illustrated in Figure 1.8.

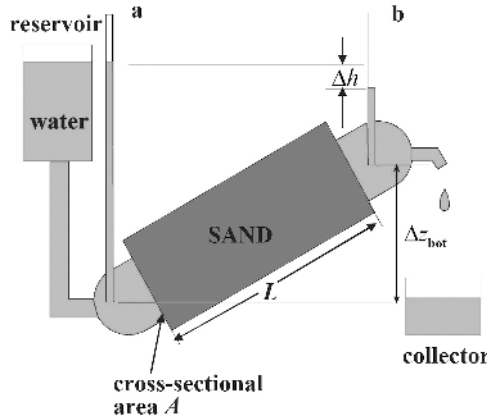


Figure 1.8: Apparatus used to demonstrate the concept of pressure measurements and later to describe the measurement of hydraulic conductivity.

In this experiment, the water moves parallel to the cylinder axis through the sand; as it does so, it loses energy. One measure of this loss of energy is the pressure decrease. While it is quite challenging to measure the pressure of the moving water in the sand directly, the pressure can be easily measured indirectly by creating a static column of water that accesses the moving fluid. The two vertical standpipes, or *manometers*, that are attached to the experimental apparatus in Figure 1.8 facilitate the measurement of the pressure in the moving water. Water rises in the manometers to the level consistent with the pressure at the access point at the base of the manometer tube. Given the height of the water in the tube, one can determine the pressure at the base of the tube using equation (1.21) and therefore in the moving fluid at that point of entry into the manometer.

If there were no flow occurring in the apparatus depicted in Figure 1.8, the water levels in the manometers would be equal such that $\Delta h = 0$. One must be careful to note that this observation does not mean that the pressure at the bases of the two manometers are equal. In fact, when there is no flow the pressures at the bases of the two manometers differ by $\rho_g \Delta z_{\text{bot}}$. A pressure difference between two points will cause flow to occur only if it is sufficient to overcome the force of gravity. The reservoir serves to provide this additional force. For the case indicated when flow is occurring, the water height in the right manometer is less than that in the left by Δh . This indicates that accompanying the flow is a loss of energy between the two points where the manometers contact the fluid. This energy loss is related to the viscous character of the fluid and its interaction with the sand; it is not related to the fact that the fluid is flowing “uphill.”

1.6 SURFACE TENSION CONSIDERATIONS

While the physical effects of pressure on flow of a single fluid in a porous medium are rather straightforward to describe, the relation between the pressures in adjacent fluid phases separated by an interface is more complex. This situation arises when more than one fluid phase is present. Before discussing the impact of this situation within a porous medium, we consider a simple experiment wherein the behavior of a bead of water on a waxed surface is observed, such as a raindrop resting on the hood of a recently waxed car. The drop surface has the geometry of an oblate spheroid (squashed sphere), perhaps approaching spherical if it is small enough that gravitational effects are negligible. A circle of contact area exists between the spherical shape and the waxed surface with the radius of the contact area being somewhere between 0 and the radius of the droplet. If the same bead of water were placed on an unwaxed hood, it would spread over the surface as a thin film. Of interest is an explanation of the factors that influence the interactions between fluids and of fluids with surfaces.

The explanation of fluid-solid interactions lies in the molecular structure of the fluid comprising the drop and the way that structure relates to the molecules at the surface of the solid. In general, water molecules attract one another. At the boundary of the drop, however, the attractive forces of molecules within the drop are not balanced by the attractive forces of molecules outside the drop. The result is a modification of the structural arrangement of the molecules at the drop surface. Although the resulting molecular arrangement cannot be formally considered as a

skin, it has characteristics often identified with a membrane under tension, such as the surface of a balloon filled with air.

The change in energy of a volume of static fluid due to an infinitesimal decrease in its volume is equal to $-pdV$. This expresses the fact that work must be done on the volume (i.e., it must be compressed by an external force per unit area) for its energy to increase. Similarly, a change in the surface area bounding a material is accompanied by a change in energy. Expansion of the surface requires that the attractive forces among the molecules be overcome. The change in energy will be designated γdA , where A is the surface area. For an interface between two different fluids, γ is referred to as the *interfacial tension*. In the case of an interface between a liquid and its own vapor, γ is called the *surface tension*. In many instances, these terms are used less precisely and interchangeably.

We emphasize that the change in energy of a surface is positive when the surface expands because work must be done to stretch that surface. On the other hand, the energy of a volume is increased by compressing that volume. The quantity, γ , has units of force per unit length, or energy per unit area. Mechanically, this can be understood by realizing that stretching a membrane may be accomplished by applying a force per unit length along the curve that bounds the membrane. Analogous to the fact that a force per unit area causes a change in volume, a force per unit length is needed to cause a change in area.

A droplet of water in air will attempt to minimize its surface area in response to the surface tension. The minimum surface area for a specified volume of fluid is a sphere. Thus one influence on the shape of a drop of water tends to cause the drop to be spherical. Gravity can cause deviation from the spherical shape, but in the immediate discussion, this force will be neglected. When the droplet is placed in contact with the solid, the force of interaction between the fluid and solid and the fact that the solid is rigid will influence the drop shape. The interface between the water and air tends to be spherical. If the water molecules are more attracted to each other than to the solid, as is the case for a waxed surface, the drop will minimize the area of contact with the solid. In the limit of no attraction to the solid, the droplet would be a sphere sitting on the solid. An increased attraction between the water and solid will cause the area of contact between the fluid and solid to increase. In the limit where the attraction to the solid is much stronger than the attraction between water molecules, the droplet will spread as a film over the solid. At intermediate levels of attraction, the surface area of contact between the fluid and solid will take on values intermediate between a complete sphere and a film. The forces acting on the surface of the droplet are the fluid pressures. At the curve at the edge of the water droplet where the solid, water, and air phases come together, the *common line*, interfacial tension and surface tension forces are operative. If the droplet surface or the common line contain significant mass, gravitational forces will also be operative.

To quantify the relationship between surface tension and the fluid pressures consider the simple geometry involved in the rise of water in a capillary tube (Figure 1.9a). If the water in the tube is in static equilibrium, then there must be a balance of forces acting on the interface between the air and the water phases. The forces that act on the interface are the pressure of the air acting on the concave side of the interface, the pressure of the water acting on the convex side, and the interfacial tension effects that act tangent to the surface. The fluid on the concave side, in this

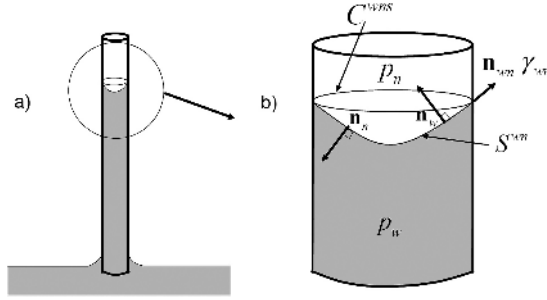


Figure 1.9: Definition sketch of the force balance between pressure and tensile forces at the static water-gas interface in a capillary tube: (a) the capillary tube; (b) forces acting on the interface.

case air, is referred to as the nonwetting fluid because it is less attracted to the solid than the other fluid. This pressure will be signified as p_n , where the subscript n indicates “nonwetting.” The fluid on the convex side of the interface, in this case water, is referred to as the wetting fluid since it preferentially wets the solid. The wetting phase pressure is indicated as p_w , where w indicates the “wetting” phase.⁵ In addition to the pressure acting on the interface, at the edge of the interfacial surface forces are applied by the interfacial tension, γ_{wn} , and the surface tensions, γ_{ws} and γ_{ns} . These forces are exerted on the common line, the curve where the three phases come together. In addition, a lineal tension of the common line can contribute to a force balance. At equilibrium, the forces that act on the interface must be balanced, as must the forces that act on the common line.

To analyze the total force balance on the interface, integrals are formulated, each of which accounts for one of the forces summed over its geometric region of application. The forces acting on the wn interface include the fluid pressures that act on the surfaces and the surface tension along the common line. Analogously with a membrane, the pressures on the two sides will influence the shape of the interface while the tensions on the edge pin the location of the boundary or allow for slippage. The total force from the pressure is obtained as the integral of the pressure over the complete surface of the interface. The force from the surface tension is obtained as an integral over the common line.

The force on the wn interface due to the nonwetting air phase acts in a direction normal to the surface and in the direction pointing out from this phase. If this normal at any point on the surface is designated as \mathbf{n}_n , the total force due to the nonwetting phase may be calculated as the vector:

$$\mathbf{F}^n = \int_{S^{wn}} p_n \mathbf{n}_n dS \quad (1.25)$$

where S^{wn} is the surface of the interface. On the other side of the interface, the wetting phase exerts a force normal to the interfacial surface in the direction tangent

⁵ Note that regardless of the chemical makeup of the two fluids in contact with the solid, the one that is more attracted to the solid is called the wetting phase. This can be confusing, for example, in the case of an oil and water mixture in contact with a plastic such that the oil is the “wetting” phase while water is referred to as “nonwetting.”

to \mathbf{n}_w , the unit vector normal to the surface that points outward from the wetting phase. This force may be obtained as the integral:

$$\mathbf{F}^w = \int_{S^{wn}} p_w \mathbf{n}_w dS \quad (1.26)$$

Finally, the force exerted by the interfacial tension along the bounding line is in a direction tangent to the unit vector \mathbf{n}_{wn} that points outward from the interface in a direction that is normal to the bounding line and tangent to the surface. The total force exerted by the interfacial tension is therefore:

$$\mathbf{F}^{wn} = \int_{C^{wns}} \gamma_{wn} \mathbf{n}_{wn} dC \quad (1.27)$$

where C^{wns} is the bounding curve where the wetting, nonwetting, and solid phases come together. Since the total force acting on the interface must be zero for the static case, the sum of the three forces in equations (1.25), (1.26), and (1.27) must be zero, or:

$$\int_{S^{wn}} p_n \mathbf{n}_n dS + \int_{S^{wn}} p_w \mathbf{n}_w dS + \int_{C^{wns}} \gamma_{wn} \mathbf{n}_{wn} dC = 0 \quad (1.28)$$

The formulation of the total force in equation (1.28) has intuitive appeal on physical grounds. However, besides the total force balance for the interface, the forces at each point on the interface must also balance at equilibrium. Direct formulation of this balance is not intuitive. Nevertheless, application of mathematical theorems, that may require the user to leave intuition behind, to the physical equation (1.28) will lead to the desired result. The mathematical expression that is useful in this analysis converts the integral over the curve bounding the surface to an integral over the surface. This relation is the *divergence theorem* for a surface and has the general form [7]:

$$\int_{C^{wns}} f \mathbf{n}_{wn} dC = \int_{S^{wn}} \nabla' f dS - \int_{S^{wn}} (\nabla' \cdot \mathbf{n}_n) \mathbf{n}_n f dS \quad (1.29)$$

where ∇' is the two-dimensional del operator acting in the surface. Application of this relation to the last term on the left side of equation (1.28) with f replaced by γ_{wn} yields:

$$\int_{S^{wn}} p_n \mathbf{n}_n dS + \int_{S^{wn}} p_w \mathbf{n}_w dS + \int_{S^{wn}} \nabla' \gamma_{wn} dS - \int_{S^{wn}} (\nabla' \cdot \mathbf{n}_n) \mathbf{n}_n \gamma_{wn} dS = 0$$

or, after collection of the terms in the integrands:

$$\int_{S^{wn}} [p_n \mathbf{n}_n + p_w \mathbf{n}_w + \nabla' \gamma_{wn} - (\nabla' \cdot \mathbf{n}_n) \mathbf{n}_n \gamma_{wn}] dS = 0 \quad (1.30)$$

Since this relation must hold, regardless of the size or portion of the interfacial surface over which the integration is performed, the integrand in equation (1.30) must be zero at every point on the surface so that:

$$p_n \mathbf{n}_n + p_w \mathbf{n}_w + \nabla' \gamma_{wn} - (\nabla' \cdot \mathbf{n}_n) \mathbf{n}_n \gamma_{wn} = 0 \quad (1.31)$$

This equation is a vector equation and has components in each of three orthogonal coordinate directions. The first, second, and fourth terms are vectors normal to the surface. The third term involves the gradient in the surface and thus is a vector tangent to the surface. Since equation (1.31) must be valid in any direction, the component of the equation in the directions tangent to the surface is obtained as:

$$\nabla' \gamma_{wn} = 0 \quad (1.32)$$

Equation (1.32) indicates that at equilibrium, the surface tension of an interface between two fluids will be constant, independent of position, since its gradient is zero.

The balance of forces in the direction normal to the interface is obtained as the dot product of equation (1.31) with the unit vector normal to the surface, \mathbf{n}_n . Note that $\mathbf{n}_n = -\mathbf{n}_w$ such that $\mathbf{n}_n \cdot \mathbf{n}_n = 1$ and $\mathbf{n}_n \cdot \mathbf{n}_w = -1$. Thus the normal component of the force balance at any point on the interface is:

$$p_n - p_w - (\nabla' \cdot \mathbf{n}_n) \gamma_{wn} = 0 \quad (1.33)$$

For the case where the interface is flat, the orientation of \mathbf{n}_n does not change with position on the surface, and the divergence of this normal will be zero. Thus for a flat interface, equation (1.33) simplifies to the condition that the pressure across the interface will be continuous with $p_n = p_w$. This is the condition that is typically imposed on large-scale systems where the curvature is small, such as the surface of a bucket of water or at the top of a swimming pool. In general, the quantity $\nabla' \cdot \mathbf{n}_n$ is equal to the sum of the curvatures of the surface in any two orthogonal directions. If the *curvature of the surface* is denoted as $2/R_c$, where R_c is the *geometric mean*, the *radius of curvature*⁶ is calculated as:

$$\nabla' \cdot \mathbf{n}_n = \frac{2}{R_c} = \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (1.34)$$

where R_1 and R_2 are the radii of curvature of any two orthogonal curves on the surface and $\nabla' \cdot \mathbf{n}_n$ is called the *mean curvature*. Each of the radii of curvature is positive when the corresponding curve is concave on the n side and negative when the corresponding curve is concave on the w side. Then equation (1.33) can be rewritten in the form:

$$p_n - p_w = \frac{2}{R_c} \gamma_{wn} \quad (1.35)$$

The *capillary pressure*, p_c , is now defined, in general, as the product of the mean curvature and the interfacial tension:

⁶For a spherically shaped surface, R_c is equal to the radius of the sphere; for a flat surface, R_c is infinite.

$$p_c = \frac{2}{R_c} \gamma_{wn} \quad (1.36)$$

Thus, equation (1.35) expresses the fact that at equilibrium:

$$p_n - p_w = p_c \quad (1.37)$$

Equation (1.35) is known as the *Laplace equation for capillary pressure*. Note that $p_n \neq p_w$ whenever $|R_c| \neq \infty$. Thus, when the surface tension is zero, the equilibrium pressure drop across an interface will be zero only if the interface is flat or at points on the interface where the radii of curvature are equal in magnitude and opposite in sign. Equation (1.35) is similar to that which describes the pressure difference across a physical membrane, such as for a balloon. If the surface tension of the membrane is inadequate to sustain the pressure difference, the balloon will burst.

Before illustrating the balance of forces on an interface between phases with an example calculation, we will develop the expression for the balance of forces on the common line. This expression provides information about the relationships among the interfacial tensions. Because the common line is located on the surface of the solid where the two fluid phases and the solid contact each other, the balance equation must account for the forces exerted by the interfaces. Consider the situation presented in Figure 1.10 where a drop of liquid is sitting on a solid surface, for example a drop of water on the hood of a car. The drop is a cap with spherical shape. A magnification of the region in the vicinity of the common line is provided as part (b) of the figure, and various unit vectors are illustrated there. The force exerted by

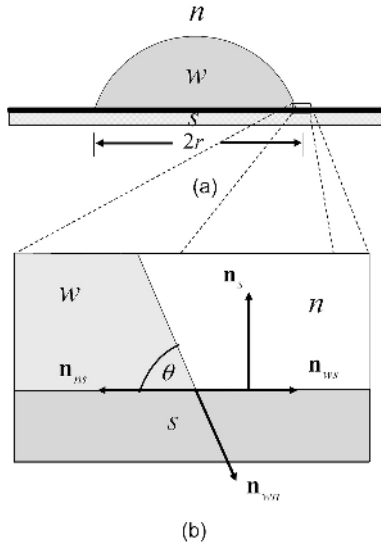


Figure 1.10: (a) Drop of water on a horizontal surface with angle of contact θ and circle of contact with radius r . (b) Enlargement of region where three phases meet with the unit normal vectors \mathbf{n}_{wn} , \mathbf{n}_{ws} , and \mathbf{n}_{ns} indicated at a point on the common line.

each interface on the common line is tangent to the interface and exerts a force on the common line trying to displace it. The total force exerted on a segment of the common line by the interfaces is therefore given as the sum of the integrals of each of the three interface forces over the common line:

$$\mathbf{F}_{\text{interfaces}} = - \int_{C^{wns}} \gamma_{wn} \mathbf{n}_{wn} dC - \int_{C^{wns}} \gamma_{ws} \mathbf{n}_{ws} dC - \int_{C^{wns}} \gamma_{ns} \mathbf{n}_{ns} dC \quad (1.38)$$

where each of the unit vectors is normal to the common line C , tangent to its corresponding interface, and points outward from the interface at the common line. In addition to these forces, the mechanical behavior of the solid and its surface roughness exert an attractive force on the common line with magnitude f_s normal to the smooth representation of the surface in the direction pointing into the solid. This force is $-f_s \mathbf{n}_s$. Finally, the common line has its own tension that acts along its axis, much like a rubber band or a spring. Thus forces are exerted at the ends of the common line segment by the line tension, γ_{wns} , in a direction tangent to the common line and pointing outward. These additional forces may be expressed as:

$$\mathbf{F}_{\text{line}} = - \int_{C^{wns}} f_s \mathbf{n}_s dC + (\gamma_{wns} \mathbf{n}_{wns})_1 + (\gamma_{wns} \mathbf{n}_{wns})_2 \quad (1.39)$$

where the subscripts “1” and “2” refer to the two ends of the segment being studied and \mathbf{n}_{wns} is the outward directed tangent vector at each end. If a curve being studied is a closed loop, the full circle of contact in the present case, the forces due to line tension will not appear as there are no ends. At equilibrium, the total force acting on the common line segment will be zero. Thus, addition of equations (1.38) and (1.39) yields:

$$\begin{aligned} & - \int_{C^{wns}} \gamma_{wn} \mathbf{n}_{wn} dC - \int_{C^{wns}} \gamma_{ws} \mathbf{n}_{ws} dC - \int_{C^{wns}} \gamma_{ns} \mathbf{n}_{ns} dC \\ & - \int_{C^{wns}} f_s \mathbf{n}_s dC + (\gamma_{wns} \mathbf{n}_{wns})_1 + (\gamma_{wns} \mathbf{n}_{wns})_2 = 0 \end{aligned} \quad (1.40)$$

The expression for the balance of forces at a point on the common line may be obtained by making use of the divergence theorem for a curve to relate the terms evaluated at the ends of the segment to integrals over the segment. This theorem has the form [7]:

$$(f \mathbf{n}_{wns})_1 + (f \mathbf{n}_{wns})_2 = \int_{C^{wns}} \nabla'' f dC + \int_{C^{wns}} (\mathbf{n}_{wns} \cdot \nabla'' \mathbf{n}_{wns}) f dC \quad (1.41)$$

where ∇'' is the one-dimensional del operator acting along the curve. Application of equation (1.41) to equation (1.40), with f replaced by γ_{wns} , to eliminate the terms at the ends of the curve then provides:

$$\begin{aligned} & - \int_{C^{wns}} \gamma_{wn} \mathbf{n}_{wn} dC - \int_{C^{wns}} \gamma_{ws} \mathbf{n}_{ws} dC - \int_{C^{wns}} \gamma_{ns} \mathbf{n}_{ns} dC - \int_{C^{wns}} f_s \mathbf{n}_s dC \\ & + \int_{C^{wns}} \nabla'' \gamma_{wns} dC + \int_{C^{wns}} (\mathbf{n}_{wns} \cdot \nabla'' \mathbf{n}_{wns}) \gamma_{wns} dC = 0 \end{aligned} \quad (1.42)$$

or, after collection of the integrands:

$$\int_{C^{wns}} [-\gamma_{wn} \mathbf{n}_{wn} - \gamma_{ws} \mathbf{n}_{ws} - \gamma_{ns} \mathbf{n}_{ns} - f_s \mathbf{n}_s + \nabla'' \gamma_{wns} + (\mathbf{n}_{wns} \cdot \nabla'' \mathbf{n}_{wns}) \gamma_{wns}] dC = 0 \quad (1.43)$$

This equality must hold regardless of the length of common line segment over which the integration is performed. Therefore, the integrand itself must be zero or:

$$-\gamma_{wn} \mathbf{n}_{wn} - \gamma_{ws} \mathbf{n}_{ws} - \gamma_{ns} \mathbf{n}_{ns} - f_s \mathbf{n}_s + \nabla'' \gamma_{wns} + (\mathbf{n}_{wns} \cdot \nabla'' \mathbf{n}_{wns}) \gamma_{wns} = 0 \quad (1.44)$$

The term in parentheses in this equation is the vector known as the *curvature* of the common line. It may be expressed in terms of two orthogonal vector components as:

$$\mathbf{n}_{wns} \cdot \nabla'' \mathbf{n}_{wns} = \kappa_n \mathbf{n}_s + \kappa_g \mathbf{n}_{ws} \quad (1.45)$$

where κ_n is the *normal curvature* and κ_g is the *geodesic curvature* [4]. Substitution of this relation into equation (1.44) yields the force balance on the common line as:

$$-\gamma_{wn} \mathbf{n}_{wn} - \gamma_{ws} \mathbf{n}_{ws} - \gamma_{ns} \mathbf{n}_{ns} - f_s \mathbf{n}_s + \nabla'' \gamma_{wns} + \kappa_n \gamma_{wns} \mathbf{n}_s + \kappa_g \gamma_{wns} \mathbf{n}_{ws} = 0 \quad (1.46)$$

This equilibrium balance of forces at a point on the common line is a vector equation that states the balance of forces in any coordinate direction. Important balance expressions may be obtained by calculating the dot product of equation (1.46) with each of the three orthogonal vectors \mathbf{n}_{wns} , \mathbf{n}_s , and \mathbf{n}_{ws} .

The dot product of \mathbf{n}_{wns} with equation (1.46) yields:

$$\mathbf{n}_{wns} \cdot \nabla'' \gamma_{wns} = 0 \quad (1.47)$$

where use has been made of the fact that all the unit vectors that appear explicitly in equation (1.46) are orthogonal to \mathbf{n}_{wns} . This equation expresses the equilibrium requirement that γ_{wns} be a constant along the common line in that its spatial derivative taken in the direction along the common line is zero.

The dot product of \mathbf{n}_s with equation (1.46) gives the balance of forces in the direction normal to the solid surface:

$$-\gamma_{wn} \mathbf{n}_{wn} \cdot \mathbf{n}_s - f_s + \kappa_n \gamma_{wns} = 0 \quad (1.48)$$

The angle between the *wn* interface and the *ws* interface at the common line is called the *contact angle* and is designated as θ . Therefore:

$$\mathbf{n}_{wn} \cdot \mathbf{n}_s = -\sin \theta \quad (1.49)$$

and equation (1.48) may be written:

$$\gamma_{wn} \sin \theta - f_s + \kappa_n \gamma_{wns} = 0 \quad (1.50)$$

This equation indicates that the force exerted on the common line by the wn interface that tends to pull the common line away from the solid is balanced by an attractive force of the solid and a tendency of the curved common line to expand (or contract) due to the lineal tension. Note that if the common line has no curvature in the direction normal to the solid (such that $\kappa_n = 0$ as in Figure 1.10), the lineal tension will not result in a force in the direction normal to the solid.

Finally, the component of balance equation (1.46) in the direction tangent to the solid surface and normal to the common line (i.e., in direction \mathbf{n}_{ws}) is obtained from the dot product of equation (1.46) with \mathbf{n}_{ws} :

$$-\gamma_{wn} \cos \theta - \gamma_{ws} + \gamma_{ns} + \kappa_g \gamma_{wns} = 0 \quad (1.51)$$

where use has been made of the facts that $\mathbf{n}_{wn} \cdot \mathbf{n}_{ws} = \cos \theta$ and $\mathbf{n}_{ws} \cdot \mathbf{n}_{ws} = -\mathbf{n}_{ws} \cdot \mathbf{n}_{ns} = 1$. This equation expresses the balance of forces in the direction tangent to the solid surface. When an imbalance exists, the common line will be displaced as one fluid spreads onto the surface. Equation (1.51) may be rearranged to the form:

$$\cos \theta = \frac{\gamma_{ns} - \gamma_{ws}}{\gamma_{wn}} + \frac{\kappa_g \gamma_{wns}}{\gamma_{wn}} \quad (1.52)$$

Typically, either from historical precedent or because the line tension and geodesic curvature are small, the last term in this expression is excluded so that the force balance becomes:

$$\cos \theta = \frac{\gamma_{ns} - \gamma_{ws}}{\gamma_{wn}} \quad (1.53)$$

Equation (1.53) is known as *Young's equation*.

The contact angle θ plays a very important role in multiphase flow. If the angle is less than 90 degrees, then the fluid w in Figure 1.10 is the wetting fluid. The fluid for which the wetting angle is greater than 90 degrees, the fluid n in the figure, is the nonwetting fluid. If $|\gamma_{ns} - \gamma_{ws}| > \gamma_{wn}$, then no equilibrium is possible as $|\cos \theta|$ would have to be greater than 1 for equation (1.53) to be satisfied. In this case, the wetting phase will spread until it completely coats the solid surface.⁷

In light of this theoretical analysis, we return to the question of why water will bead on a waxed car surface but not on an unwaxed surface. The explanation lies in the magnitude of the contact angle between the water and the painted surface as opposed to the contact angle between the water and the waxed surface. Water beads on the waxed solid surface because the contact angle between the water and the wax is greater than 90 degrees such that the air is the “wetting fluid” in this case. On the other hand, the contact angle between water and the unwaxed surface is less than 90 degrees such that the water tends to wet this surface. When the magnitude

⁷The wettability of various fluids can be influenced by additives that affect the surface tension of the fluids.

of the right side of equation (1.53) is greater than 1, as is the case for a poorly waxed car in need of a new paint job, the water tends to spread in sheets over the surface. In this comparison the *wettability* of the painted surface is said to be greater than that of the waxed surface.

Consider an experiment whereby a 0.10 cc droplet of water is placed on the hood of a car at a place where the hood is horizontal. Assume that the drop is small enough that its shape may be considered spherical. The contact angle between the water and solid phase is observed to be 100° such that the size of the droplet is more than half a sphere. The volume of the drop may be related to the radius of the *ws* circle of contact, r , and the contact angle, θ , according to:

$$V = \frac{\pi}{3} \left(\frac{r}{\sin \theta} \right)^3 (1 - \cos \theta)^2 (2 + \cos \theta) \quad (1.54)$$

For this system, where the surface is concave in the wetting phase, the mean radius of curvature is the negative of the radius of the drop cap:

$$R_c = -\frac{r}{\sin \theta} \quad (1.55)$$

If two variables from among V , r , θ , and R_c are observed, then the remaining variables may be calculated from the last two equations. If more than two of the variables are observed, the equations can serve as measures of the accuracy of the measurements. For the present case with $V = 0.1$ cc and $\theta = 100^\circ$, rearrangement of equation (1.54) yields:

$$r = \left(\frac{3V}{\pi} \right)^{1/3} \left(\frac{1}{1 - \cos \theta} \right)^{2/3} \left(\frac{1}{2 + \cos \theta} \right)^{1/3} \sin \theta = 0.331 \text{ cm} \quad (1.56)$$

and equation (1.55) provides $R_c = -0.336$ cm. At room temperature, the surface tension of an air water interface⁸ is approximately $\gamma_{wn} = 72.5$ dynes/cm [2]. Thus, from equation (1.36) the capillary pressure of the *wn* interface is:

$$p_n - p_w = p_c = \frac{2}{R_c} \gamma_{wn} = -4.32 \times 10^2 \text{ dynes/cm}^2 \quad (1.57)$$

where n refers to the air phase, w to the water phase, and the difference in the pressures is negative since the air preferentially “wets” the solid as indicated by the fact that the air-solid contact angle is less than 90° . For context, it may be helpful to note that this pressure is the same as the decrease experienced at the bottom of a glass of water if the depth of water is decreased by 0.44 cm. Although this magnitude of capillary pressure is small, it should seem reasonable that for flow in porous media where the curvatures can be orders of magnitude higher, capillary pressure is important.

⁸Surface tension for an air-water interface is approximately $\gamma_{wn} = 75.6 - 0.15 T$ dynes/cm, where T is temperature in degrees Celsius.

With the information obtained thus far, we can also make use of equation (1.53) to determine the difference in interfacial tensions between the fluids and the solid:

$$\gamma_{ns} - \gamma_{ws} = \gamma_{wn} \cos \theta = 72.5 \frac{\text{dynes}}{\text{cm}} \cos 100^\circ = -12.6 \frac{\text{dynes}}{\text{cm}} \quad (1.58)$$

Although this result provides the magnitude by which $\gamma_{ws} > \gamma_{ns}$ for this system, no information is obtained about the values of each of these interfacial tensions.

Also, the result neglects the effects of common line tension. In fact, values of common line tensions involving a solid and a pair of fluids vary depending on the way the solid is prepared. The common line effects are considered to be small in porous media applications relative to other difficulties involving heterogeneity and scale. Nevertheless, one should be aware that this approximation is employed.

The wn interfacial tension exerts a force normal to the solid surface that is countered by the attraction of the solid to the common line. This attraction may be calculated using equation (1.50). Because the surface is flat and the force we are investigating acts normal to the surface on the curve, the normal curvature is zero. Therefore, the lineal tension does not affect the results for geometric reasons, and not by assumption. Equation (1.50) thus provides the attraction force per unit length of common line as:

$$f_s = \gamma_{wn} \sin \theta = 72.5 \frac{\text{dynes}}{\text{cm}} \sin 100^\circ = 71.4 \frac{\text{dynes}}{\text{cm}} \quad (1.59)$$

The preceding discussion and examples involve the effects of surface tension and capillary pressure at the microscale. The study of these phenomena in porous media columns or in the field is undertaken at the macroscale. At this scale, rather than looking at a particular interface or the points on an interface, the aggregate effects of interfacial processes within a representative region of the medium are accounted for. The term *capillarity* is commonly employed to refer to the fact that one fluid is preferentially drawn into a porous medium. This phenomenon is attributable to surface tension influences. Some aspects of this effect will now be examined briefly.

Generally, when water is brought into contact with dry soil, it is drawn into the soil. If the soil is above the water, the elevation to which the water will be drawn against gravity depends on the material that composes the soil and the pore sizes and geometry. To some degree, water will exist in soil above a saturated region and will be hydrodynamically connected to that region. The *water table* is the location in the subsurface where the water saturates the medium and where the pressure is equal to atmospheric. In fine-grained soil, water tends to be found at elevations higher above the water table than under similar conditions in more coarse soil. To demonstrate the reason this occurs, another simple experiment is considered.

The ends of two vertical clean glass tubes (*capillary tubes*) with inside diameters of 0.5 mm and 1.0 mm, respectively, are dipped into a beaker of water as depicted in Figure 1.11. The glass tubes are the solid phase, indicated as material s_g . After a short time, water is observed to have entered the tubes and risen above the level of

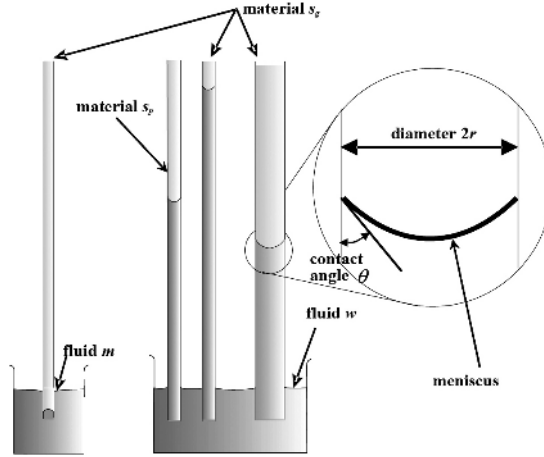


Figure 1.11: A suite of experiments demonstrating the relative wettability of glass and plastic in contact with air, water, and mercury.

the water in the beaker. Moreover, the water level in the 0.5 mm diameter tube is approximately twice as high as in the 1.0 mm tube.

This experiment demonstrates that the rise in the water level is roughly linearly inversely proportional to the radius of the tube. Also, at a horizontal observation level below the surface of the water in the beaker, the pressure in the water will be constant. Therefore if a mathematical plane is located such that it intersects a capillary tube, the water pressure in the tube at that position should be equal to the water pressure on the outside of the tube.

From this observation, the pressure of the water in the capillary tube at elevations above the water surface in the beaker can be calculated. Since the pressure difference between the air and the atmosphere across a flat surface will be zero according to equation (1.35), the water pressure at the water surface in the beaker is atmospheric. Therefore, the pressure in the capillary tube above this surface will be less than atmospheric. Pressure relative to atmospheric is called *gauge pressure*, and thus the pressure in the capillary tube is referred to as being *negative pressure*. Furthermore, since the water in the tube is static, the pressure decreases in direct proportion to elevation in the tube according to equation (1.21) in the form:

$$p_w = p_{\text{atm}} - \rho g Z \quad (1.60)$$

with a change in coordinate such that Z is the distance above the water level in the beaker and p_{atm} is atmospheric pressure. The higher the elevation above the water surface, the more negative will be the gauge pressure of the water. Since the density of air is very small, the pressure in the air may be considered to be constant in the study region (i.e., gravitational effects on the air pressure are negligible). At the top of the water column in the capillary tube, a jump in pressure takes place between the water and air phases. This jump is accounted for in equation (1.35). If the height of water in the capillary tube is designated as $Z = h$, combination of equations (1.35) and (1.60) gives:

$$p_w gh = \frac{2}{R_c} \gamma_{wn} \quad (1.61)$$

This equation indicates that *capillary rise* can occur in a capillary tube only if the surface tension between the two fluids is nonzero and the interface between the fluids is curved with the interface being convex (i.e., bulging outward) from the air side. If the interface is concave from (i.e., bulging into) the air side, the capillary rise will be negative such that the liquid level will decrease in a *capillary depression*. Equation (1.61) will be discussed further subsequently.

Now extend the experiment by dipping into the water a tube made of plastic material, denoted s_p , and with an inside diameter equal to that of the smaller glass tube, 0.5 mm (as indicated in Figure 1.11). Despite the equality of the tube diameters, the water does not rise as high in the plastic tube as in the glass tube. The interfacial tension of the air-water interface is unchanged, so based on equation (1.61), the lower rise in the plastic tube must be accompanied by a larger value of the radius of curvature of the interface, R_c , reflective of different interaction between the tube materials and the water.

As a final element of this experiment, dip a smaller diameter glass tube into a beaker of mercury (fluid m in Figure 1.11). In this case, the mercury does not penetrate the bottom of the tube and flow into the tube unless one pushes the tube deeper into the beaker. Indeed, the air displaces the mercury slightly as the mercury level in the tube is lower than that outside. In addition, the curved meniscus between the air and the fluid, that has thus far been convex from the air side, is now concave.

The explanation of the behavior of the water and mercury interactions with the tubes is found in the concept of *wettability*. In the air-water-solid systems, water preferentially wets the sides of the capillary tubes relative to air, and wets glass more enthusiastically than it wets plastic. The water is drawn up in the capillary tube because of its affinity for the sides of the tube and its ability to sustain a pressure jump across its interface with air.

The height of capillary rise is determined from the balance of forces as indicated in equation (1.61) at the meniscus between the water and the air. The contact angle between the meniscus and the tube wall, θ in Figure 1.11, is generally considered to be a property of the three phases. Although the roughness of the solid surface can impact the value of the contact angle, this effect will be neglected here. For the small capillary tubes under consideration, assume that the interface is essentially spherical such that the radius of curvature, R_c , is related to the tube radius, r , according to:

$$r = R_c \cos \theta \quad (1.62)$$

Substitution of this equation into equation (1.61) and rearrangement yields the height of the capillary rise as:

$$h = \frac{2\gamma_{wn} \cos \theta}{r\rho_w g} \quad (1.63)$$

Equation (1.63) demonstrates that the smaller the tube radius, the higher the meniscus will be drawn into the tube. As long as the tube is small enough that the approximation of a spherical interface applies, the capillary rise is linearly proportional to the inverse of the radius. Similarly, in naturally occurring fine-grained material, which would typically have smaller diameter pores than coarse-grained material, water is more easily held in the region above the water table. The observation that water does not rise as high in the plastic tube as in the glass tube suggests that the wettability of water relative to air on plastic is less than on glass. Finally, the observation that there is a depression rather than rise of mercury in the glass tube indicates that mercury does not wet glass relative to air.

While a capillary tube can, to a limited degree, be a surrogate for the channels in a porous medium, the analogy has some serious limitations. The pores in a porous medium are irregular in geometry and variable in shape. The cross-sectional characteristic length of a pore will vary over at least a couple of orders of magnitude. Pores are also connected to each other and allow flow to follow a complex, multi-directional path.

To obtain some insight into how a variable pore diameter might affect the behavior of multiphase fluids, consider yet another simple experiment. Figure 1.12 depicts a capillary tube with a small, but variable, diameter that is a simple surrogate for pores. The experiment begins by immersing the lower, flanged end of the capillary tube into a beaker of water. The tube is lowered very slowly until the water has just entered the tube up to point “1” in Figure 1.12b, the minimum constriction. This process is the *imbibition stage*, as water moves into the tube displacing the air that flows upward to leave the tube. If the capillary tube is lowered further into the water, for example by a distance δ , the water level in the capillary will increase only by an amount between 0 and δ . The reason the capillary rise is not sustained in this process is that the capillary forces are less effective because of the increased diameter of the tube. This difference will be minimized when the tube has been lowered such that the water just rises to point “2”. If the tube is lowered further, the height of the water level in the capillary relative to the level in the beaker once again increases. This is due to the decrease in capillary diameter that gives rise to an increase in the

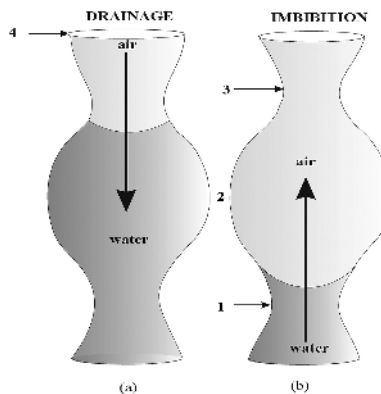


Figure 1.12: The constriction in the capillary tube tends to retain water at a higher elevation on drainage (a) and to preclude the water level from reaching a higher elevation on imbibition (b).

capillary force. Once location “3” is reached, the process continues in the same fashion as the tube is immersed further.

Let us now immerse the capillary tube to the location marked 4 in Figure 1.12a. Now slowly raise the capillary tube so the water moves downward in the capillary. In this, the *drainage stage*, the minimum cross section of the capillary tends to influence the behavior of the fluid by maintaining it at a level above the larger pore. Note that maintaining this higher level depends on the radius of the pore, the surface tension, and the wettability. The capillary forces are not influenced by the larger cross-section geometry of the capillary below the neck where the interface is established.

On the other hand, during imbibition the wider opening associated with the larger pore (or a large pore in a network in a natural soil) does not provide as attractive a region for water flow as does a small opening.⁹ From another perspective, with all other factors being equal, the air-water interface tends to remain where the radius of the pore is the smallest. Thus water is precluded from advancing until the pressure is sufficient to overcome the impediment of the larger pore.

From this example it is evident that the physical behavior of the modified capillaries shown in Figure 1.12 is influenced by whether the water is draining or imbibing. In the macroscale study of porous media, the capillary pressure is related to the saturation. Thus it is not surprising that the equilibrium relationship between saturation and capillary pressure is not single-valued. The equilibrium relation depends on whether imbibition or drainage has occurred prior to examination of the state of the system. This situation is described by saying that the capillary pressure is a *hysteretic* function of saturation, that is, the relationship is dependent upon the history of the porous media system. Thus different equilibrium states (that is, distributions of fluid) may be obtained for the same external pressure conditions, depending upon the path taken to get to the new state. There are other reasons for hysteresis, and these will be considered in the chapter on constitutive relationships.

In summary, it is fair to say that the description of a porous media system composed of two or more fluids and a solid is complicated in comparison with the case of a single fluid and a solid by the presence of the interface between the fluids. The interactions between the fluids and between each of the fluids and the solids must be considered to obtain a complete description of the physical processes. Capillary effects allow for discontinuity of pressure across the fluid-fluid interfaces that is an important factor in modeling multiphase flow.

1.7 CONCEPT OF CONCENTRATION

One final basic concept, the *concentration* of a chemical species in a fluid phase, will be introduced here to conclude this chapter. The relatively short length of this section does not imply that the study of concentrations of species is simple, unim-

⁹ Recall that water rises more readily in a small diameter capillary than one of large diameter.

portant, or straightforward. In fact, the study of the transport and reaction of chemicals within a phase and their transfer between phases is a challenging and timely problem that is seldom easy. As with saturation, porosity, and pressure, concentration is one of the primitive variables in mathematical simulation. Its evolution is described by a conservation equation, and properties of a fluid depend on the concentrations of its chemical constituents. Additionally, the concentration of a material is reflective of its amount in the total solution. Thus, issues of scale involving the size of the sample in which a concentration is measured are important. An average concentration of a contaminant in a groundwater system does not indicate whether hot pockets of concentration threaten water supply wells. In this section measures of the concentration of constituents dissolved in a fluid are explored. If the chemicals are dissolved in a water phase, they are referred to as the solutes in the water solvent, and the phase is referred to as an aqueous solution.

Concentration is generally expressed in terms of mass of solute per unit volume of solution. If, for example, one had a mass of 10 g of salt in a solution of one liter, the concentration could be expressed as a concentration of 10 g/1000 cc, or 0.01 g/cc. Alternatively, one could express the concentration as the number of grams of salt per given weight of solution. In the above example this would yield 10 g/1010 g, or 0.01. For dilute solutions, the difference between these two measures is insignificant.

In field situations, one normally works with concentration in terms of parts per million (ppm) defined as the dimensionless ratio:

$$\text{ppm} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6 \quad (1.64)$$

Alternatively, the concentration is sometimes expressed as parts per billion (ppb) where:

$$\text{ppb} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^9 \quad (1.65)$$

For the case of ten grams of salt in a liter of water, the concentration is ten thousand parts per million or ten million parts per billion. Concentrations in terms of parts per billion are often used in studying organic contamination of water. Some chemicals are considered to be health hazards in concentrations on the order of 1 ppb. At such a low concentration, the dissolved chemical may have minimal impact on the flow properties of the phase. Nevertheless, the movement of the chemical relative to the phase is important to study.

Concentrations are also expressed in terms of moles of a constituent per volume. However, in this text, all references to concentration will be on a mass basis. When a contaminant adheres to a solid phase, its concentration relative to the solid may also be expressed as mass per mass of solid. Material attached to subsurface solids is immobile unless it dissolves into the fluids in contact with the solid. The scope of this text is primarily limited to subsurface fluid phases. However, it is not possible to completely isolate interacting components of environmental problems.

1.8 SUMMARY

The purpose of this chapter is to introduce the reader to the basic concepts that must be considered in studying flow in porous media. After introduction of several fundamental porous media properties, current methodology for quantification of porosity and grain-size distribution was presented.

Pressure has been described and defined for both saturated (single-phase flow) and unsaturated (multiphase, air-water) flow. Capillarity, a multiphase phenomenon, was introduced to demonstrate how negative gauge pressure can arise in water in air-water flow. The importance and behavior of the interface between fluid phases was presented along with the influence of surface tension, curvature, common lines, and hysteresis. Commonly used measures of solute concentration were briefly discussed.

1.9 EXERCISES

1. Indicate whether each of the following items exists at the microscale or the macroscale. For items that exist at both scales, propose a relation between the microscale and macroscale measures: (a) pressure; (b) velocity; (c) density; (d) porosity; (e) saturation; (f) capillary pressure; (g) chemical species concentration; (h) temperature.
2. Find the minimum pore diameter in a cubic packing of equal-sized spheres of radius R .
3. For the soil described by the data provided in Table 1.2, determine the coefficient of uniformity, C_u , the coefficient of curvature, C_c , and the possible soil type.
4. A porous medium is made up of grain particles with a density of 2.65 g/cc, water with a density of 1.0 g/cc, and air. A 1 cc sample taken from the medium has a mass of 2.05 g. If the porosity of the sample is 0.3, determine the water saturation and the water content.
5. A porous medium is constructed that is a collection of hollow spheres. A second porous medium is constructed using a similar collection of spheres except that these spheres are not hollow. Which medium has a higher porosity? Justify your answer.
6. The *void ratio* is defined as the volume of voids (i.e., the volume not occupied by solid particles) divided by the volume of solid particles in a sample of porous medium. Obtain a mathematical relation between the void ratio, e , and the porosity, ϵ .
7. Consider a 20 cm vertical column of water in a right circular cylinder. The pressure in the water is hydrostatic. Calculate the average pressure in the water obtained by averaging over the volume of the water. Compare this result with the average pressure in the water calculated by averaging over the surface that bounds the water. Can any general conclusions be drawn from this result?

8. Now consider a container that is a cylindrical column with radius R_1 for the bottom 10cm and radius R_2 for the next 10cm. Note that if $R_1 = R_2$, the system is the same as in the last problem. Calculate the average pressure of a 20cm column of water in this cylinder based on averaging over the volume and then based on averaging over the surface that bounds the water. What are the implications of this result in relation to a porous media system in which the water content is not constant.
9. A capillary tube is constructed as an alternating sequence of water-wet and air-wet materials. Suppose that the air-wet material is the first (bottom) segment. Describe the behavior of the system as the tube is dipped into a beaker of water, pushed into the water, and withdrawn from the water. How would the behavior be different if the bottom segment were water-wet?
10. Consider a cone with the point on the bottom and with the angle at the tip designated as ϕ . Suppose the cylinder is filled to a depth of water b such that the radius of the common line circle is R . Provide expressions for the curvature of the common line, the normal curvature, and the geodesic curvature. Also provide a sketch that illustrates these quantities.

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