# Steady Flow through Porous Media

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**The increasing demands for oil, water, and food produced in an environmentally sound manner have placed emphasis on the manner of their production, a major part of which is concerned with flow through porous media.**

**The movement of materials through porous media is of interest in many disciplines: in chemical engineering—adsorption, chromatography, filtration, flow in packed columns, ion exchange, reactor-engineering; in petroleum engineering—displacement of oil with gas, water and miscible solvents including surface-active agent solutions and description of reservoirs; in hydrology—movement of trace pollutants in water systems, recovery of water for drinking and irrigation, salt water encroachment into fresh water reservoirs; in soil physics—movement of water, nutrients, and pollutants into plants; in biophysics—life processes such as flow in the lung and the kidney.**

**This paper reviews the fundamentals of steady flow through porous media: it discusses the pseudotransport coefficients permeability, capillary pressure, and dispersion and relates these coefficients to the geometry of porous media. It also discusses single-fluid flow, multifluid immiscible flow, and multifluid miscible flow including the effects of heterogeneity, nonuniformity, and anisotropy of media.**

## INTRODUCTION

A porous medium is a solid with holes in it. Usually the number of holes or pores is sufficiently large that a volume average is needed to calculate its pertinent properties. Pores which occupy some definite fraction of the bulk volume form a complex network of voids. In describing flow in porous media, we are usually interested in interconnected pores since these are the ones that affect flow. However, dead-end pores, that is, pores with only one entry (or exit), must also be considered in flow phenomena where mass transfer takes place.

The matrix of a porous medium is the material in which the holes or pores are imbedded. The manner in which the holes are imbedded, how they are interconnected, and the description of their location, size, shape, and interconnection characterize the porous medium. The porosity is a quantitative property that describes the fraction of the medium that is voids. When we are concerned with flow, the pores or portion of the medium that contribute to flow is called effective porosity.

An extremely large array of materials can be classified as porous media. Broadly speaking, porous media are classified as unconsolidated or consolidated and as ordered or random. Examples of unconsolidated media are beach sand, glass beads, catalyst pellets, soil, gravel, and packing, such as charcoal. Examples of consolidated media are most of the naturally occurring rocks, such as sandstones, limestones, and so forth. In addition, concrete, cement, bricks, paper, cloth, and so forth are man-made consolidated media. Wood can be considered a consolidated medium, as can the human lung. Ordered media are regular packing of various types of materials, such as spheres, column packings, wood, and so forth. Random media are media without any particular correlating factor. They are hard to find, since with almost any media one can correlate some factor.

Since our main interest is the passage of materials into and out of the pore space, we characterize or describe porous media in terms of the properties of the matrix that affect flow. The flow properties which describe the matrix from the point of view of the contained fluid are pseudotransport properties: permeability, the conductance of the medium; dispersion, the mixing caused by the tortuous paths in the medium and other factors; and capillary pressure, the interfacial force due to surfaces. These properties depend on the structure of the matrix. They are bulk properties and have meaning only when applied to a medium having some minimum number of pores—a piece large enough to be volume-averaged. These properties are normally useful only in equations that are at the same level of description as the properties themselves.

Darcy's law (Darcy, 1856) relates the volumetric flow rate $Q$ of a fluid flowing linearly through a porous medium directly to the energy loss, inversely to the length of the medium, and proportionally to a factor called the hydraulic conductivity, $K$.

Darcy's law is expressed as:

$$Q = \frac{KA(h_1 - h_2)}{\Delta l} \tag{1}$$

where

$$\Delta h = \Delta z + \frac{\Delta p}{\rho} + \text{constant} \tag{2}$$

Darcy's law is empirical in that it is not derived from first principles; it is rather the result of experimental observation. Thus, although Darcy's law is empirical, DeWiest (1965) has heuristically demonstrated that it is the empirical equivalent of the Navier-Stokes equations.

Darcy's law is usually considered valid for creeping flow where the Reynolds number as defined for a porous medium is less than one. The Reynolds number in open conduit flow is the ratio of inertial to viscous forces and is defined in terms of a characteristic length perpendicular to flow for the system. The hydraulic radius of a porous medium is defined as the void volume of a porous medium divided by the surface area of the medium. The value of the hydraulic radius for a medium of spherical particles is:

$$R_H = \frac{\text{void volume}}{\text{surface area of spheres}} \tag{3}$$

The Reynolds number for flow in a pipe is:

$$Re = \frac{vd\rho}{\mu} \tag{4}$$

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Equation 4 using $4R_H$ for diameter and $v\infty = \phi v$ yields a Reynolds number for the porous medium as:

$$Re = \frac{4R_H v\infty \rho}{\mu} = \frac{2}{3(1-\phi)} \frac{D_p v_\infty \rho}{\mu} \tag{5}$$

Usually the Reynolds number is defined without numerical constants:

$$Re_p = \frac{D_p v_\infty \rho}{\mu(1-\phi)} \tag{6}$$

In some equations the $(1 - \phi)$ is also dropped. Darcy's law is usually considered valid in the creeping flow regime (where $Re_p$ is less than 1).

The hydraulic conductivity, $K$, defined by Darcy's law, Eq. 1, is dependent on the properties of the fluid as well as the pore structure of the medium. The hydraulic conductivity is temperature-dependent, since the properties of the fluid, density and viscosity, are temperature-dependent. Hydraulic conductivity can be written more specifically in terms of the intrinsic permeability and the properties of the fluids:

$$K = \frac{k\rho g}{\mu} \tag{7}$$

where $k$ is the intrinsic permeability of the porous medium and is a function only of the pore structure. The intrinsic permeability is not temperature-dependent. Darcy's law is often written in differential form, so that in one-dimension:

$$\frac{Q}{A} = q = -\frac{k}{\mu}\frac{dp}{dx} \tag{8}$$

The minus sign results from the definition of $\Delta p$ which is equal to $p_2 - p_1$, a negative quantity. The term $q$ is called the seepage velocity and is equivalent to the velocity of approach $v_\infty$ which was used in the definition of the Reynolds number.

It is usually assumed that Darcy's law is valid in three dimensions, that the permeability $\underline{k}$ is a second-order tensor-dependent on the directional properties of the pore structure, and that $\underline{q}$ is a vector,

$$\underline{q} = -\frac{\underline{k}}{\mu} \underline{\nabla} p \tag{9}$$

Permeability is normally determined using linear flow in the incompressible or the compressible form, depending on whether a liquid or gas is used as the flowing fluid. Most often liquid is used as the flowing fluid since one does not have to correct for compressible effects or slip flow. The volumetric flow rate $Q$ (or $Q_m$) is determined at several pressure drops. $Q$ (or $Q_m$) is plotted vs. the average pressure $p_m$. The slope of this line will yield the fluid conductivity, $K$, or, knowing the fluid density and viscosity, the intrinsic permeability, $k$. For gases, the fluid conductivity depends on pressure so that:

$$\bar{K} = K\left(1 + \frac{b}{p}\right) \tag{10}$$

where $b$ is a parameter-dependent on the fluid and the porous medium. Under such circumstances, a straight line results as with a liquid, but it does not go through the origin; instead, it has a slope of $bK$ and intercept $K$. This difference between the liquid and gas flow was pointed out by Klinkenberg (1941). The explanation for this phenomenon is that gases do not always stick to the walls of the porous medium. This slip shows up as an apparent dependence of the permeability on pressure.

## DESCRIPTION OF POROUS MEDIA

The main interest in describing porous media is to understand and to predict the passage of materials into and out of the media. It is possible to break down the description or characterization of porous media in terms of geometrical or structural properties of the matrix that affect flow and in terms of the flow properties which describe the matrix from the point of view of the contained fluid. The problem of description of a porous medium is one of describing the geometrical or structural properties in some average fashion and relating these average structural properties to the flow properties.

There are two levels of description. At the microscopic level, the description is statistical—in terms of "pore-size" distribution. This description of "pore size" is considered nebulous because it depends on how one describes such a distribution. It is opposed to macroscopic description which describes the media in terms of the average or bulk properties and their variation at sizes or scales much larger than pores. In other words, for a piece of media large enough to have meaning in some volume-averaged sense, the macroscopic level may be based on Darcy's law.

A microscopic description characterizes the structure of the pores. The objective of pore structure analysis is to provide a description that can be related to the macroscopic or bulk flow properties. The bulk properties that we want to relate to pore description are porosity, permeability, dispersion, tortuosity, capillarity, connectivity, relative permeability, adsorption, and wettability. When one examines different samples of the same medium, such as sandstone, it is apparent that the number of pore sizes, shapes, orientations, and interconnections is enormous. Because of this complexity, pore structure description is most often a statistical distribution of apparent pore sizes. This distribution is apparent because to convert measurements to pore sizes we resort to models which provide "average" or model pore sizes. One way to define a pore-size distribution is to model the porous medium as a bundle of straight cylindrical capillaries. The diameters of the model capillaries are distributed according to some distribution function.

A common method of obtaining a pore-size distribution is from capillary pressure measurements or mercury porosimetry. The capillary pressure is a multifluid property—related to the specific free energies of the interface between fluids and fluids and pore walls. The capillary pressure is an equilibrium property—directly related to the interfacial tension (Morrow, 1970). At equilibrium, the surface free energy between the fluids is a minimum. The equilibrium condition is expressed by the Laplace equation:

$$p_c = \gamma_{12}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{11}$$

where $p_c$ is the capillary pressure; $\gamma_{12}$ is the specific free energy of the interface between fluids 1 and 2 and is equivalent to $\sigma$ the interfacial tension between the two fluids; and $r_1$ and $r_2$ are the two principal radii of curvature of the interface at any point.

Consider a straight cylindrical circular capillary. The radius of curvature for such a capillary is the harmonic average of the two principal radii which is the term in parentheses in Eq. 11; therefore,

$$p_c = \frac{2\gamma_{12}}{r} \tag{12}$$

For two immiscible fluids in contact with the solid walls of the capillary, the fluid-fluid interface intersects the solid surface at an angle

$$\cos\theta = \frac{\gamma_{s1} - \gamma_{s2}}{\gamma_{12}} \tag{13}$$

The curvature of the meniscus is:

$$r = \frac{\delta}{2\cos\theta} \tag{14}$$

and

$$p_c = \frac{4\gamma_{12}\cos\theta}{\delta} = \frac{2\sigma\cos\theta}{r} \tag{15}$$

where $\delta$ is the capillary diameter, Eq. 15 is for a capillary tube where we usually assume $\gamma_{12} = \sigma$. For fluid surrounding a bundle of rods $\gamma_{s2} = 0$ and $\gamma_{s1} = \gamma_{12} = \sigma$, then $\cos\theta = 1$ and

$$p_c = \frac{4\sigma}{\delta} = \frac{2\sigma}{r} \qquad (16)$$

Imagine a porous medium to be a bundle of capillaries—the pressure in all the capillaries is the capillary pressure of such a medium. If we apply a given pressure to a fluid-filled porous medium, the saturation of the medium will be a function of the applied pressure. The relation between saturation and capillary pressure at a given applied pressure $p_c$ is:

$$S = \int_{\delta}^{\infty} f(\delta) d\delta \qquad (17)$$

Figure 1 is a typical capillary pressure-wetting fluid saturation curve showing hysteresis. These curves were determined in a sandstone where the fluid system was oil and water. The drainage curve begins with the sample saturated with the water. The imbibition curve begins with the sample saturated with the nonwetting fluid, oil. The hysteresis in the capillary behavior may be due to two mechanisms:

- A difference in the advancing and receding contact angles in the fluid in contact with the solid surfaces.
- An ink bottle effect.

In the ink bottle effect, one assumes a pore shape which contains two equal, small radii at each end and a middle section with a large radius. On the drainage curve the pore will empty to the upper radius. Thus, the fluid saturation will be higher than with the imbibition curve. The fluid saturation will be lower on imbibition, since the fluid fills to the lower radius. A real situation is more complicated since there will be several radii and many different connections.

If the pores are not straight capillaries, Eq. 11 still applies. To find the actual expression between saturation and capillary pressure for a porous medium, we must know the average interfacial curvature as a function of saturation. Since this is difficult to determine, we generally use the capillary model. The capillary model does not have to be circular nor the capillaries of equal lengths, although normally we assume them to be of equal length. Brutsaert (1966a,b) describes how to obtain a pore-size distribution from capillary pressure data.

Another method of defining pore size distributions used with photomicrographs is to use the mean intercept length to characterize pore size. One measures the mean intercept length by taking the arithmetic average of all the chords obtained by intersecting the pores in a photomicrograph with parallel straight lines in all directions. With photomicrographic interpretation, the additional problem of interpreting a two-dimensional surface in three dimensions exists, although the field of stereology provides theoretical relationships between two and three dimensions.

In this method of obtaining a pore-size distribution, a photomicrograph of a thin section of a porous medium is made and the pore sizes inferred by direct measurement of the pores on a set of such photomicrographs. By a set we mean a set large enough so that the number of measurements gives a good statistical average. For this approach, a stereologically sound method of "measuring" pores must be used; that is, it must correctly infer the three-dimensional geometry from an interpretation of the two-dimensional photograph. Further, it must be correct for known pore sizes. If a mean intercept length (or a grid or a sequence of circles) is used, the approach should correctly infer known geometries. The approach used to interpret the photomicrographs depends most often on the equipment that is available to interpret them. Dullien and coworkers (1970, 1971, 1972, 1973, 1974) have discussed photomicrographic methods in detail.

Pore structure for unconsolidated media is inferred from a particle-size distribution, the geometry of the particles, and the manner in which the particles are packed. The theory of packing has been determined for symmetrical shapes, especially spheres. A knowledge of particle size, symmetry, and the theory of packing allows one to establish relationships between pore-size distributions and particle-size distributions.

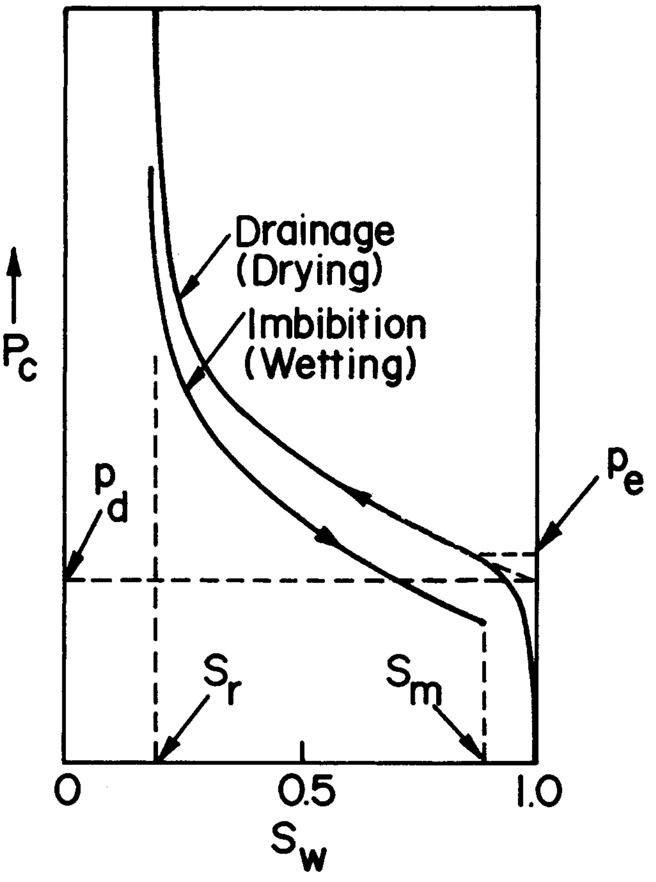

Figure 1. Capillary pressure as a function of saturation (Corey, 1977).

The common regular packing of identical spheres is described by the geometry of the packing. The packing of spheres has two extreme cases (Graton and Fraser, 1935). A cubic packing is one extreme. This packing has a calculated porosity of 0.4764. The other extreme is a rhombohedral packing, and has a calculated porosity of 0.2595. The model of Mayer and Stowe (1965) is defined in terms of a single angle $\sigma$ which is determined by the edges of the rhombohedron formed by connecting the centers of a set of spheres. This model may be utilized to calculate porosities of intermediate packings of uniform spheres.

Haughey and Beveridge (1966) used the porosity to model the coordination number—the number of points of adjacent contacts for a single imbedded sphere. The coordination number $n$ describes the packing. For example, $n$ is 6 for cubic packing, 8 for orthorhombic, 10 for tetragonalsphenoidal, 12 for rhombohedral. For random packing,

$$n = 22.47 - 39.39\,\phi; \quad 0.254 \le \phi \le 0.5 \qquad (18)$$

Statistical models are often useful to relate the micro- and macro-structure of a porous medium. Guin, Kessler, and Greenkorn (1971, 72) discuss generalized models for a network of randomly intersecting straight capillaries. They show that the ergodic assumption—that spatial averages coincide with mathematical expectation—is not necessarily satisfied in all models (Haring and Greenkorn, 1970; Matheron, 1967; Scheidegger, 1957; Saffman, 1959). Dullien (1979) gives an excellent review of statistical models. It is interesting that MacDonald, El-Sayed, Mow, and Dullien (1979) conclude that network models composed of tubes or channels are satisfactory to predict flow rate and pressure drop.

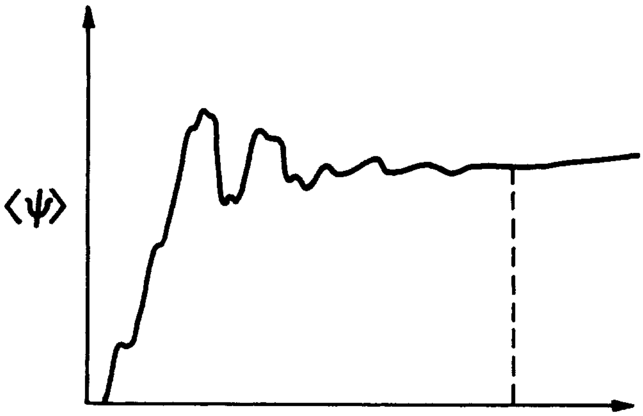

**Figure 2. Dependence of average on averaging volume (Whitaker, 1970).**

A macroscopic description of a porous medium is a description in terms of average or bulk properties at sizes much larger than a single pore. When we reach the point of characterizing a porous medium macroscopically, we must cope with the scale of description. The scale used will depend on the way and on what size we wish to model the porous medium. For a macroscopic reading, assume, if possible, that a given medium is "ideal," that is, homogeneous, uniform, and isotropic. The term homogeneous normally implies that an average property can be used to replace the entire media; for example, a single value of permeability can be used for a "homogeneous" reservoir. And this value of permeability will characterize flow in this reservoir. Unfortunately, a medium which is "homogeneous" in this sense for one property may not be "homogeneous" for another.

The term "reservoir description" often means description in the sense of homogeneous as opposed to heterogeneous, as discussed above. Reservoir description means describing the reservoir at a level where a property changes enough so that more than a single average must be used to model flow. In this sense, a reservoir composed of a section of coarse gravel and a section of fine sand where these two materials are separated and have significantly different permeabilities, is heterogeneous. Defining the dimensions locating the area and determining the average properties of the gravel and the sand is reservoir description. This description is satisfactory for reservoir-level problems; however, if one studies mechanisms of fluid flow or a process at a given scale and wants to use this data at a different scale, the effects of nonideal media at a given scale require more specific definitions.

Slattery (1972) describes averages to use in volume-averaging the equations of change for flow in porous media. Equations describing imcompressible creeping flow of a new-Newtonian fluid of constant viscosity through a porous medium are the continuity equation:

$$(\underline{\nabla} \cdot \underline{v}) = 0 \tag{19}$$

and the void distribution function:

$$\alpha(\delta) = \begin{cases} 1 \text{ if } \delta \text{ is in the pores} \\ 0 \text{ if } \delta \text{ is in the matrix} \end{cases} \tag{20}$$

Since $\alpha(\delta)$ is unknown, we volume-average the equation of continuity and equation of motion.

Assume for every point in space an average volume which contains the volume of the fluid, $V_f$. The porosity of this space is:

$$\phi = \frac{1}{V} \int_V \alpha(\delta) dV \tag{21}$$

Assume a microscopic characteristic length, $d$, over which there is significant variation in point velocity. Further assume that a macroscopic characteristic length, $L$, representative of the distance over which significant variation in the average velocity, $\langle v \rangle$, takes place. Let $d$ approximate pore diameter or grain size and $L$ approximate the length of the system. The volume average of a point quantity associated with the fluid is:

$$\langle \psi \rangle = \frac{1}{V} \int_V \psi dV \tag{22}$$

If we plot $\langle \psi \rangle$ vs. $V$, starting with $V$ in the solid, as $V$ increases portions of the fluid are contained within $V$. The volume average $\langle \psi \rangle$ passes through several fluctuations until $V$ reaches a size where $\langle \psi \rangle$ smooths. Figure 2 (Whitaker, 1970) is a schematic picture of $\langle \psi \rangle$ vs. $V$. For values of $V$ larger than at the dashed line on Figure 2 the volume average $\langle \psi \rangle$ is smooth. However, it is not necessarily constant.

Let $l$ be a characteristic macroscopic length for the average value and $d << l$ and $\langle \langle \psi \rangle \rangle = \langle \psi \rangle$, then the volume average of $\langle \psi \rangle$ is:

$$\langle \langle \psi \rangle \rangle = \frac{1}{V} \int_V \langle \psi \rangle \, dV \tag{23}$$

which leads to $l << L$. Whitaker (1970) shows for the above restrictions that the volume and area averages are essentially equivalent.

Bear (1972) uses porosity as a point quantity in a porous medium and a Representative Elementary Volume (REV) to characterize a medium macroscopically. This definition is a specific case of the more general discussion of Whitaker (1970). The size of the REV around a point $P$ is smaller than the total medium so it can represent flow at $P$. There must be enough pores to allow statistical averaging. If porosity varies the maximum length is the characteristic length that indicates the rate of change of porosity. The minimum length is the pore size. The REV is equivalent to the generalized value defined by Whitaker (1970) as the dashed line in Figure 2. $\langle \psi \rangle$ is porosity. Bear replaces the porous medium in a "continuum sense" with a model which gives the correct average porosity at any point in the medium.

The terms heterogeneity, nonuniformity, and anisotropy must be defined in the volume-average sense. Since the definitions for nonideal properties are arbitrary it seems reasonable to define them in direct relation to flow. The definitions of heterogeneity, nonuniformity, and anisotropy can be defined at the level of Darcy's law in terms of permeability. Permeability is more sensitive to conductance, mixing, and capillary pressure than porosity.

Greenkorn and Kessler (1970) define heterogeneity, nonuniformity, and anisotropy in reference to permeability as follows. First, by macroscopic they imply averaging over elemental volumes of radius $\epsilon$ about a point in the media, where $\epsilon$ is large enough that Darcy's law can be applied for appropriate Reynolds numbers. In other words, volumes are large with respect to that of a single pore. Further, $\epsilon$ is to be the minimum radius that satisfies such a condition; otherwise, by making $\epsilon$ too large, certain nonidealities may be obscured by burying their effects far within the elemental volume. Obviously one can, for all practical purposes, remove certain effects by scale.

The definitions of heterogeneity, nonuniformity, and anisotropy are based on the probability density distribution of permeability of random macroscopic elemental volumes selected from the medium. For a uniform medium, the probability density function for permeability is either a Dirac delta function or a linear combination of $N$ functions that satisfy the relation:

$$f(k) = \sum_{i=1}^{N} \xi_i \delta \tag{24}$$

where

$$\sum_{i=1}^{N} \xi_i = 1 \tag{25}$$

If the probability density function cannot be constructed with a finite number of weighted delta functions, then the medium is nonuniform. An homogeneous medium has a unimodal permeability distribution, whereas one that is heterogeneous is at least bimodal. The medium can be described as isotropic if the permeability is independent of direction and is anisotropic otherwise.

There has been a recent revival of the discussion of nonideal porous medium systems in the soil physics literature. (Bakr et al., 1978; Gutjahr et al., 1978; Dagan, 1979; Delhomme, 1979; Freeze, 1975; Philip, 1980). Similar discussions occurred in the 1960's in petroleum literature with miscible recovery of oil. This discussion continues as part of the topic often called reservoir description. Several frameworks exist to describe nonideal media. There is a need for more experimental field data interpreted in an appropriately scaled manner.

## SINGLE FLUID FLOW

The equations of change for single fluid flow can be obtained from limited cases for multifluid flow. However, the inherent simplicity of one fluid allows simplification in the flow modeling such that it is useful to treat this limited case, single fluid flow, separately.

The parameters that relate the medium and flow in this case are porosity, permeability, tortuosity, and connectivity. These parameters are usually defined with reference to single fluid flow. Complex potentials can be used to model single fluid flow problems since Laplace's equation results from steady single-fluid flow situations. Darcy's law is an empirically determined relation for single fluid flow in a linear system. Slattery (1969) raises several problems concerning Darcy's law. Whitaker (1970) poses the problems raised by Slattery (1969) as follows. For the creeping flow of a constant viscosity single Newtonian fluid in a rigid porous medium, the continuity equation of the fluid is:

$$\frac{\partial \rho}{\partial t} + (\underline{\nabla} \cdot \underline{v}) = 0 \tag{26}$$

The equation of motion for the fluid is:

$$\frac{\partial \rho \underline{v}}{\partial t} + (\underline{\nabla} \cdot \rho \underline{v}\underline{v}) - (\underline{\nabla} \cdot \underline{\underline{\tau}}) - \rho \underline{F} = 0 \tag{27}$$

where $\underline{\underline{\tau}}$ are the stresses in the fluid and $\underline{F}$ are body forces. With these two equations we require a void distribution function:

$$\alpha(\delta) = \begin{cases} 1, & \text{if } \delta \text{ is in the fluid} \\ 0, & \text{if } \delta \text{ is in the solid} \end{cases} \tag{28}$$

We cannot determine Eq. 28 and we cannot solve Eqs. 26 and 27. The method posed to overcome the dilemma is to volume average the equations of change.

In order to volume average the equations of change we need gradients of averages and averages of gradients. Slattery (1969) derived a theory for the volume average of a gradient from the general transport theorem:

$$\langle \underline{\nabla} \underline{\underline{\psi}} \rangle = \underline{\nabla} \langle \underline{\underline{\psi}} \rangle + \frac{1}{V} \int_{A_i} \underline{\underline{\psi}} \underline{n} dA \tag{29}$$

where $\underline{n}$ is the outward directed normal for $V$ or $V_f$ and $A_i$ is the area of the solid-fluid interface. The divergence theorem is:

$$\langle (\underline{\nabla} \cdot \underline{\underline{\psi}}) \rangle = (\underline{\nabla} \cdot \langle \underline{\underline{\psi}} \rangle) + \frac{1}{V} \int_{A_i} (\underline{\underline{\psi}} \cdot n) dA \tag{30}$$

Consider a point, $z$, in a porous medium of closed surface, $S$, and volume, $V$. $z$ is either in the matrix or in a pore or on the boundary, as sketched in Figure 3 (Slattery, 1972). Apply Eqs. 29 and 30 to the equation of continuity, Eq. 26, and the equation of motion, Eq. 27, for the region enclosed by S in Figure 3. The mass balance for the fluid inside the closed surface S is:

$$\int_{V_f} \left[ \frac{\partial \rho}{\partial t} + (\underline{\nabla} \cdot \rho \underline{v}) \right] dV = 0 \tag{31}$$

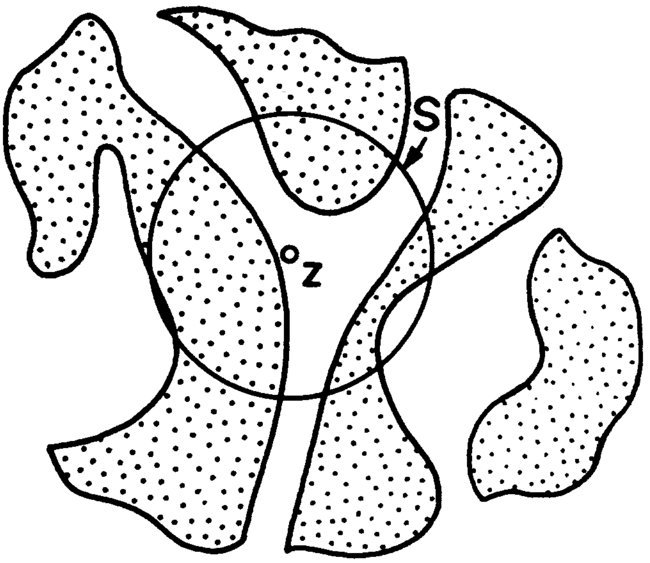

Figure 3. Averaging surface S to be associated with every point z in the porous medium (Slattery, 1972).

Using Eqs. 29 and 30:

$$\frac{\partial \langle \rho \rangle}{\partial t} + (\underline{\nabla} \cdot \langle \rho \underline{v} \rangle) = 0 \tag{32}$$

The equation of motion for the fluid inside the closed surface S is:

$$\int_{V_f} \left[ \frac{\partial \rho \underline{v}}{\partial t} + (\underline{\nabla} \cdot \rho \underline{v}\underline{v}) - (\underline{\nabla} \cdot \underline{\underline{\tau}}) - \rho \underline{F} \right] dV = 0 \tag{33}$$

Applying Eqs. 29 and 30 again:

$$\frac{\partial \langle \rho \underline{v} \rangle}{\partial t} + (\underline{\nabla} \cdot \langle \rho \underline{v}\underline{v} \rangle) - (\underline{\nabla} \cdot \langle \underline{\underline{\tau}} \rangle) - \langle \rho \underline{F} \rangle - \frac{1}{V} \int_S (\underline{\underline{\tau}} \cdot \underline{n}) dS = 0 \tag{34}$$

For an incompressible fluid without any inertial effects present and with body forces represented by a potential function $\underline{F} = -\underline{\nabla}\hat{\phi}$:

$$(\underline{\nabla} \cdot \{\langle \underline{\underline{\tau}} \rangle - \rho \hat{\phi} \underline{\underline{I}}\}) + \frac{1}{V} \int_{S_w} (\{\underline{\underline{\tau}} - \rho \hat{\phi} \underline{\underline{I}}\} \cdot \underline{n}) dS = 0 \tag{35}$$

where $S_w$ is the interface between the fluid and the solid.

Slattery (1972) shows that the second term of Eq. 35 is a function of the difference between the local average fluid velocity $\langle \underline{v} \rangle$ and the local average solid velocity $\langle \underline{u} \rangle$. Therefore, the force per unit volume an incompressible fluid exerts on an anisotropic (oriented) porous medium is supplementary to the hydrostatic force and the local pressure. Let $\mathfrak{p} = p - p_0 + \rho g$, then Eq. 35 can be written:

$$\underline{\nabla} \mathfrak{p} - \mu \nabla^2 \langle \underline{v} \rangle + \mu \underline{\underline{k}}^{-1} \langle \underline{v} \rangle = 0 \tag{36}$$

The second term in Eq. 36 represents viscous drag at the boundaries and was recognized heuristically by Brinkman (1949). Howells (1974) and Hinch (1977) confirm the validity of Eq. 36 by considering slow flow in random arrays of fixed spheres and for suspensions, respectively. Normally, this viscous drag term is neglected and

$$\langle \underline{v} \rangle = -\frac{\underline{\underline{k}}}{\mu} \underline{\nabla} p \tag{37}$$

If $\langle \underline{v} \rangle$ is equal to $\underline{q}$, Eq. 37 is Darcy's law in three dimensions for an anisotropic porous medium. The permeability tensor $\underline{\underline{k}}$ is symmetric.

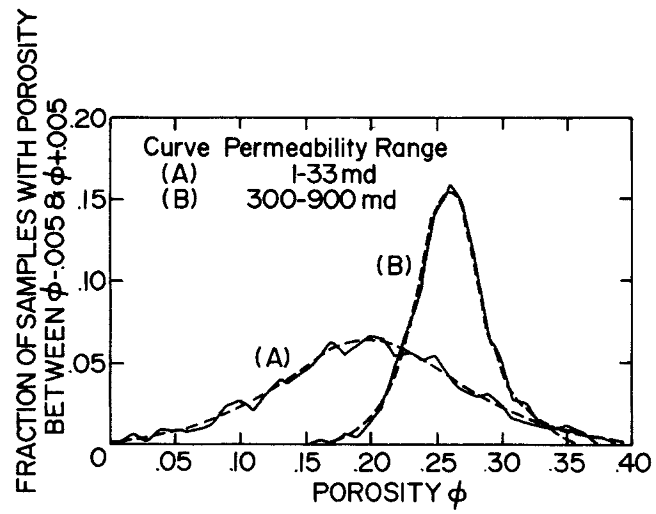

Figure 4. Porosity distributions. (Collins, 1961)

The following are the equations of change for single-fluid flow in a porous medium. The equation of continuity is:

$$\phi \frac{\partial \rho}{\partial t} + (\underline{\nabla} \cdot \rho \underline{q}) = 0 \tag{38}$$

where $\phi$ is the porosity of the medium, $\rho$ is the density of the fluid in the pores. The equation of motion—Darcy's law—in three dimensions is:

$$\underline{q} = -\frac{k}{\mu} \underline{\nabla}\left(p - \frac{d}{dz} \rho g z\right) \tag{39}$$

Four macroscopic properties of nonideal porous media which may be used to describe single-fluid flow will be discussed. (Inversely, single-fluid flow may be used to infer these properties.) To calculate flow through a nonideal porous medium the effects of heterogeneity, nonuniformity, and anisotropy must be considered on these macroscopic properties. These four properties are described as follows:

*Porosity* macroscopically characterizes the effective pore volume of the medium. The porosity is directly related to the size of the pores relative to the matrix. When porosity is substituted, we lose the details of the structure.

*Permeability* — the conductance of the medium defined with direct reference to Darcy's law. The permeability is related to the pore-size distribution since the distribution of the sizes of entrances, exits, and lengths of the pore walls makes up the major resistances to flow. The permeability is the single parameter that reflects the conductance of a given pore structure. The permeability and porosity are related since if the porosity is zero the permeability is zero. Although there may be a correlation between porosity and permeability, permeability cannot be predicted from porosity alone since we need additional parameters which contain more information about pore structure. These additional parameters are the next two macroscopic properties.

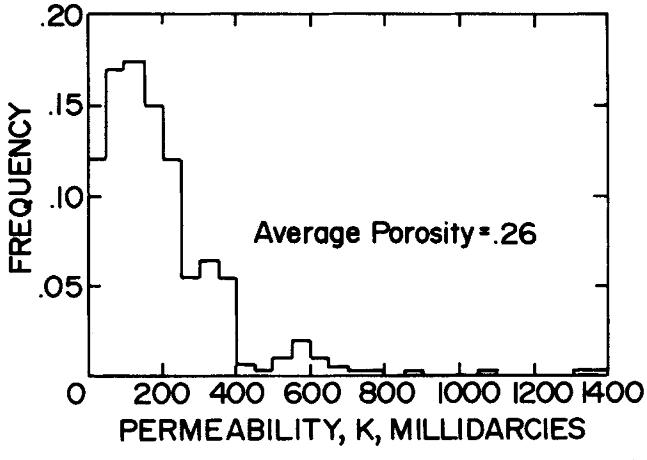

Figure 5. Permeability distribution for a natural sandstone (Law, 1944).

*Tortuosity* — the relative average length of a flow path, the ratio of the average length of the flow paths to the length of the medium. The tortuosity is a macroscopic measure of both the sinuousness of the flow path and the variation in pore size along the flow path. Like porosity, tortuosity correlates with permeability but cannot be used alone to predict permeability except in some limiting cases.

*Connectivity* — the manner and number of pore connections. When all the pores are the same size, connectivity is the average number of pores per junction (Fatt 1956a). The connectivity is a macroscopic measure of the number of pores at a junction and, further, the manner of connection, that is, the different sizes of the pores at the junction. Like porosity and tortuosity, connectivity correlates with permeability but cannot be used alone to predict permeability except in certain limiting cases. The real problem lies in the conceptual simplifications which result from replacing the real porous medium with macroscopic parameters that are averages and that relate to some idealized model of the medium. Tortuosity and connectivity represent different features of the pore structure and are useful to interpret such macroscopic flow properties as permeability, capillary pressure and dispersion.

Kozeny (1927) represents a porous medium as an ensemble of channels of various cross-sections of the same length and solves the Navier-Stokes equations for all channels passing a cross-section normal to the flow to obtain:

$$S^2 = \frac{c\phi^3}{k} \tag{40}$$

where the Kozeny constant $c$ is a shape factor which takes on different values depending on the shape of the capillary ($c = 0.5$ for a circular capillary). $S$ is the specific surface of the channels. For other than circular capillaries, Leverett (1941) included a shape factor:

$$r^2 = \frac{ck}{\phi} \tag{41}$$

The specific surface for cylindrical pores is:

$$S_A = \frac{n2\pi rL}{n\pi r^2 L} = \frac{2}{r} \tag{42}$$

and

$$S_A^2 = \frac{2\phi}{\sqrt{8}\, k} \tag{43}$$

If we replace $2/\sqrt{8}$ with a shape parameter $c$ and $S_A$ with a specific surface,

$$S = \phi S_A \tag{44}$$

we obtain the Kozeny equation.

The tortuosity, $\tau$, was introduced as a modification to the Kozeny equation to account for the fact that in a real medium the pores are not straight—the length of the most probable flow path is longer than the overall length of the porous medium and

$$S^2 = \frac{c\phi^3}{\tau k} \tag{45}$$

Many authors include a shape factor in the tortuosity. In any event, there is an inferred relationship between permeability, porosity, tortuosity, and pore structure.

The tortuosity is difficult to relate to the nonuniformity and the anisotropy of a medium. If we attempt to predict permeability from a pore structure model, tortuosity is needed to correct the model for pore length. For a given model including nonuniformity and anisotropy—tortuosity is constant (2.25 for the model of Haring and Greenkorn, 1970; 1 for the model of Fatt, 1956a). Tortuosity enters the problem significantly through fluid flow, that is, in diffusion in pores and in dispersion when we are concerned with flow of miscible fluids. In mass transfer by diffusion in pores, the tortuosity is used to relate diffusivity and effective diffusivity in the pores (Satterfield and Sherwood, 1963).

$$\mathfrak{D}_{eff} = \frac{\mathfrak{D}}{\tau} \tag{46}$$

With dispersion of two miscible liquids where diffusion effects are present (at slow velocities), the effective diffusion or dispersion is described by tortuosity. According to Whitaker (1967):

$$D_{eff} = D(\delta_{jk} + RB_{jk}) \tag{47}$$

where $RB_{jk}$ is the tortuosity effect.

The connectivity must be related to the permeability since the manner and number of intersections affects the flow resistance. Fatt (1956a, 1956b) uses connectivity to relate the structure of his model to permeability. Since the tortuosity of his model is one, tortuosity does not enter the problem. It would seem that the Kozeny relation must be modified so that tortuosity includes the geometric effect and a connectivity parameter that itself includes the effect of intersections:

$$S^2 = \frac{a\phi^3}{\tau k} \tag{48}$$

where $a$ is connectivity.

To find the average porosity of a homogeneous but nonuniform medium, we determine the correct mean of the distribution of porosity. It has been observed that data on porosity of both natural and artificial media usually are normally distributed (Law, 1944; Bennion and Griffiths, 1966). Figure 4 shows the porosity distribution of samples from a heterogeneous sandstone: there are two distinct distributions with widely differing permeabilities. The two distributions are nonuniform. Also, in Figure 4 for both sets the distribution of the nonuniform porosity is approximately normal. The mean of the normal distribution based on a sample size $n$ is:

$$\langle \phi \rangle = \frac{\sum_{i=i}^{n} \phi_i}{n} \tag{49}$$

the arithmetic average. The average porosity of a heterogeneous nonuniform media as in Figure 4 is the volume weighted average of the number average, Eq. 49.

$$\langle\langle \phi \rangle\rangle = \frac{\sum_{i=1}^{m} V_i \langle \phi_i \rangle}{\sum_{i=1}^{m} V_i} \tag{50}$$

For the case of Figure 4, $m = 2$, since there are two distinct distributions.

The average nonuniform permeability is a function of position. For a homogeneous but nonuniform medium, the first moment is the appropriate estimate of the mean of the permeability distribution function. Permeability of a nonuniform medium is usually skewed, Figure 5 (Law, 1944). Most data for nonuniform media show permeability to be log normally distributed (Csallany and Walton, 1963; Law, 1944; Seaber and Hollyday, 1966). The appropriate average for a homogeneous, nonuniform permeability, assuming it is distributed as a log normal, is the geometric mean.

$$\langle k \rangle = \left[ \prod_{i=1}^{n} k_i \right]^{1/n} \tag{51}$$

For reservoirs where heterogeneity may be three-dimensional and flow is essentially two-dimensional, we usually assume layers at a given point and compute the average according to:

$$\langle\langle k \rangle\rangle = \frac{h \ \langle k_1 \rangle + h_2 \langle k_2 \rangle + \dots}{h} \tag{52}$$

where $h$, $h_2$, are layer thicknesses and $h$ is the total thickness.

To determine an overall average between points when the heterogeneity is restricted to layers, find the geometric averages of the layers and combine them into one average using Eq. 52. To determine an overall average where the heterogeneities are three-dimensional, compute the average at one point according to Eq. 51 and combine these averages as a weighted harmonic average (Johnson and Greenkorn, 1962).

$$\langle\langle k \rangle\rangle_s = \frac{L}{\frac{L_1}{\langle k_1 \rangle} + \frac{L_2}{\langle k_2 \rangle} + \dots} \tag{53}$$

where $L$ is the length of a layer.

The permeability in general is a tensor and we determine the elements of the tensor in anisotropic systems. Again, in natural systems we have the dilemma of deciding whether directional effects are oriented heterogeneities, or whether permeability is really tensorial in that the directional effect is a point property. (Interestingly enough, in most situations either will give a usable answer.) Permeability is a volume-averaged property for a finite but small volume of a medium. Anisotropy in natural or artificially packed media may result from particle (or grain) orientation, bedding of different sizes of particles, or layering of media of different permeability. It is difficult to say at what level we should treat a directional effect as anisotropy or as an oriented heterogeneity. Assuming the problem of scale is solved let's look at directional effects represented by the permeability tensor.

In principle, simply use the general form of Darcy's law, where, neglecting gravity:

$$\underline{q} = -\frac{\underline{\underline{k}}}{\mu} \underline{\nabla} p \tag{54}$$

The significance of the tensor, $\underline{\underline{k}}$, is that in an anisotropic (oriented) medium, the velocity, $\underline{q}$, and the pressure gradient, $\underline{\nabla} p$, are not in the same direction.

We have an additional dilemma in that in order to determine anisotropy experimentally finite chunks of porous media must be used and, unfortunately, there are two extremes of possible conditions plus the intermediate possibilities (Scheidegger, 1957; Marcus, 1962). For one extreme, permeability is measured in the direction of pressure gradient—the velocity component parallel to the pressure gradient is:

$$q_n = (\underline{n} \cdot \underline{q}) \tag{55}$$

The directional permeability measured is:

$$k_n = (\underline{n} \cdot [\underline{\underline{k}} \cdot \underline{n}]) \tag{56}$$

For the other extreme, permeability is measured in the direction of flow—the component of pressure parallel to the flow is:

$$(\underline{\nabla} p)_n = (\underline{n} \cdot \underline{\nabla} p) \tag{57}$$

The directional permeability measured is:

$$k'_n = \frac{1}{([\underline{n} \cdot \underline{\underline{k}}^{-1}] \cdot \underline{n})} \tag{58}$$

The error is a maximum at 45° from the principal axis of the permeability tensor. The error is small, fortunately, unless the difference between the values of $k_{11}$ and $k_{22}$ is large. Parsons (1964) makes this point in discussing the papers of Marcus (1962) and of Greenkorn, Johnson, and Shallenberger (1964). The difference between the two extremes is not large, if the ratio of $k_{11}/k_{22}$ is small.

It is interesting to speculate whether or not pure creeping flow is required everywhere through the pores to use permeability as the conductance parameter in single fluid flow. If the overall pressure drop is linear with velocity, and if there is form drag (noncreeping flow) in addition to the wall resistance and entrance-exit effects, the length and shape of the flow path (tortuosity) and the manner and number of intersections (connectivity) must affect permeability. Further, it is interesting to speculate whether or not permeability is reciprocal in a noncreeping but linear flow regime since form drag will be different in different directions.

### MULTIFLUID IMMISCIBLE FLOW

The equations of change for multifluid immiscible flow are similar to those for single-fluid flow. However, the equations are written for each fluid and connected using the capillary pressure and saturation of the various fluids. The additional parameters wettability, capillary pressure, relative tortuosity, and relative permeability are introduced.

Immiscible flow is modeled by ignoring capillary pressure as in the Buckley-Leverett (1941) displacement model or by assuming that a distinct boundary exists and moves as in the Muskat (1937) model. Transient flow is normally modeled in much the same manner as single fluids, by writing an average expression.

Muskat et al. (1937) assume Darcy's law is valid for each flowing fluid when the fluids are a gas, 1, and a liquid, 2.

$$q_1 = -\frac{\underline{k}k_{r1}}{\mu}\underline{\nabla}p_1 \tag{59}$$

and

$$\underline{q}_2 = -\frac{\underline{k}k_{r2}}{\mu_2}\underline{\nabla}p_2 \tag{60}$$

The product $\underline{k}k_{r1}$ is the effective permeability of the medium to fluid 1 with fluid 2 present, $\underline{k}_1$. The product $\underline{k}k_{r2}$ is the effective permeability of the medium to fluid 2 with fluid 1 present, $\underline{k}_2$. Effective permeabilities depend on both pore structure and the fluids present in the porous medium. The values of $k_{r1}$ and $k_{r2}$ are called the relative permeabilities, and are defined by:

$$k_{r1} = \frac{\underline{k}_1}{\underline{k}} \tag{61}$$

$$k_{r2} = \frac{\underline{k}_2}{\underline{k}} \tag{62}$$

The relative permeabilities depend on saturation (and wettability and saturation history). The continuity equations for each fluid are:

$$\phi\frac{\partial \rho_1 S_1}{\partial t} = -(\underline{\nabla}\cdot\rho_1\underline{q}_1) \tag{63}$$

and

$$\phi\frac{\partial \rho_2 S_2}{\partial t} = -(\underline{\nabla}\cdot\rho_2\underline{q}_2) \tag{64}$$

where $S_1$ is fractional saturation of fluid 1, $S_2$ is fractional saturation of fluid 2. These saturations must add up to 1 so that:

$$S_1 + S_2 = 1 \tag{65}$$

For immiscible fluids, the interfacial tension between the two fluids causes a pressure discontinuity at the boundary separating the two fluids. This pressure is the capillary pressure and is related to saturation so that:

$$p_c(S_1) = p_2 - p_1 \tag{66}$$

The extension of Darcy's law to the flow of two immiscible fluids in a porous medium is heuristic. Slattery (1968, 1970) introduced the concept of local averaging to each fluid in multifluid immiscible flow in a porous medium to obtain:

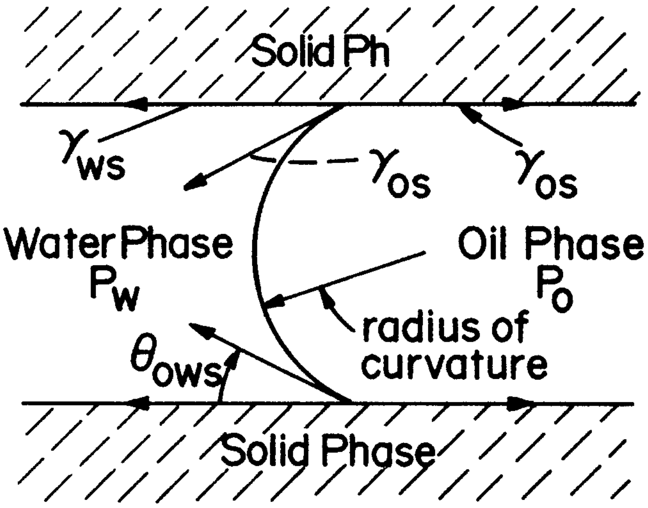

**Figure 6. Hydrostatic equilibrium—two fluid phases in contact with a solid phase (Melrose and Bradner, 1974).**

$$\nabla(p - p_o)^i + L_i\underline{q}_i = 0 \tag{67}$$

where $p_o$ is a reference pressure and $L_i$ is a resistance coefficient. Thus a relative permeability concept results from volume averaging the equations of continuity and motion for multifluid immiscible flow.

In summary, for multifluid immiscible flow of compressible fluids, in an isotropic porous medium with no gravity:

$$\underline{q}_i = -\frac{k_i(S_i)}{\mu_i}\underline{\nabla}p_i \tag{68}$$

and

$$\frac{\partial S_i}{\partial t} = -(\underline{\nabla}\cdot\underline{q}^i) \tag{69}$$

$$\sum_{i=1}^{n} S_i = 1 \tag{70}$$

$$p_c(S_w) = p_n - p_w \tag{71}$$

where $n$ and $w$ stand for nonwetting and wetting fluids, respectively.

Morrow (1970) discusses the thermodynamics of surfaces between immiscible fluids and between fluids and solids with reference to the superficial surface free energy, surface free energy, and surface (interfacial) energy and shows

$$\frac{F_S}{A} = \sum_{i=1}^{k}\mu_i\Gamma_i + \sigma \tag{72}$$

Equation 72 defines the superficial surface free energy per unit area. For a single component system composed of a pure liquid and its vapor the dividing surface in the model can be located so that $\Gamma = 0$, the superficial surface free energy per unit area $F_S/A$, and the surface tension are equal.

The interfacial tension is numerically equal to the reversible work of extension per unit area,

$$\sigma = \left(\frac{\partial F}{\partial A}\right)_{T,V,n} \tag{73}$$

If the interfacial tension is constant,

$$\sigma\Delta A = (\Delta F)_{T,V,n} \tag{74}$$

which defines the surface free energy. In systems where the interfacial tension changes with the surface area, such as systems containing surface active agents,

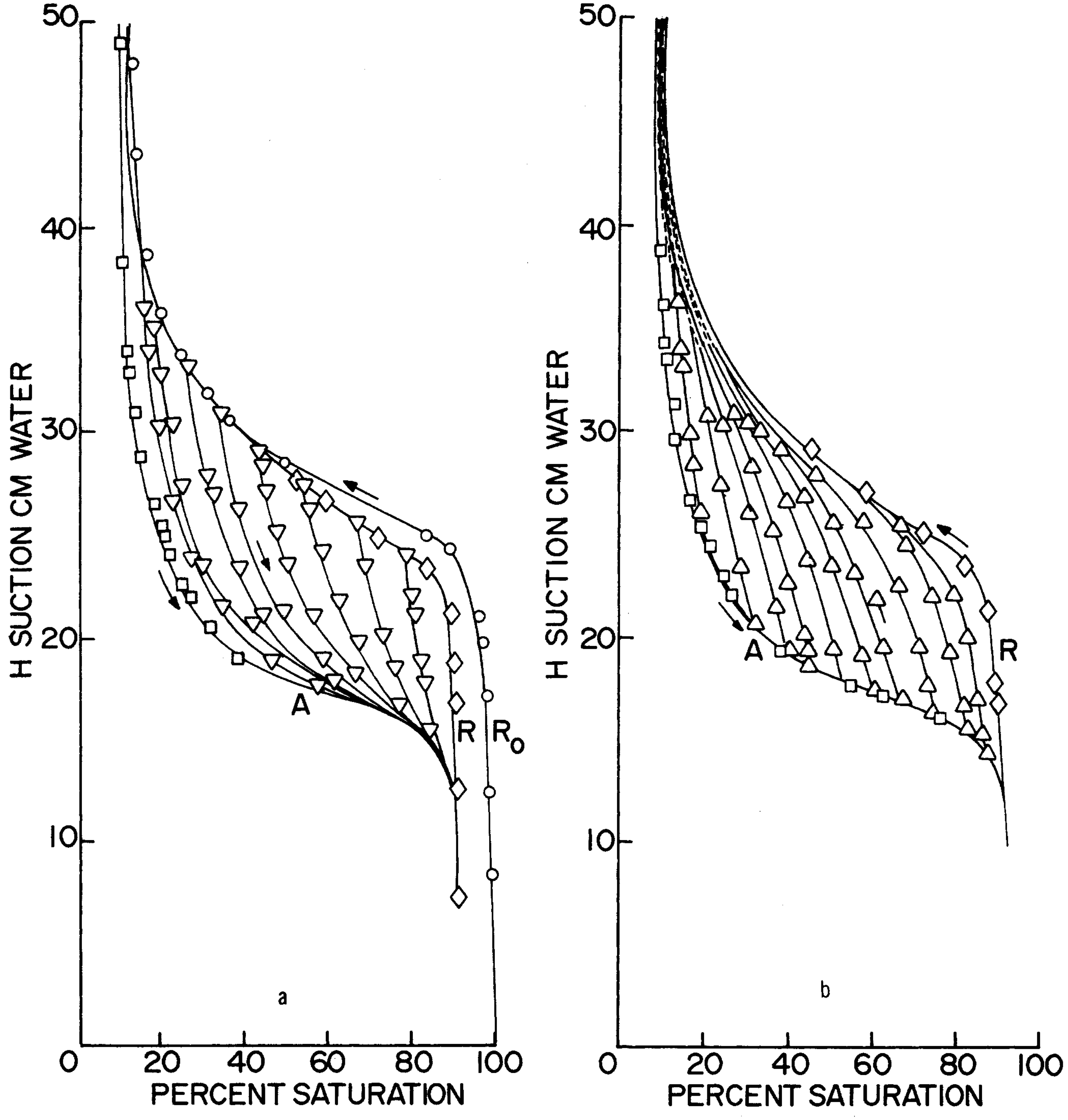

**Figure 7. (a) Imbibition scanning curves originating from the secondary desaturation curve *R*. (b) Desaturation scanning curves originating from the pendular imbibition curve A. (Morrow and Harris, 1965).**

$$(\Delta F)_{T,V,n} = \int_{A_1}^{A_2} \sigma(A)dA \tag{75}$$

Consider two immiscible fluids, oil and water, contained in the interstices of a porous medium. Further, concentrate on an individual idealized pore containing the two immiscible fluids and a hypothetical interface as in Figure 6 (Melrose and Brandner, 1974). At equilibrium, two hydrostatic equations define the state of the interface, Laplace's equation, and Young's equation. Laplace's equation can be written as:

$$p_o - p_w = \sigma_{ow}/R_{ow} \tag{76}$$

$p_o$ is the pressure in the oil, $p_w$ is the pressure in the water, $\sigma_{ow}$ is the interfacial tension between the two fluids, and $R_{ow}$ represents the curvature of the interface. Young's equation is:

$$\sigma_{os} = \sigma_{ws} + \sigma_{ow} \cos\theta_{ows} \tag{77}$$

where the subscript $s$ stands for the solid. $\sigma_{os}$ is the interfacial tension between the oil and the solid, $\sigma_{ws}$ is the interfacial tension between the water and the solid, and $\theta_{ows}$ is the angle of contact measured through the water that the fluid-fluid interface makes with the solid surface.

The contact angle $\theta_{ows}$ in Eq. 77 is used to define the wettability of the solid surface. In Figure 6, the solid surface is water wet if $\theta_{ows} < 40°$; the solid surface is oil wet if $\theta_{ows} > 140°$; and for $40° < \theta_{ows} < 140°$, the solid surface is said to have neutral wettability. The contact angle, $\theta_{ows}$ (and therefore the wettability) may show hysteresis, that is, the angle may be different depending on whether the fluid-fluid interface is moving to the left or to the right. Wettability of a given surface may also depend on surface viscosity, which influences the speed at which a given wetting fluid covers the surface. It is possible for solid surfaces to have mixed wettability, that is, different areas of the solid surface have different wettabilities (different contact angle or speed of wetting).

For porous media of intermediate and low permeabilities, for glass beads and sand, the pores are small enough that we can assume: pressure is constant in each of the fluids; the interfacial tension between the two fluids does not depend on the radius of curvature; and the curvature of the fluid-fluid interface is constant. The expressions for the curvature of the interface, $R_{nw}$, are still complex with these assumptions except for simple geometries. (Here, *n* and *w* represent nonwetting and wetting, respectively.) The expression for curvature $R_{nw}$ will contain both first and second derivatives. Laplace's equation may be written in terms of the two principle radii of curavture $r_1$ and $r_2$ and Eq. 76 defines the capillary pressure $p_c$ at a point as:

$$p_c = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right) \tag{78}$$

In an actual porous medium which contains a complex network of nonuniform pores, many stable interface configurations in the pores are possible. Since there are many stable configurations if one stops imbibition and begins draining in a medium at arbitrary points, a series of scanning loops will be obtained as shown in Figure 7 (Morrow and Harris, 1965). The scanning curves result from intermediate stable configurations in the pores. Notice that if the drainage curve is measured a second time after imbibition, the loop starts where imbibition saturation stopped.

Fluid-fluid interfaces in a pore may be stable or unstable in certain configurations depending on the geometry of the pores, the saturation, and the pressure drop across each pore. The limiting number of stable configurations gives rise to the hysteresis discussed earlier. If the interface takes on an unstable shape (or corresponding position in a pore), there will be sudden local flow in which one fluid will displace the other. This stuttering flow which restores equilibrium was first reported by Haines (1930) and the jumps in flow are often referred to as "Haines jumps."

The drainage and wetting capillary pressure curves in Figure 1 have certain limiting values of capillary pressure and saturation. The drainage capillary pressure curve approaches a minimum saturation of the wetting fluid, $S_r$ that appears to be reached asymptotically as the capillary pressure increases. An explanation for the residual saturation is that at this saturation the wetting fluid exists only as unconnected pendular rings in the pore spaces and the wetting fluid does not flow. Another explanation for the residual saturation is that the wetting fluid remains in very small pores. In oil-water systems, the residual saturation is referred to as connate water; in air-water systems, as the minimum water content. It is generally observed that the broader the pore size distribution, the higher the value of $S_r$. Any change in wettability of a system changes the residual saturation.

Another characteristic of the drainage curve in Figure 1 is that the capillary pressure drops off from a relatively constant value decreasing rapidly to zero very close to $S_w = 1$. When a certain threshold value is reached, pressure decreases rapidly. This threshold or entry pressure value is ambiguous. In oil-water systems the entry or threshold pressure is called the displacement pressure, $p_d$. It is defined as the first $p_c$ at which desaturation of the drainage curve occurs. $p_d$ is determined by extrapolating the drainage curve in a straight line fashion to $S_w = 1$, Figure 1. The saturation at which $p_d$ occurs is called $S_d$. In air-water systems the entry or threshold pressure, $p_e$, is defined at the inflection point of the $p_c$ curve; it is called the bubble pressure, the air pressure required to force air through an initially water-saturated sample.

The wetting curve has a critical saturation, $S_m$. For imbibition, the nonwetting fluid becomes trapped in a pore or cluster of pores and the wetting fluid bypasses this trapped nonwetting fluid. Prediction of $S_m$ has not been accomplished; it would be a most useful number for oil-water systems. Values may be as high as 30 to 40% of the nonwetting fluid. Since the nonwetting fluid for $S_w \geq S_m$ is not interconnected, it does not have a unique capillary pressure. It is generally observed that the broader the pore size distribution, the larger the $S_m$.

Brooks and Corey (1964, 1966) empirically define the effective saturation:

$$S_e = \frac{S_w - S_r}{1 - S_r} \tag{79}$$

(since the pore space containing the wetting fluid at $S_r$ contributes relatively little to the flow). The effective saturation can be related to the dimensionless ratio of displacement pressure over capillary pressure by:

$$S_e = \left(\frac{p_d}{p_c}\right)^{\lambda} \tag{80}$$

Leverett (1941) suggested plotting a reduced capillary pressure function vs. saturation as a means of correlating capillary pressure data for different media. The *J* function defined by Leverett is usually written as:

$$J = \frac{p_c}{\sigma f(\theta)}\left(\frac{k}{\theta}\right)^{1/2} \tag{81}$$

If the wetting fluid saturation of a porous medium decreases, the fluid "particles" of the wetting fluid must take an increasingly longer path to move between two points (since the nonwetting fluid is in the way). Burdine (1953) suggested

$$\tau_w(S_e) = \frac{\tau_1}{S_e^2} \tag{82}$$

where $\tau_w$ is the relative tortuosity of the wetting fluid. $\tau_1$ is the tortuosity of the wetting fluid at $S_e = 1$. For the nonwetting phase

$$\tau_n(S_e) = \frac{\tau_1}{(1 - S_e)^2} \tag{83}$$

Eqs. 82 and 83 are not valid for anisotropic media.

We need effective permeabilities to use the extended form of Darcy's law for such multifluid flow as water and oil. The effective permeabilities can be found if we know the intrinsic permeability of a medium and the relative permeabilities of the wetting (water) and nonwetting (oil) fluids as functions of saturation. Relative permeability may be based on intrinsic permeability, dry air permeability, or at $S_w = 1$ and $S_r$. We will use the latter in the discussion that follows. The relative permeability is a function of saturation and also depends on pore-size distribution, wettability, and saturation history. Figure 8 is a sketch of effective wetting and nonwetting fluid relative permeability

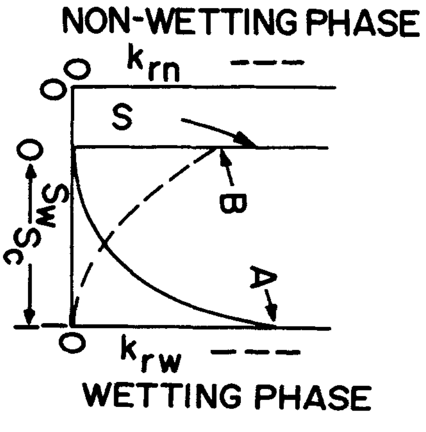

Figure 8. Relative permeability vs. saturation.

curves determined from drainage measurements. The relative permeability of the wetting fluid is usually defined as the ratio of the effective permeability at a given wetting fluid saturation to the effective permeability of the wetting fluid at a wetting fluid saturation $S_w = 1$ (Point A of Figure 8). The relative permeability of the nonwetting fluid is similarly defined as the ratio of the effective permeability of the nonwetting fluid at a given saturation to the effective permeability at residual wetting fluid saturation (Point B of Figure 8). If we plot relative permeability as a function of effective saturation, $S_e$ as defined by Eq. 79 for media with a different pore-size distribution index, $\lambda$, introduced in Eq. 80, we will obtain different relative permeability curves.

Burdine (1953) proposed the following relations for relative permeability based on drainage capillary pressure written in terms of effective saturation defined by Eq. 79:

$$k_{rw} = S_e^2 \frac{\int_o^{S_e} \frac{dS_e}{p_c^2}}{\int_o^1 \frac{dS_e}{p_c^2}} \tag{84}$$

and

$$k_{rn} = (1 - S_e)^2 \frac{\int_{S_e}^1 \frac{dS_e}{p_c^2}}{\int_o^1 \frac{dS_e}{p_c^2}} \tag{85}$$

Purcell (1949) used a capillary model to relate relative permeability and capillary pressure. Corey (1977) writes equations similar to Purcell in terms of the average of the square of the hydraulic radius of the pores as:

$$\langle R_w^2 \rangle = \frac{\sigma^2 \cos^2\theta}{S} \int_o^S \frac{dS}{p_c^2} \tag{86}$$

and

$$\langle R_n^2 \rangle = \frac{\sigma^2 \cos^2\theta}{S} \int_o^S \frac{dS}{p_c^2} \tag{87}$$

The Kozeny-Carman equation for permeability for single fluid flow is:

$$k = \frac{\phi^3}{c\tau^2} \tag{88}$$

where the tortuosity, $\tau$, is about 2 for sand and the shape factor, $c$, is about 2.5. Combining the generalized form of Darcy's law with Eqs. 86 and 87 leads to a generalized Kozeny-Carman expression for effective permeabilities.

Most practical flow situations in oil reservoirs have present three immiscible fluids, water, oil, and gas. In such situations we need three fluid relative permeabilities—usually called three-phase relative permeabilities—to use the modified form of Darcy's law. We can extend the treatment of Burdine (1953) which was used above for two fluids.

Schneider and Owens (1970) measured three-phase water-oil-gas-relative permeabilities in sandstones and carbonates. They summarized general relative permeability characteristics based on their measurements and those of other investigators (Corey et al., 1956; Land, 1968; Narr and Wygal, 1961; Saraf and Fatt, 1967; Sarem, 1966). The relative permeabilities in the two materials, sandstone and carbonate, did not show different behavior. Wettability has the most influence. The effects of heterogeneity, nonuniformity, and anisotropy were not considered. The water relative permeability is a function of its own saturation. Therefore, water relative permeabilities as determined in two-phase systems can be used in three-phase systems that have the same wettability characteristics. Oil phase relative permeabilities are related to their own saturations and saturation histories. The relative permeability of a gas in oil-wet system is not sensitive to residual oil saturation. The relative permeability of gas in a water-wet system is decreased by the presence of residual oil. The relative permeability of oil in an imbibition process does not depend on the flowing gas phase when gas saturation is increasing. The relative permeability of oil in an imbibing process increases when gas saturation decreases. In systems with no strong wetting preference, three-phase relative permeabilities cannot be predicted from two-phase relative permeability. Stone (1970) presents a model to estimate three-phase relative permeabilities for systems with a strong wetting preference, that is, based on two-phase data.

For the movement of water in dry soil, a diffusion-type equation is sometimes used since $p_c$ is a single-valued function of wetting fluid saturations (Richards, 1931). The basic assumptions are (Handy, 1960): both water and air are continuous behind the imbibing front; pressure gradient in the gas is negligible both ahead of and behind the imbibing water front; the capillary pressure gradient over any increment of length provides the driving force for overcoming the viscous forces in that same increment of length. Combining Darcy's law, the equation of continuity, and the capillary pressure equation yields:

$$\phi \frac{\partial S_w}{\partial t} = - \frac{\partial}{\partial x} \left[ \left( \frac{k_w}{\mu_w} \frac{\partial p_c}{\partial S_w} \right) \frac{\partial S_w}{\partial x} \right] \tag{89}$$

We assume the term in parenthesis is a saturation dependent diffusion coefficient type term.

$$\hat{D} = \frac{k_w}{\mu_w} \frac{\partial p_c}{\partial S_w} \tag{90}$$

and

$$\phi \frac{\partial S_w}{\partial t} = - \frac{\partial}{\partial x} \left( \hat{D} \frac{\partial S_w}{\partial x} \right) \tag{91}$$

## MULTIFLUID MISCIBLE FLOW

The equations of change for multifluid miscible flow are the same as with single-fluid flow. However, if the two fluids begin flowing separately, a mixed region separates them. Much of the modeling for miscible flow is concerned with modeling the mixed region and the parameter associated with the mixing—the dispersion coefficient. Dispersion results from the complex nature of the flow paths in the media although diffusion and turbulence also affect mixing.

In principle, the overall equations of motion and continuity for multi-fluid miscible flow are the same as for single-fluid flow. The equation resulting from the combination of Darcy's law and the overall continuity equation is also the same. Appropriate single-fluid viscosities and densities are used if the fluids are commingled. In multifluid miscible flow, we are sometimes interested in the regions between the fluids where the relative concentrations of the fluids are different—in the mixed region. Outside of the mixed region, the single-fluid equations apply directly.

To describe the mixing or dispersion of multifluid miscible flow, one must assume two fluids of equal viscosity and equal density, where one of the fluids is displacing the other fluid from a porous medium. If we assume initially that the flow is in one dimension, Darcy's law for the flow of each fluid and the sum of the flows is:

$$q = - \frac{k}{\mu} \frac{dp}{dx} \tag{92}$$

The equation of continuity for the total flow is:

$$\phi \frac{\partial \rho}{\partial t} + \frac{\partial \rho q}{\partial x} = 0 \tag{93}$$

Combining Eqs. 92 and 93 with an equation of state gives:

$$\phi c_f \frac{\partial p}{\partial t} = \frac{k}{\mu} \frac{\partial^2 p}{\partial x^2} \tag{94}$$

For an incompressible fluid:

$$\frac{\partial^2 p}{\partial x^2} = 0 \tag{95}$$

The problem of miscible flow is very complicated, even in one dimension with fluids of equal properties, since mixing occurs both longitudinally, in the direction of flow, and transversely, perpendicular to the flow. Imagine that we inject a "dot" of traced fluid of concentration $c_0$ at $t = 0$ rather than over the entire face. As the dot moves from one end to the other it will spread in the direction of flow and perpendicular to the flow. At the end the dot will have transformed into an elipse with concentration varying across it.

There are several possibilities for obtaining the partial differential equations which describe the concentration behavior of the mixed zone as a function of time and position. Kramers and Albreda (1953) apply the mixing cell model for studying the frequency response of continuous flow in a packed tube to obtain:

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} \tag{96}$$

where $D$ is the dispersion coefficient and $v_x$ is the averaged interstitial velocity, $q_x/\phi$. Scheidegger (1954) assumes that the motion of a tracer through a porous medium at each point is uncorrelated. He applies the central limit theorem to show that the concentration of marked particles is represented by an error function which is the solution to the differential equation:

$$\frac{\partial c}{\partial t} + v_x \frac{\partial c}{\partial x} = \frac{\partial}{\partial x}\left(D \frac{\partial c}{\partial x}\right) \tag{97}$$

Nikolaevskii (1959) obtained a model for dispersion analogous to diffusion in homogeneous isotropic turbulence. He applies the central limit theorem to marked particles of fluid moving with the mean velocity so that at an arbitrary instant in time there exists a three dimensional probability density of finding particles at some point $(x, y, z)$. The concentration of marked particles is:

$$c(x, y, z, t) = \frac{(2n)^{3/2}}{\sqrt{\sigma_x^2 \sigma_y^2 \sigma_z^2}} \exp\left\{-\frac{1}{2}\left(\frac{x^2}{\sigma_x^2} + \frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right)\right\} \tag{98}$$

Equation 98 is a solution of the diffusion equation of the form:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_x \frac{\partial c}{\partial x}\right) + \frac{\partial}{\partial y}\left(D_y \frac{\partial c}{\partial y}\right) + \frac{\partial}{\partial z}\left(D_z \frac{\partial c}{\partial z}\right) \tag{99}$$

Where the dispersion, $D_x$, is:

$$D_x = \frac{\sigma_x^2}{2t} \tag{100}$$

and similarly for $D_y$ and $D_z$.

Since the coefficient of dispersion is different along each of the axes $\underline{\underline{D}}$ must be a second order tensor. Assuming $\underline{\underline{D}}$ is invariant to rotation about the direction of the mean velocity and mirror reflections relative to planes including the mean velocity vector or perpendicular to this vector, the dispersion coefficient has the following form:

$$D_{ij} = A\tilde{v}_i\tilde{v}_j + B\delta_{ij} \tag{101}$$

where $\tilde{v}_i$, $\tilde{v}_j$ are the components of the perturbation of the average velocities. Then, superimpose the average motion of the fluid, Darcy's law, and Eq. 99 in fixed coordinates:

$$\frac{\partial c}{\partial t} + v_i \frac{\partial c}{\partial x_i} = \frac{\partial}{\partial x_i}\left(D_{ij} \frac{\partial c}{\partial x_j}\right) \tag{102}$$

All of the above approaches are statistical in that they obtain an equation for the mass balance by first postulating a solution and then relating the solution to the partial differential equation. The partial differential equation whose solution will describe the breakthrough curve can be used experimentally to determine $D$. The procedure is to curve fit the appropriate solution of Eq. 102 by adjusting the coefficient $D$.

Rifai, Kaufman, and Todd (1956) followed reasoning similar to that of Scheidegger (1954b) to arrive at the expression for the breakthrough curve from the normal probability density function.

$$c/c_o = \frac{1}{2}\, erfc \left\{\frac{x - v_x t}{2\sqrt{Dt}}\right\} \tag{103}$$

Equation 103 is a solution of Eq. 102 in one dimension. However, if we use the initial and boundary conditions:

$$\begin{aligned} c/c_o\,(x, 0) &= 0, \quad x \geq 0 \\ c/c_o\,(0, t) &= 1, \quad t \geq 0 \\ c/c_o\,(\infty, t) &= 0, \quad t \geq 0 \end{aligned} \tag{104}$$

the solution of Eq. 102 in one dimension with these conditions is:

$$c/c_o = \frac{1}{2}\left[erfc \frac{x - v_x t}{2\sqrt{Dt}} + e^{v_x x/D}\, erfc \frac{x + v_x t}{2\sqrt{Dt}}\right] \tag{105}$$

Ogata and Banks (1961) analyzed experimental results in linear systems using both Eqs. 105 and 103. Considering experimental errors, they determined if $D/v_x x < 0.002$ the maximum error in approximating Eq. 105 with Eq. 103 is 3% or less. Equation 103 is used to determine dispersion coefficients from measured breakthrough data. For an ideal medium, $D$ may be determined from the slope of the breakthrough curve $V/V_0 = 1$ since

$$D = \frac{1}{4\pi} \frac{L v_x}{\left(\dfrac{\partial c/c_o}{\partial V/V_0}\right)^2_{VV_0=1}} \tag{106}$$

where $V/V_0$ is the ratio of effluent volume to the pore volume of the media. For nonideal media, Eq. 105 is fit to the breakthrough data.

Based on statistical arguments and the volume averaging technique, it is reasonable to accept Eq. 102 as a model for the mixed zone as a function of time and position. As mentioned earlier, this is a mixing zone model as is the relative permeability model. In the dispersion model, mixing results from fluctuations of the individual fluid velocities superimposed on the average velocity of the composite. In the relative permeability model, each fluid has its own velocity; and mixing is built into the relative-permeability-saturation relationship.

One may imagine a variety of mechanisms that cause macroscopic mixing. However, the following nine mechanisms account for most of the mixing:

*Molecular Diffusion.* If time scales are sufficiently long, dispersion results from molecular diffusion.

*Mixing Due to Obstructions.* The fact that the flow channels in a porous medium are tortuous means that fluid elements starting a given distance from each other and proceeding at the same velocity will not remain the same distance apart.

*Presence of Autocorrelation in Flow Paths.* Dispersion can result from the fact that all pores in the porous medium are not accessible to a fluid element after it has entered a particular flow path. In other words, the connectivity of the medium is not complete.

*Recirculation Caused by Local Regions of Reduced Pressure.* Dispersion can be caused by a recirculation arising from flow restrictions. The conversion of pressure energy into kinetic energy gives a local region of low pressure; and, if this region is accessible to fluid which has passed through the region previously, a recirculation is set up similar to a venturi-manometer combination which contains no manometer fluid.

*Macroscopic Dispersion.* Caused by nonidealities which change the directions of gross streamlines.

*Hydrodynamic Dispersion.* Macroscopic dispersion is produced in a capillary even in the absence of molecular diffusion because of the velocity profile produced by the adherence of the fluid to the wall. This causes fluid particles at different radial positions to move at different velocities relative to one another so that a series of mixing-cup samples at the end of the capillary exhibit dispersion.

*Eddies.* If the flow within the individual flow channels of the porous medium becomes turbulent, mixing results from eddy migration.

*Dead-End Pores.* Dead-end pore volumes cause mixing in unsteady flow (concentration profiles varying) because, as a solute-rich front passes the pore, diffusion into the pore occurs by molecular diffusion. After the front passes, this solute will diffuse back, and disperse, for example, a step concentration input to the system. This pore volume also causes confusion in experimental interpretation because it is measured as porosity, even though this porosity does not contribute to the available flow cross section.

*Adsorption.* Adsorption is an unsteady-state phenomenon. Just as with dead-end pores, a concentration front will deposit or remove material; therefore, will tend to flatten concentration profiles in the interstitial fluid.

Generally we include the first seven mechanisms in the dispersion coefficient. Dead-end pores usually are assumed to cause early breakthrough and increase the length of the tail of the breakthrough curve. The early breakthrough results because the effective flow porosity is less than that used to calculate the velocity, therefore, the concentration front moves faster than predicted when the porosity is not corrected for dead-end pores. The tail-off results because even though dead-end pores do not contribute to flow, there will be diffusion of the displacing fluid into and out of pores, thus dragging out the breakthrough curve. Coats and Smith (1964) considered the possible effect of dead-end pores using the three-parameter capacitance model of Deans (1963) to account for the mass transfer into and out of the dead-end pores. Their results showed that the solutions of Eq. 102 for three different sets of boundary conditions gave the same dispersion coefficient as the capacitance model. In some cases the three-parameter capacitance model gave a better fit to the asymmetrical tail. All four solutions seemed to fit the breakthrough data about equally well. The effects of adsorption are usually modeled by adding a rate dependent term to Eq. 102.

Pfannkuch (1963) plotted the existing data for longitudinal dispersion as in Figure 9, plotting $D_L/v$ vs. $f(vd/\mathfrak{D})$, where $d$ is a characteristic dimension perpendicular to flow usually referred to as the effective particle diameter; $\mathfrak{D}$ is the diffusion coefficient of the tracer; and the dimensionless group $vd/\mathfrak{D}$ is the Peclet number (*Pe*). If the dispersion coefficient replaces the diffusion coefficient in the dimensionless group so that it is $vd/D$, the group is called the Bodenstein number (*Bo*).

Perkins and Johnston (1963) use the mixing-cell approximation of Aris and Amundson (1957) to model this region. The model assumes the medium is a series of pore spaces connected by small openings with complete mixing in each chamber.

Much of the discussion concerning dispersion originated in reference to capillary network models for uniform isotropic porous media (deJosselin de Jong, 1958; Saffman, 1959; Scheidegger, 1959) and for nonuniform and anisotropic porous media (Greenkorn and Kessler, 1969; Haring and Greenkorn, 1970; Guin et al., 1972).

The equation for dispersion from the statistical model does not include diffusion. According to Biggar and Nielsen (1962) mixing due to coupling of molecular diffusion and dispersion is important in field systems.

Pakula and Greenkorn (1971) measured the parameters of the pore-size distribution of unconsolidated glass beads and other structure-related properties to determine a physical model of the beads. They measured values of $D_L$ and $D_T$ by imbedding electrodes in the model and actually measuring the variance of longitudinal and transverse dispersion during flow.

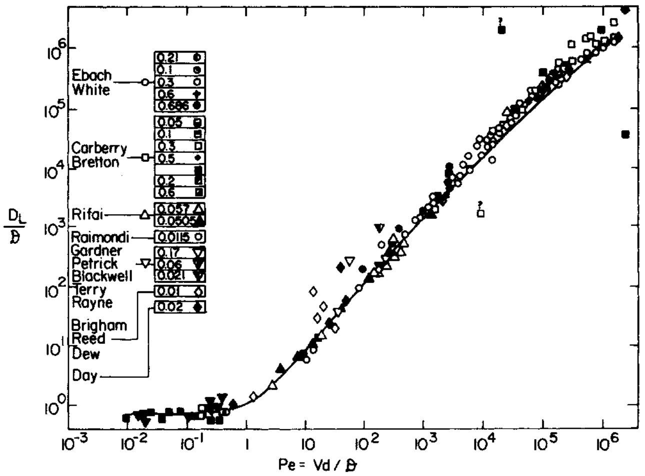

**Figure 9. Relationship between molecular diffusion and convective dispersion (Pfannkuch, 1962).**

The effects of nonuniformity on longitudinal dispersion have been investigated experimentally by Raimondi et al. (1959), Brigham et al. (1961), and Nieman (1969). Raimondi et al. (1959) constructed packed porous media where the permeability of the media is constant—the mean pore size is the same—but the pore-size distributions are different. Their results are represented by:

$$D_T = 0.5\sigma v\delta \tag{107}$$

$\sigma$ is a measure of the nonuniformity. Perkins and Johnston (1963) used the data of Raimondi et al. (1959) and Brigham et al. (1961) to plot $\sigma$ vs. particle diameter for random packs of spheres. They use $\sigma$ to modify their empirical correlation of dispersion coefficients for nonuniform media so that

$$D_L = \frac{1}{F\phi} + 0.5\sigma Pe, \quad Pe < 50 \tag{108}$$

$$D_T = \frac{1}{F\phi} + 0.055\sigma Pe, \quad Pe < 100 \tag{109}$$

where $F$ is the electrical resistivity factor of the formation.

There seems to be general agreement among investigators that the appropriate equation for mixing is:

$$\frac{\partial c}{\partial t} + v_i \frac{\partial c}{\partial x_i} = \frac{\partial}{\partial x_i}\left(D_{ij}\frac{\partial c}{\partial x_j}\right) \tag{110}$$

The coefficient of dispersion is a symmetric second-order tensor of the form:

$$D_{ij} = a_{ijkl}\frac{v_k v_l}{|v|} \tag{111}$$

The coefficient of dispersivity is a fourth order tensor and represents the structure of the media. Two of the elements of the dispersivity, $a_{ijkl}$, represent the nonuniformity and the remaining ones represent the orientation of the pore structure. If the velocities are the correct ones relative to the most probable path, then dispersivity should not be a function of velocity. Guin et al. (1973) show that for the equation of change represented by Eq. 110 the $a_{ijkl}$ depend on velocity. Greenkorn and Kessler (1970) summarize the effect of nonuniformity by tabulating the ratio of the longitudinal to transverse dispersion as represented by various models.

If one accepts the form of Eq. 110, the effect of heterogeneity can be incorporated by defining $D_{ij}$ as a function of position. Any useful predicted results will be made using numerical techniques for solving Eq. 110.

The effect of nonuniformity is incorporated in the form of the dispersion tensor and is summarized in terms of the ratio of the longitudinal to transverse dispersion coefficients for one-dimensional flow. These models and the data can be made to agree, except in the case of Whitaker (1967) whose results seem to show that for the assumptions made to get to a comparable result the medium is uniform. (Otherwise, the form of the ratio is a complex function of several tensors.) The results of Poreh (1965) include three elements of the dispersivity tensor and a dependence on velocity such that in the limit the dispersion matches hydrodynamic dispersion in a single capillary. (See Taylor, 1953; Aris, 1956.)

Including anisotropy of the media in the description of dispersion is complex since the mixing due to orientation of the pores is stored in the fourth order dispersivity tensor. Scheidegger (1961) introduces several symmetry relations to show that the dispersivity tensor may be reduced to 36 independent elements to describe the effects of nonuniformity and anisotropy. In this discussion he shows two elements remain for isotropic media. Shamir and Harleman (1967) modeled, both physically and mathematically, layered porous media where one model had layers of sand of different permeability perpendicular to flow and the other had two layers parallel to flow. In their investigation, they determined the dispersion in each system experimentally; they fit solutions for one dimension of Eq. 110 and calculated an overall dispersion coefficient from the breakthrough curve. Assuming the flow pattern within the changing layers is irrelevant to the problem they used convolution integrals to solve Eq. 110 for each layer and calculated the dispersion in each layer as the fluid flowed.

Moranville et al. (1977a,b) used the model of Guin et al. (1972) to obtain forms of the dispersion tensor for transversely isotropic porous media. Moranville et al. (1977a,b) used several different cases including the measurements of Goad (1970) for cylinders approximating various angles of layered systems. In his systems, Goad (1970) found dispersion is greater for flow perpendicular to the axis of symmetry than parallel to it.

It was implied in portions of the earlier discussion that the effect of heterogeneity on dispersion must be handled by making the dispersion coefficient position dependent. At one level the experiments discussed above could be considered as oriented heterogeneities and handled in this way.

Currently there exist several dilemmas concerning dispersion and the interpretation of laboratory measurements for use on a field scale. Field dispersivity may be orders of magnitude larger than for the same material in the laboratory. Biggar and Nielsen (1962) have emphasized the importance of considering molecular diffusion on a field scale. The possible dependence of the dispersivity on velocity seems to be indicated by theoretical studies. This means that the velocity with which we imagine the coordinate system to be translated when we interpret laboratory measurements may be incorrect.

It is not clear if we scale the ratio of average microscopic pore diameter to permeability that this assures scaling of microscopic and macroscopic lengths. The question of velocity dependence, whether due to connectivity or the limiting cases of plug and parabolic flow, is not clearly answered. Finally, can we really use the same constitutive relationships to treat anisotropy at the macroscopic and microscopic levels?

## SUMMARY

This paper presents an overview of the development and current state of the field of steady flow-through porous media. The macroscopic description of flow phenomena has primarily been presented because it has the most practical value.

The description of the porous media has provided the basis for analyzing the resultant flow phenomena. Three broad categories partition the models of fluid flow. Single-fluid flow is the most general fluid flow model. Multifluid immiscible flow models are similar to those for single fluid flow except that additional parameters such as wettability and capillary pressure are introduced. The most complex flow phenomena is multifluid miscible flow because there is a region of mixing where fluid properties deviate from their respective component values.

The multitude of fluid flow studies presented have been employed in resolving some of the current problems in this field. Due to the variety of conditions and intertwining flow phenomena, increased research in this area is guaranteed.

## NOTATION

$A$ = area $[L^2]$
$a$ = connectivity, accessibility [1]
$b$ = parameter in slip flow expression for $K$ $\left[\frac{t^2L}{M}\right]$
$C$ = shape factor [1]
$c$ = concentration $[L^{-3}]$
$D$ = diameter $[L^2]$
$D$ = dispersion $\left[\frac{L^2}{t}\right]$
$D_L$ = longitudinal dispersion $\left[\frac{L^2}{t}\right]$
$D_p$ = particle diameter $[L]$
$D_T$ = transverse dispersion $\left[\frac{L^2}{t}\right]$
$\hat{D}$ = soil water "diffusion" $\left[\frac{L^2}{t}\right]$
$\mathfrak{D}$ = binary diffusion coefficient $\left[\frac{L^2}{t}\right]$
$d$ = characteristic microscopic length $[L]$
$d$ = differential operator [1]
$F$ = Helmoltz free energy $\left[\frac{L^2M}{t^2}\right]$
$\underline{F}$ = body forces $\left[\frac{LM}{t^2}\right]$
$g$ = acceleration due to gravity $\left[\frac{L^1}{t^2}\right]$
$h$ = energy per unit weight of fluid $[L]$ (hydraulic head for water)
$\underline{\underline{I}}$ = unit matrix [1]
$J$ = Leverett $J$ factor, reduced capillary pressure [1]
$K$ = hydraulic conductivity $\left[\frac{L}{t}\right]$
$\tilde{K}$ = slip conductivity $\left[\frac{L}{t}\right]$
$k$ = effective permeability to water as a function of water content $[L^2]$
$k_{ri}$ = relative permeability [1]
$k_{rw}$ = relative permeability of water [1]
$L$ = characteristic macroscopic length $[L]$
$l$ = pore length $[L]$
$n$ = coordination number, ratio of void to total volume [1]
$\underline{n}$ = outward directed normal
$Pe$ = Peclet number $\frac{d_pV}{K}$ [1]
$\mathfrak{p}$ = $p - p_o + \rho\phi$ $\left[\frac{M}{t^2L}\right]$
$p$ = pressure $\left[\frac{M}{t^2L}\right]$
$p_c$ = capillary pressure $\left[\frac{M}{t^2L}\right]$
$Pd$ = displacement pressure $\left[\frac{M}{t^2L}\right]$
$P_e$ = threshold pressure $\left[\frac{M}{t^2L}\right]$
$p_m$ = arithmetic average pressure $\frac{p_1 + p_2}{2}$ $\left[\frac{M}{t^2L}\right]$
$Q$ = volumetric flow rate $\left[\frac{L^3}{t}\right]$

$Q_m$ = volumetric flow rate at average pressure $p_m$ $\left[\frac{L^3}{t}\right]$
$\underline{q}$ = seepage velocity $\left[\frac{L}{t}\right]$
$Re$ = Reynolds number [1]
$Re_p$ = Reynolds number based on particle diameter [1]
$R_H$ = hydraulic radius $[L]$
$r$ = radius $[L]$
$r_1$, $r_2$ = radii of curvature in Laplace Eq. $[L]$
$S$ = saturation [1]
$S$ = specific surface [1]
$S_A$ = surface area of pores $[L^2]$
$S_e$ = effective saturation [1]
$S_o$ = oil saturation [1]
$S_w$ = water saturation [1]
$t$ = time $[t]$
$u$ = displacement $[L]$
$V$ = volume $[L^3]$
$V_o$ = total pore volume of medium $[L^3]$
$V_f$ = fluid volume $[L^3]$
$v$ = velocity $\left[\frac{L}{t}\right]$
$\langle v \rangle$ = area averaged velocity $\left[\frac{L}{t}\right]$
$v_\infty$ = velocity of approach $\left[\frac{L}{t}\right]$
$x$ = coordinate $[L]$
$y$ = coordinate $[L]$
$z$ = coordinate (direction of gravity) $[L]$
$\alpha(\delta)$ = void distribution factor [1]
$\Delta$ = difference
$d$ = pore diameter $[L]$; Dirac delta, Eq. 24
$\underline{\nabla}$ = vector partial differential operator $\left[\frac{1}{L}\right]$
$\underline{i}\frac{\partial}{\partial x} + \underline{j}\frac{\partial}{\partial y} + \underline{k}\frac{\partial}{\partial z}$
$\nabla^2 = \frac{\partial}{\partial x^2}\frac{\partial}{\partial y^2}\frac{\partial}{\partial z^2}\left[\frac{1}{L^2}\right]$
$\gamma_{12}$ = specific free energy of interface between fluids 1 and 2 $\left[\frac{L^2M}{t^2}\right]$
$\gamma_{s1}$ = specific free energy of interface between the solid and fluid 1 $\left[\frac{L^2M}{t^2}\right]$
$\lambda$ = pore-size distribution index [1]
$\mu$ = viscosity
$\nu$ = kinematic viscosity $\left[\frac{L^2}{t}\right]$
$\Phi$ = potential
$\phi$ = porosity [1]
$\theta$ = contact angle of liquid solid interface
$\rho$ = density $\left[\frac{M}{L^3}\right]$
$\sigma$ = interfacial tension $\sigma \equiv \gamma_{12}$, $\left[\frac{M}{t^2}\right]$
$\tau$ = fluid stress $\left[\frac{M}{Lt^2}\right]$
$\tau$ = tortuosity [1]

### Overscores

$\hat{}$ = identifying mark
$\langle\ \rangle$ = space average
— = time average

### Subscripts

$i$ = coordinates
$n$ = nonwetting
$o$ = oil
$w$ = water
$w$ = wetting

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# Properties of Bismuth Oxide Catalysts for Oxidative Dehydrogenation Dimerization of Propylene

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The electronic properties of bismuth oxide shed light on the mechanism of its catalytic activity for the oxidative dehydrogenation dimerization of propylene. Variations in the electrical conductivity and thermoelectric power, as the gas phase contacting a pellet of this *p*-type semiconductor was changed, provided information about the nature of species adsorbed at reaction temperature.

## SCOPE

The complete investigation of any heterogeneous catalytic system includes characterization of the bulk solid, determination of the nature of the surface active sites, and identification of the type(s) of adsorbed species that are formed on the surface. When the solid has sensitive electrical properties, it may be possible to use changes that occur in these properties to gain insight into some of these characteristics. Bismuth oxide is such a material (it is a *p*-type semiconductor), and it is a catalyst for several reactions among them being the dimerization of propylene to form 1,5-hexadiene (and ultimately benzene through cyclization) in the presence of oxygen at high temperature (OXDD).

The purpose of these experiments was to study the interaction of the reactants oxygen and propylene with $Bi_2O_3$. To a pellet of the material were attached electrical leads and thermocouples which allowed one to measure simultaneously the temperature, electrical conductivity, and thermoelectric power as the partial pressures of the adsorbates were changed. The observations were analyzed according to an electrical conductivity model which assumes that the individual catalyst particles in the compressed solid pellet are each composed of an interior core and an external shell.

Whereas earlier studies of the electronic properties were conducted in closed systems, a flow reactor was used in this investigation so as to reproduce the reaction conditions at which the kinetic data were collected. It is desirable to make the maximum number of observations of the catalytic system at reaction conditions in order to deduce with less ambiguity some of the details of the reaction mechanism; these experiments were designed to extend the amount of information available for the bismuth oxide catalyst.

## CONCLUSIONS AND SIGNIFICANCE

The electronic properties studied in this work, the conductivity and thermoelectric power (Seebeck Effect), indicate that both of the reactants for the OXDD reaction, propylene and oxygen, were adsorbed on the surface of the oxide. Based on the data of this work and data from similar catalytic systems, a model is advanced to explain the adsorption-desorption phenomena. From this model it was concluded that the oxygen is adsorbed as a negative species (perhaps $O^{-2}$) and that there is more than one type of charge carrier (positive cation vacancy "holes" due to rapid electron exchange between $Bi^{+3}$ and $Bi^{+5}$, plus some other type) responsible for the pellet conductivity. The oxygen adsorption sites are probably these bismuth cation centers. The electrical effects observed with oxygen are reversible as the partial pressure is cyclically changed.

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