Thermodynamic Basis of Capillary Pressure in Porous Media

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Important features of multiphase flow in porous media that distinguish it from single-phase flow are the presence of interfaces between the fluid phases and of common lines where three phases come in contact. Despite this fact, mathematical descriptions of these flows have been lacking in rigor, consisting primarily of heuristic extensions of Darcy's law that include a hysteretic relation between capillary pressure and saturation and a relative permeability coefficient. As a result, the standard capillary pressure concept appears to have physically unrealistic properties. The present paper employs microscopic mass and momentum balance equations for phases and interfaces to develop an understanding of capillary pressure at the macroscale. Next, the standard theories and approaches that define capillary pressure at the macroscopic scale are described and their shortcomings are discussed. Finally, an approach is presented whereby capillary pressure is shown to be an intrinsic property of the system under study. In particular, the presence of interfaces and their distribution within a multiphase system are shown to be essential to describing the state of the system. A thermodynamic approach to the definition of capillary pressure provides a theoretically sound alternative to the definition of capillary pressure as a simple hysteretic function of saturation.

INTRODUCTION

Capillary pressure and capillary action play a central role in the description of multiphase (and unsaturated) flow in porous media. Although processes determining the distribution of fluids are extremely complicated, the main theoretical and practical tool currently in use for characterizing the nature of this distribution is an empirical relationship between capillary pressure and saturation \( p^c = p^c(s^*) \). The unfulfilled premise of the traditional capillary theory is that this simple model provides a suitable basis for accounting for all effects and processes that influence the fluid distribution such as immiscibility, surface tension, presence of microscopic scale fluid-fluid interfaces, fluid viscosity, wettability of solid surfaces, grain size distribution, macroscale and microscale heterogeneities, solid matrix deformation, fluid composition, etc. All of these effects are essentially lumped into the \( p^c(s^*) \) relationship. Although a myriad of theoretical and experimental works exist that attempt to delineate the influence of the individual factors on the capillary pressure versus saturation relationship, a rigorous and consistent thermodynamic theory of capillarity that provides a phenomenological correspondence among the relevant processes is still lacking. The need for a rigorous theory of capillarity has been enunciated by Scheidegger [1974, p. 61]: "A consistent theory of capillary pressure in porous solids should provide an explanation of the fundamental relationship between saturation and capillary pressure (or interfacial curvature). To date, this does not seem to have been obtained." Two decades later, such a fundamental relationship is still not available and the information on a thermodynamic basis of capillary pressure seems to be somewhat fragmentary. Some studies are based on the microscopic relationships for capillary pressure in tubes or pores of very simple geometry. The resulting equations are thus only an extrapolation of those microscopic relationships to the macroscale. Furthermore, experimental studies often examine only equilibrium conditions and the results of these studies are merely assumed to apply under dynamic conditions also.

In recent years, some progress has been made in laying the foundation for a coherent and systematic theory of multiphase flow in porous media. Two parallel and somewhat related approaches have been followed. Marle [1972], Kalaydjian [1987], and Pavone [1989] employ nonequilibrium thermodynamics, and Hassanizadeh and Gray [1990] and Gray and Hassanizadeh [1991b] use the Coleman and Noll method in developing their theories. Two very important characteristics of these approaches, absent in other theories, are (1) all parts of a multiphase system including bulk phases, interfaces, and contact lines are modeled, and (2) constitutive relationships describing the behavior of the system are developed at the macroscopic scale. In the nonequilibrium thermodynamic approach, however, fluid pressure is introduced at the microscale and a number of thermodynamic relationships known for a single phase fluid continuum are assumed a priori to hold for a multiphase medium at the macroscopic scale. As a result, the thermodynamic equation for capillary pressure obtained by Kalaydjian [1987] and Pavone [1989] is somewhat lacking in generality.

In the present paper, first a description of the capillary action in a capillary tube at the microscale is provided based on momentum balances for interfaces and a contact line. These equations provide the theoretical bases for the Laplace equation for an interface and Young's equation for a contact line, respectively. Hysteresis in microscopic capillary pressure is discussed and explained based on the interaction forces between the contact line and solid-fluid interfaces. Next the present theories and approaches that define capillary pressure at the macroscale are described and
their shortcomings are discussed. Finally, an alternative definition of macroscale capillary pressure is given based on the theories developed by Hassanizadeh and Gray [1990] and Gray and Hassanizadeh [1991b]. Capillary pressure is shown to be an intrinsic property of the system under study expressed in terms of the change in free energy of the phases and interfaces due to a change in saturation. It is shown that capillary pressure is equal to the difference between nonwetting and wetting phase pressures only at equilibrium, and a first-order nonequilibrium expression is provided. Hysteresis in capillary pressure is argued to be due to lumping of too many effects in the $p^\sigma - (\gamma^\alpha - \gamma^\omega)$ relationship. In particular, the presence of interfaces and their distribution in the porous medium is considered to be important to describing the state of the system. An expanded dependence of capillary pressure on saturation as well as the specific interfacial area of fluid-fluid interfaces is suggested as an appropriate functional relationship that will exhibit reduced hysteresis.

**Microscale Momentum Balance Equation for a Surface**

A full discussion of capillary dynamics at the microscale is best carried out in the context of the momentum balance equations for the interface between two phases and for the curve where three phases meet. In a capillary filled with two immiscible fluids, interfaces may form between the two fluids and between each of the fluids and the solid. These three interface types are depicted in Figure 1. Additionally, the curve where the three interfaces intersect, the common line or contact line, is also indicated in Figure 1.

The movement of the fluid-fluid interface is governed by the balance of the forces exerted by the two fluids on the interface and the forces present within the interface. In Appendix A, the momentum balance equation for a fluid-fluid interface is developed. The interface is considered to behave as a viscous Newtonian fluid to obtain a microscopic constitutive theory. For the case where the viscous interaction of the fluid phases with the interface are negligible and the inertial contributions to the interfacial flow are neglected, the tangential and normal components of the momentum balance are

\[ \nabla^\sigma \gamma^{wn} = -(\nabla^\sigma \cdot \gamma^{wn}) \cdot I^\sigma \]

\[ -\gamma^{wn}(\nabla^\sigma \cdot N) + (p^n - p^w) = -(\nabla^\sigma \cdot \gamma^{wn}) \cdot N \]

respectively, where

- $\gamma^{wn}$ interfacial tension of the interface between the $w$ and $n$ phases;
- $N$ unit vector as in Figure 1;
- $p^n$ pressure in the $\alpha$ phase;
- $\gamma^{wn}$ denotes the interfacial viscous forces present when the interface is in motion;
- $I$ identity tensor;
- $I^\sigma$ surficial identity tensor, $I - NN$.

The term $\nabla^\sigma \cdot N$ may be expressed in terms of the mean curvature of the surface $R$ by the relation [e.g., Aris, 1962]

\[ \nabla^\sigma \cdot N = 2/R \]

such that (2) becomes

\[ -\frac{2\gamma^{wn}}{R} + (p^n - p^w) = -(\nabla^\sigma \cdot \gamma^{wn}) \cdot N \]

Additionally in Appendix A, a constitutive equation is given for the surface stress tensor of a fluid-solid interface modeled as an elastic surface. Although such an interface is not of primary interest in the current work, the effects of the fluid-solid interfaces on the contact line dynamics are important and must be accounted for. Indeed, the tendency of the contact line to move in a particular direction is opposed or assisted by the forces within the solid-fluid interfaces.

The contact line is actually a transition zone where molecular forces from the two fluid phases and the solid interact. In a continuum approach at the microscale, this zone is treated as a one-dimensional continuum. The dynamics of the contact line are treated as being governed by forces originating from interactions among solid-fluid and fluid-fluid interfaces. Note that when the contact line is fixed to the solid surface, elastic forces are present within the solid-fluid interface contributing to the balance of momentum of this curve. These stresses are caused by infinitesimal deformation of the solid surface in response to the pull of the meniscus on the contact line. The deformations are visible for very thin or deformable materials such as a mica sheet [Tabor, 1969] or a solidified paraffin crust [Chappuis, 1977].

In Appendix B, the momentum balance for the contact line is developed and presented as (B6) when the inertial effects are negligible. The components of this balance equation tangent and orthogonal to the contact curve are obtained by taking its inner product with the unit vector $\Lambda$ and the tensor $I - \Lambda \Lambda$, respectively:

\[ \Lambda \cdot \nabla^\sigma \gamma^{wn} = \Lambda \cdot F \]

\[ \gamma^{wn} \Lambda \cdot \nabla^\sigma \Lambda - \nu^{wn} \gamma^{wn} - \nu^{ws} \gamma^{ws} - \nu^{ns} \gamma^{ns} = (I - \Lambda \Lambda) \cdot F \]

where

- $\gamma^{wn}$ contact curve compression;
- $\Lambda$ unit vector tangent to the contact curve;
- $F$ resultant of the elastic surface forces acting on the contact line;
- $\gamma^{\alpha\beta}$ interfacial tension of the interface between the $\alpha$
Fig. 2. Forces acting on the wns contact line when a capillary tube intersects a wn interface.

and β phases;

\( \nu_{αβ} \) unit vector normal to the contact curve and tangent to the αβ interface.

Equation (B5) relates \( \mathcal{F} \) to the infinitesimal deformation of the solid-fluid interface. Experimental evidence for the existence of \( \mathcal{F} \) may be found in the work by Chappuis [1977, 1982]. This quantity may also be considered to be a formal representation of the adhesion forces between a fluid and solid that is widely discussed in the literature and is said to be at least partially responsible for contact angle hysteresis (see, for example, Slattery and Flumerfelt [1982] and Chappuis [1982]). Furthermore, Bartell and Merrill [1932] discuss the friction between fluid and solid and the energy that is expended as a liquid moves over a solid surface. As such, \( \mathcal{F} \) may be viewed as the frictional force exerted by the solid-fluid interfaces on the moving contact line. Equations (5) and (6) will be used here in investigating the equilibrium of the contact line and hysteresis in the contact angle.

**Capillary Pressure at the Microscale**

In the first part of this discussion, the phenomenon of capillarity at the microscale is briefly analyzed in the context of a simple hypothetical experiment and using momentum balance equations (1) and (4) for an interface and (5) and (6) for the contact line. Although the experiment discussed will involve transition of an interface from one state to another, the dynamics of the transition will not be considered here. Only equilibrium states attained at the end of various transitions will be discussed.

Consider a large diameter vessel containing two immiscible fluids, \( \omega \) and \( \eta \), separated by an interface. Assume that the \( \omega \) phase is denser than the \( \eta \) phase and fills the bottom portion of the container. The normal vector to the interface \( \mathbf{N} \) is taken to be positive pointing into the \( \omega \) phase. Since the container is large, at some distance from its wall, the interface between the two phases may be considered to be essentially horizontal. Therefore \( \nabla \cdot \mathbf{N} = 0 \) at this location. If the system is at rest, \( \mathbf{U} = 0 \) such that the viscous forces given by \( \tau^{\eta\omega} \) will be zero, and (2) reduces to

\[
\rho^{\omega} - \rho^{\eta} = 0 \quad (7a)
\]

indicating that the fluid pressures are equal. The momentum balance in the surface, obtained from (1), is

\[
\nabla \cdot \mathbf{\gamma}^{\omega\eta} = 0 \quad (7b)
\]

Because the solid surface is preferentially wetted by the \( \omega \) phase,

\[
\mathbf{\gamma}^{\omega\eta} < \mathbf{\gamma}^{\eta\omega} \quad (7c)
\]

This equilibrium situation may now be disturbed by slowly lowering a capillary tube that is preferentially wetted by the \( \omega \) phase into the center of the container from above. The solid material of the capillary tube will be indicated as the \( s \) phase. The instant the tube penetrates the \( \omega \eta \) interface and enters the \( \omega \) phase, an \( \omega s \) interface and an \( \omega s \eta \) curve, or common line, are formed. At this instant, as depicted in Figure 2, the part of the interface at the center of the tube will not sense any disturbance. Information must propagate from the tube wall to the tube center. Thus the interface at the tube center will momentarily remain at equilibrium and balance equations (7a) and (7b) will apply there. However, at the common line, the equilibrium state will not exist. Forces acting on this common line will be active and tend to disturb the interface from its flat configuration. The common line will tend to move upward and will cause the \( \omega s \eta \) interface to become concave when viewed from above. As a result, the interface equilibrium is disturbed and (7a) will not apply. The curvature of the interface requires that a pressure difference across the interface be established for equilibrium. Thus the interface, as well as the common line, will move upward and will reach a new equilibrium position when the forces acting on the common line and the interface attain equilibrium separately, as is depicted in Figure 3.

In Figure 2, \( \gamma^{\eta\alpha} \) is the interfacial tension between the nonwetting fluid and the solid, and \( \gamma^{\omega\alpha} \) is the interfacial tension between the wetting fluid and the solid. Because the solid phase is preferentially wetted by the \( \omega \) phase, \( \gamma^{\omega\alpha} > \gamma^{\eta\alpha} \) and the common line tends to move upward. If static resistance to this movement is overcome, the common line will move until it reaches a new equilibrium state (see Figure 3). At this new equilibrium state, (5) and (6) apply. The three components of the contact line momentum balance at equilibrium in the directions \( \mathbf{A} \), \( \mathbf{e}_r \), and \( \mathbf{e}_\theta \) obtained from these equations for a vertical cylindrical capillary tube are

\[
\mathbf{A} \cdot \nabla \cdot \mathbf{\gamma}^{\omega s} = \mathbf{F} \cdot \mathbf{A} \quad (8a)
\]

\[
-\frac{\gamma^{\omega s}}{r} + \gamma^{\omega s} \sin \theta = \mathbf{F} \cdot \mathbf{e}_\rho = f_\rho \quad (8b)
\]
and

\[ \gamma_w \cos \theta_e + \gamma_{ws} - \gamma_{ns} = F \cdot e_z = -C^f e_z \quad (8c) \]

respectively, where

- \( e_r \) unit vector positive normal to the wall out of the fluid phases;
- \( e_z \) unit vector positive upward;
- \( r \) radius of the capillary tube;
- \( f_e \) solid bonding force on the contact line at equilibrium;
- \( \theta_e \) equilibrium contact angle;
- \( C^f \) resistance coefficient that ranges from positive to negative values.

The expression on the left side of (8c) is sometimes referred to as "spreading pressure" [Schiegg, 1986].

For this case of a vertical capillary tube in which the equilibrium common line is a circle, \( \gamma_{ws} \) will be considered to be a constant property of the common line because of symmetry. Therefore \( V^e \gamma_{ws} e \) in (8a) is zero as is \( F \cdot A \). Thus for the experimental configuration under consideration, the solid surface exerts no force on the common line in the direction tangent to the line at equilibrium [see also Chapuis, 1982]. Note that in this analysis, the elastic forces in the solid-fluid interfaces (with their resultant \( F \)) are treated as forces resisting the movement of the contact line. The component of \( F \) resisting the inward pull is given by \( f_e \) as defined in (8b). The balance provided by (8c) indicates that the elastic stresses in the solid-fluid interfaces acting on the contact line can introduce a resistance to its slippage tangent to the capillary tube wall. One would therefore expect the component \( C^f f_e \) to be acting downward, such that \( C^f \) is positive, when the contact line (and the meniscus) is pushed upward as in the transition from the situation in Figure 2 to the state of Figure 3. Conversely, the coefficient \( C^f \) will be negative when the interface is pushed downward. The phenomenon of hysteresis in both microscopic capillary pressure and contact angle can be explained on the basis of variations in \( C^f \) and \( f_e \), as is discussed at the end of this section.

For this experiment, the curvature of the interface requires that a pressure difference across the interface be established at equilibrium. The interface momentum as the transition to a new equilibrium state occurs will be governed by (1) and (4). When the new equilibrium state is reached, the viscous forces \( \tau_w \) vanish, and the equations reduce to

\[ \nabla^e \gamma_w = 0 \quad (9a) \]

\[ (p^n - p^w)_e = 2\gamma_w R \quad (9b) \]

respectively. This latter relation, commonly called the Young-Laplace equation, is the equilibrium relation between the pressures on the two sides of an interface. Note that it also applies for a flat interface where \( R = \infty \) such that (7a) is recovered. Although the interfacial viscous term on the right side of (4) is expected to be negligible for almost all practical situations of two-phase flow in capillaries, the Young-Laplace equation must be viewed as a relation that applies only when the interface is at equilibrium.

Commonly, the left side of (9b) is called capillary pressure \( p^c \) such that

\[ p^c = p^n - p^w \quad (10a) \]

Then, under the assumption that (9b) holds at all times, the following is commonly concluded:

\[ p^c = \gamma_w (V^e \cdot N) = 2\gamma_w R \quad (10b) \]

The disadvantage of the definition given in (10a) is that this "capillary pressure" cannot be considered as an intrinsic property of the interface in a given capillary because it is related to the difference in fluid pressures rather than to the interface properties. A more appropriate approach is to define capillary pressure by (10b). By this formalism, (10a) will be obtained as an equilibrium relationship giving the balance of forces acting on the interface. Because \( \gamma_w \) relates to the change of interfacial free energy per unit change in interfacial area, \( p^c \) as defined in (10b) may be viewed as a state variable of the interface. On the other hand, \( p^n - p^w \) is not a state variable of the interface. That is, \( p^n - p^w \) may be varied by external effects causing a movement of the interface. When the definition of capillary pressure given by (10b) is substituted into (2), the result describes the motion of the interface during the dynamic change from one state to another and reduces to (10a) when equilibrium is reached.

Equation (10b) is valid for a meniscus of general shape. For a spherical meniscus in a vertical tube with a circular cross section of radius \( r \), the mean curvature of the meniscus is related to the radius of the tube by \( r = R \cos \theta \) such that (10b) becomes

\[ p^c = \frac{2\gamma_w}{r} \cos \theta \quad (11) \]

At this state, no forces act on the contact line in the vertical direction. The equilibrium state reached by the meniscus within the capillary tube under the influence of interfacial forces may be called a state of natural (or neutral) equilibrium. Thus \( F \cdot e_z = 0 \) and the natural equilibrium equations for the contact line are given by (8b) and (8c) with \( C^f \) set equal to zero such that

\[ \frac{-\gamma_{ws}}{r} + \gamma_w \sin \theta_0 = f_0 \quad (12a) \]

\[ \gamma_w \cos \theta_0 + \gamma_{ws} - \gamma_{ns} = 0 \quad (12b) \]

where the subscript zero indicates the natural state. The existence of this equilibrium state has been discussed by previous researchers. For example, Bartell and Merrill [1932] have performed experiments showing that both receding and advancing contact angles approach a common equilibrium value if the system is allowed to come to rest.

Equation (12b), known as Young's equation, is commonly used to calculate the contact angle at the natural equilibrium state from knowledge of the interfacial tension for the three interfaces. For all other states, the actual contact angle does not have a unique value. It is possible to perturb the interface from its natural state to one with slightly different curvature such that a range of contact angles is obtained without translation of the interface. If one attempts to force one fluid to move against the other in a capillary, the meniscus and the contact line resist displacement. That is, for a sufficiently small change in pressure, the curvature of the meniscus will adjust, changing the contact angle, so that the change in pressure difference can be accommodated...
without translation of the contact line. Only with sufficiently large changes in \( p^n - p^w \) will the interface recede or advance in the tube. This has been observed in many experiments.

Slattery and Flumerfelt [1982, p. 1-225] give the following examples: "Poynting and Thomson [1902] forced mercury up a capillary tube and then gradually reduced the pressure. Instead of falling, the mercury first adjusted itself to the reduced pressure by altering the curvature of the air-mercury interface. When the pressure gradient finally grew too large, the configuration of the meniscus became unstable and the mercury fell a short distance in the tube before stopping, repeating the deformation of the interface and falling again when a new instability developed. Yarnold [1938] saw the same sticking phenomenon as a liquid index moved slowly through a glass capillary tube." Also, "... irregular jerking and sticking of the common line (was) seen by Elliott and Riddiford [1967]..."

In the context of the experiment discussed here, if one infinitesimally decreases the pressure in the \( n \) phase from a state of natural equilibrium, the curvature of the interface will decrease so that the contact angle will increase. This will cause solid-fluid interfacial stresses to develop opposing movement of the contact line. In this case, \( C^s \) will be positive. An expression for the equilibrium capillary pressure may be obtained by eliminating \( \gamma_{wn} \) and \( f_e \) by combining (8b), (8c), and (11) such that

\[
p^c = (p^n - p^w) + \frac{2\gamma_{ns} - \gamma_{wn} + 2C^s\gamma_{ns}}{r^2(1 + C^s \tan \theta_s)}
\]

(13)

Subsequent decrease of \( p^n \) (and thus of \( p^c \)) will cause further increase of \( C^s \) and \( \theta_e \) up to some maximum magnitudes. At this point, the bond between the contact line and the solid surface will be overcome such that the meniscus will start moving upward.

Similarly, if one disturbs the system from natural equilibrium by infinitesimally increasing the pressure in the \( n \) phase (or decreasing the pressure in the \( w \) phase), the interface will tend to move downward in the tube. Thus \( C^s \) will be negative and the interface will stretch such that its curvature increases while the contact angle decreases. In this process, the capillary pressure will increase. With subsequent increase of \( p^n - p^w \), the interface will continue to deform. Eventually, \( C^s \) will reach a minimum value. Further increase of \( p^n - p^w \) will create a force on the contact line that will overcome the static bond between the interface and the solid along the common line and then the contact line and interface will move to a new equilibrium position.

Each time the interface moves up or down in the capillary tube, it will come to rest at a new equilibrium position. Then the process of pressure modification causing drainage or imbibition may be repeated at each equilibrium position attained. Successive infinitesimal changes in values of \( p^n \) or \( p^w \) will eventually result in the common line moving along the tube wall until a new equilibrium state is obtained. The equilibrium states that exist at minimum capillary pressure (with minimum \( C^s \) value and maximum \( C^f \) magnitude) will be identified here as "imbibition equilibria," since they occur while experimenting such that the \( w \) phase tends to be imbibed by the capillary tube. Likewise, equilibrium states that exist for a particular location of the contact line at maximum capillary pressure will be called "drainage equilibria," since they occur while increasing \( p^c \) such that the \( w \) phase tends to drain from the capillary tube. An idealized plot of the capillary pressure versus location of the common line on the tube wall (i.e., the fraction of the tube volume filled with wetting phase) appears in Figure 4.

It is important to emphasize that Figure 4 provides a plot of \( p^c \) at equilibrium states, not while the contact line or interfaces are moving. Equilibrium states of the interface, including the state of natural equilibrium, may be found at values of capillary pressure between the two equilibrium boundaries. The dashed lines indicated as "scanning curves" are indicative of the range of values of \( p^c \) that may be achieved for a fixed position of the contact line by varying the pressure of one of the phases by small amounts without causing the interface to deform so much that the contact line moves. The distance between the two equilibria boundaries will depend on the magnitude of the resistance of the solid to movement of the contact line across its surface (i.e., the maximum variation in the magnitudes of \( C^f \) that can be achieved). Because the capillary pressure is not uniquely determined by the location of the contact line in the tube, microscopic capillary pressure is said to exhibit hysteresis. The primary source of this hysteresis is the fact that the stresses in the solid-fluid interfaces will develop such that they will always oppose the movement of the contact line (and translation of the interface).

The approach presented here and the consideration of solid-fluid interfacial elastic stresses have another advantage over the common approach where the contact angle is the only factor varying among multiple equilibrium stages. Neglect of the term \( C^sf_e \) would mean that (12b) would be valid for all states. Therefore because \( \gamma_{wm}, \gamma_{ws}, \) and \( \gamma_{ns} \) are commonly taken to be invariant when the meniscus is perturbed from its natural equilibrium, only one value of \( \theta_e = \theta_0 \) could be calculated from the equation. In essence, the existence of advancing and receding contact angles cannot be explained without taking fluid-solid interfacial elastic stresses into account.

The apparent hysteretic behavior in Figure 4 is commonly called "contact angle hysteresis" because the equilibrium contact angle is not unique [Hillel, 1980, Miller and Noegi, 1985; Schiegg, 1986; Soll, 1991]. These authors indicate that the main causes of contact angle hysteresis include roughness of the solid surface, adsorption effects, and surface impurities. These phenomena affect the solid-fluid interfacial properties accounted for by \( C^f, \gamma_{nm}, \) and \( \gamma_{ws} \) in the theory presented here. Soll [1991] measured contact angles for an oil-water-glass system and found the static contact angle to be \( \theta_e = 51.5^\circ \pm 10^\circ \). For an air-water-glass system, the...
hysteresis reported by Soll [1991] was less, with $\theta_e = 34.75^\circ \pm 2.0^\circ$. It should be noted that the utility of contact angle in the definition of capillary pressure in a tube as given by (11) is limited to the case of a vertical tube with circular cross section. In all other cases, the contact angle has no constant value and no simple relation exists between the meniscus curvature and the contact angle. In general, one must employ the definition given by (10b).

Of greatest significance is the fact that the apparent hysteresis in Figure 4 is an artifact of the abscissa chosen for the plot. Figure 4 shows that a tabulation of $p_c$ versus volume fraction of the wetting phase does not give a unique functional relationship. The difference in $p_c$ at the drainage and imbibition equilibria boundaries is dependent on the range of contact angles that can be sustained by the system without causing the contact curve to move. However, based on (10b), the capillary pressure is a unique, nonhysteretic function of the curvature of the interface between the phases. Thus if one were to plot capillary pressure versus interfacial area (for a particular capillary tube), no hysteresis in the capillary pressure data would be observed. Note also that if one were to perform this experiment using a capillary tube whose cross-sectional area were a function of position, the position of the interface along the axis (i.e., the volume fraction of the wetting phase) would also be an important factor in determining the degree of apparent hysteresis. Recognition of the fact that selection of appropriate independent variables for correct phenomenological characterization of capillary pressure is a crucial element of examination of capillary pressure at the macroscale.

**Capillary Pressure at the Macroscale: Standard Approaches**

For the study of flow and transport in porous media, equations are needed at a scale larger than the microscale. This scale is referred to as the macroscale and the quantities modeled are averages over the neighborhood of position of interest. This neighborhood is commonly called a representative elementary volume (REV) and has a characteristic length much larger than that of a typical pore diameter. Thus the average values of microscopic functions are taken to be representative of measurements that might be taken at a porous medium scale. Some degree of rigor in averaging from the microscale to the macroscale is often compromised in order to try to enhance physical understanding. However, failure to explicitly recognize the approximations made can cause confusion rather than clarification.

In the existing literature, by analogy with the equilibrium relationship (10a) between the microscale capillary pressure and the pressure difference between adjacent phases, the macroscopic capillary pressure, is almost universally defined as [e.g., Bear, 1972; Scheidegger, 1974; de la Cruz and Spanos, 1983; Anderson, 1987; Bear and Verruijt, 1987]

$$p_c = \langle p \rangle_n - \langle p \rangle_w$$  (14)

where $p_c$ is the macroscopic capillary pressure, $\langle p \rangle_n$ is the pressure of the $n$ phase averaged over the portion of the REV containing phase $n$, and $\langle p \rangle_w$ is the pressure of the $w$ phase averaged over the portion of the REV containing phase $w$.

At first thought, it might seem possible to obtain this relation by averaging its microscopic equilibrium counterpart, $p_c^{\text{equilibrium}} = (p_n^e - p_w^e)$, given in (10a), over the REV. However, (10a) applies only on the interface and thus could be averaged only over that interface and not over a volume. Thus pressures appearing in the right side of (14) would be surface averages rather than averages over the phases. These averages are not necessarily equal. Therefore even if one extends the equilibrium relation for microscopic capillary pressure as applying to the dynamic case, (14) will not follow from any systematic averaging procedure unless one is prepared to employ heuristic assumptions. At best, (14) may be viewed as a working statement assigning some function to the difference in the (macroscopic) pressures of the fluid phases at equilibrium. It must not, however, be regarded as a relation providing a balance of forces. Furthermore, $p_c$ as defined by (14) may not be related arbitrarily to other thermodynamic properties of the system.

In the literature, (14) is typically presented as a generally applicable "result" valid during all dynamic situations and not merely as an equilibrium relationship. Furthermore, to explain the behavior of the macroscopic capillary pressure $p_c$, appeal is made to the (microscopic) equation (9b). This mixing of scales has been an obstacle to a more complete understanding of macroscopic capillary pressure. Some of the resulting misconceptions will be identified here.

An empirical relation for $p_c$, measured indirectly as the difference between the externally maintained pressures of the $n$ and $w$ phases is usually proposed. A functional form hypothesizing $p_c$ to be a function of the wetting phase saturation $s_w$ may be stated as

$$p_c = \mathcal{F}(s_w)$$  (15)

The explicit functional form is considered to be specific to the combination of the pair of fluids and the porous skeleton, and also dependent on the medium temperature and the chemical composition of the fluids. The function $\mathcal{F}$ is also known to exhibit hysteresis in that the equilibrium value of $p_c$ as a function of $s_w$ is found to be dependent on the direction of the process (i.e., drainage or imbibition) leading up to the equilibrium state. A schematic depiction of the $p_c$ versus $s_w$ curves is given in Figure 5.

A few comments concerning Figure 5 are in order before proceeding. The curves identified as equilibrium curves in Figure 5 are bounds on equilibrium. Equilibrium states may also be achieved at points between the two curves. How-
ever, if one begins with a saturated medium and performs a set of sequential experiments, replacing a little of the \( w \) phase with the \( n \) phase and then waiting for equilibrium to be established at each step, the equilibrium states will lie on the upper curve. Conversely, if one performs a sequence of experiments with imbibition occurring prior to awaiting equilibrium, the equilibrium states will lie on the lower curve. One can achieve equilibrium states between the two curves (i.e., move to equilibrium states on the scanning curves) by intermixing drainage and imbibition within the sequence of experimental steps. Because equilibrium states exist not only along a curve but within a region of \( P^c-s^w \) space, it is more appropriate to call a plot of capillary pressure versus saturation a "\( P^c-s^w \) plane" instead of "\( P^c-s^w \) curve." Interestingly, the abscissa and ordinate in Figure 5 are macroscopic counterparts of the microscopic abscissa and ordinate used to generate Figure 4 for a single capillary tube. Indeed, the primary change in depicting the macroscopic situation for a complex porous medium in comparison to a highly simplified microscopic situation seems to be that the equilibria boundaries are sloped rather than horizontal and the scanning curves are loops rather than vertical lines. The equilibrium hysteresis in the \( P^c \) versus \( s^w \) plot of Figure 5 is perhaps not a property of the macroscopic situation or of system dynamics but is an artifact of the choice of independent variable selected for the functional form of (15). This fact will be demonstrated subsequently.

A number of laboratory methods exist for measuring capillary pressure-saturation relationships such as that schematized in Figure 5. They may generally be divided into two groups: displacement methods and dynamic methods. In both types of methods, the fluid saturation is varied in incremental steps. At each step, enough time is allowed for an equilibrium to be reached so that saturation will not change anymore. The capillary pressure is determined indirectly from (14) by measuring the pressure of the fluids entering and/or leaving the sample. It is important to note that the fluid pressures are almost always measured externally.

As is illustrated in Figure 5, it is commonly believed that an irreducible wetting phase saturation \( s^r \) exists for which further increase of the externally measured capillary pressure will not have any effect on the fluid saturation. Formally, the capillary pressure is said to go to infinity at the wetting phase irreducible saturation. The concept of infinite capillary pressure at an asymptotic irreducible saturation is questionable for a number of reasons. First, infinitely large pressure differences (corresponding to a large positive pressure of the \( n \) phase and/or a large tension in the \( w \) phase) are physically unrealistic under most natural conditions [Gray and Hassanizadeh, 1991b]. Second, the existence of a nonzero irreducible saturation is questioned by some researchers. Dullien et al. [1986] have observed, in a number of experiments, that the wetting phase saturation can be reduced far below the reported values of \( s^r \) when the external pressure of the nonwetting phase is increased and the experiments are run for a couple of months. Third, capillary pressure is actually related to the pressure difference between phases within the porous medium, whereas in standard measurements, the difference in pressure of fluids in reservoirs outside the medium is measured. Numerous comments in the literature indicate that externally measured capillary pressure near residual or irreducible saturation

The traditional definition of capillary pressure in terms of the difference in the external pressure of the fluid phases, as given by (14), becomes problematical when one tries to establish relationships between \( P^c \) and other medium properties. In fact, capillary pressure defined in this manner cannot be thermodynamically related to the properties of the system because external pressures can be varied arbitrarily. Nevertheless, various researchers have tried to provide empirical and theoretical explanations of the \( P^c-s^w \) relationships and dependencies described above. These expressions, although superficially appealing, are inherently inconsistent and incapable of providing a definitive description of capillarity in multiphase systems. In the remainder of this section, a number of these typical approaches are described and the resulting relationships are discussed.

The most straightforward approach to obtaining a \( P^c-s^w \) relationship has been to simply extrapolate the defining relationship for microscopic capillary pressure, (10b), to the macroscale:

\[
P^c = 2(\gamma w n) / (R)
\]  

(16a)

A similar approximation is alternatively obtained as an extrapolation of (11):

\[
P^c = 2(\gamma w n) / (r) \cos (\theta_e)
\]  

(16b)

where all terms in these two equations are considered to "have the meaning of a statistical average taken over the void space in the vicinity of a considered point in the porous medium" [Bear, 1972, p. 445]. It does not, however, seem possible to obtain (16a) from (10b) or (16b) from (11) following a rigorous averaging procedure, at least not for a
general porous medium. Indeed, since (10b) and (11) apply only at interfaces, the interpretation of a statistical average of these equations taken over void space is, at best, obscure.

Besides this fundamental problem, and the question of how the average values might relate to other medium properties, two additional significant difficulties with these definitions exist. First, there is the practical difficulty of uniquely defining a macroscopic (as well as a microscopic) contact angle and/or radius of curvature of menisci in a porous medium. Morrow [1970] finds (16b) applicable only to extremely simple geometries. Scheidegger [1974] points out that an average interfacial curvature can be defined only if the porous medium is made of a regular assemblage of capillary tubes, but the large majority of natural and artificial porous media are not. Therefore even at the microscopic scale, one cannot identify contact angles or curvature uniquely. At the macroscopic scale this identification becomes even more complicated because with capillary pressure specified as a function of saturation, (16a) and (16b) would require \( \theta_r \) and/or \( R \) to be functions of saturation. Scheidegger [1974] finds it a very difficult proposition to define an average interfacial curvature as a function of saturation. Morrow [1970] points out the practical difficulties of treating contact angle as an acceptable macroscale variable for any quantitative analysis of porous media processes. One should acknowledge that macroscopic relationships such as (10b) are certainly useful aids in studying processes in porous media. However, it must also be realized that their validity in explaining macroscopic processes is limited.

A second problem with (16a) and (16b) is that they fail to explain the observed behavior of interfaces and traditional capillary pressure. According to standard measurements, capillary pressure is zero at full saturation and asymptotically goes to infinity at the irreducible saturation. Attempts are made to explain the rise of the capillary pressure to infinity by means of (10b) or (16a) and (16b). It is argued that at irreducible saturation, the wetting phase exists only in very small pore spaces such that the radius of curvature of the meniscus are very small; and the capillary pressure will be very large. This argument may be acceptable when the porous medium is made of an array of capillary tubes including microcapillaries of very small radius. However, in natural porous media the smallest spaces are formed at the points of contact of the grains. Whether the capillary pressure will approach infinity at these sites is certainly questionable. What is more, some researchers have reported that at irreducible saturation, the wetting phase forms a thin film around the solid grains (see, for example, Morrow [1970], Dullien et al. [1986], Marsily [1986], and Jerauld and Slater [1990]). In those situations, the curvature of the interface would imply the existence of a negative capillary pressure instead of a very large positive one. This is, of course, not acceptable.

Similar inconsistencies are encountered in studying (16a) and (16b) when \( s^w \) approaches 1. Ample experimental evidence shows that as a medium becomes saturated, the nonwetting phase recedes into larger pore spaces where the radius of curvature of the meniscus is relatively large such that capillary pressure decreases. At some point, the nonwetting phase breaks up and forms isolated globules within the wetting phase (see, for example, Bear [1972, Figure 9.2.3], Scheidegger [1974, Figure 9], and Marsily [1986, Figure 2.9]). At that stage, the magnitude of the radius of curvature will decrease because a portion of a spherical surface is transformed into a closed sphere (with decreasing radius). This means, according to (16a), that the capillary pressure, instead of reaching zero near full saturation, will have to increase. For capillary pressure to become zero (16a) requires the radius of curvature of the meniscus to be very large. That certainly is not the case when the \( n \) phase is being expelled from the porous medium and \( s^w \) is near 1.

The discussion illustrates the fact that equations such as (16a) or (16b) and the typical behavior of macroscopic capillary pressure are inconsistent.

Another intuitive generalization of microscopic equilibrium equation (9b) is given by Carman [1941], who replaces the radius of curvature \( R \) with a term \( m \) defined to be the volume of the column of water in a capillary divided by the area of wetted surface of capillary such that

\[
p^c = p_w - p^w = 2\gamma w/n/m \tag{17}
\]

Carman assumes that (17) is applicable to soils. He sets \( m = e/a \), where \( e \) is the porosity and \( a \) is the specific surface of the saturated porous medium and employs this relation to find the (minimum) rise of water above the groundwater table in a given soil. He assumes that the pressure difference between air and water at the top of the capillary fringe, \( p^w - p^w \) is equal to \( g \). (It is not clear whether this is considered to be true for macroscopic as well as microscopic capillary pressure because some confusion between the two scales occurs.) With these assumptions, Carman [1941] obtains for \( h \), the height of capillary rise in soil:

\[
h = 2\gamma w/a/p_g e \tag{18a}
\]

Then if \( a = 3(1 - e)/r \), this equation becomes

\[
h = 6\gamma w/(1 - e) \tag{18b}
\]

Based on these relations, Scheidegger [1974] suggests the following macroscopic relation for capillary pressure:

\[
P^c = \rho g h = 6\gamma w/(1 - e) e r \tag{19}
\]

Note that there is a fundamental difference between (18b) and (19). The latter is meant to be valid throughout the unsaturated domain, whereas the former is only an estimation of the thickness of the capillary fringe. Although (19) seems to be independent of saturation, one may reinterpret \( r \) to be the mean radius of the largest pore space being filled with water at a given saturation. In this way, \( r \) will be a function of saturation, and (19) will then be comparable to (16b). Thus it will also suffer from the same drawbacks discussed about (16b).

Another well-known relationship is due to Leverett [1941]:

\[
P^c = \gamma w^2/(e/k)^{1/2} J(s^w) \tag{20}
\]

where \( k \) is the permeability of the medium and \( J(s^w) \) is a dimensionless function of saturation called the Leverett function. This function is basically equivalent to \( 1/(R) \) in (16a) and \( 1/m \) in (17). The advantage of scaling by \( (e/k)^{1/2} \), according to Leverett [1941], is that \( J(s^w) \) will be independent of soil properties (at least for a given class of soils such as, say, all unconsolidated sandy soils). Therefore once
\( J(s^w) \) is obtained, (20) can be used to provide a capillary pressure versus saturation relationship for a given class of soils. The form obtained for \( J(s^w) \) is very similar to the equilibrium curves for \( P^c \) in Figure 5.

Although (20) is useful in practical applications, it does not provide any insight into the behavior and processes of capillarity at the macroscale. At best, (20) should be seen as a mathematical correlation of the curves in Figure 5 for a given class of soils.

A generalization of (16b) has been given by Slattery [1968]. Employing definition (14), \( P^c = (p^w) - (p^s) \), for macroscopic capillary pressure, he proposes that \( P^c \) is a function of a characteristic length of the porous medium \( L \), the surface tension \( \gamma^w \), the contact angle \( \theta \), and saturation \( s^w \) such that

\[
P^c = \mathcal{F}(L, \gamma^w, \theta, s^w) \tag{21}
\]

Then, he applies the Buckingham-Pi theorem to obtain, for geometrically similar porous media:

\[
P^c = \frac{\gamma^w}{L} \mathcal{g}(\theta, s^w) \tag{22}
\]

This equation may also be regarded as a generalization of (20), allowing for a dependence on contact angle, and thus formally including hysteresis in the \( P^c-s^w \) relation. However, (22) cannot really serve as a phenomenological equation for \( P^c \). Together with definition (14) for macroscopic capillary pressure, it may be used to determine \( \mathcal{g}(\theta, s^w) \) from equilibrium experiments. Obviously, \( \mathcal{g}(\theta, s^w) \) will have the typical form commonly exhibited by capillary pressure versus saturation curves. This work seems to be the first attempt to incorporate an additional independent variable to \( s^w \) in the definition of the functional form of \( P^c \). Unfortunately, the analysis suffers from using independent variables from two different scales, the microscopic contact angle and the macroscopic saturation.

A more fundamental approach to obtain a phenomenological relationship for \( P^c \) has been to employ principles of equilibrium thermodynamics. In doing so, thermodynamic relationships known for single continua (thus valid at the microscale) are commonly assumed to be equally valid for multiphase media at the macroscale. For example, Leverett [1941] considers an element of sand containing only water and oil, in hydraulic contact with a water reservoir. Leverett argues that "since \( P^c \) is the free energy increase (the isothermal reversible work necessary) accompanying the transfer of a unit volume of water from the sand to the zero curvature reservoir at the same level" [Leverett, 1941, p. 161], he then proposes

\[
P^c = \delta \mathcal{A}^w/\delta V^w \tag{25a}
\]

where \( \mathcal{A}^w \) is the Helmholtz free energy of the water. If one introduces free energy per unit mass of water \( \mathcal{A}^w \), (25a) may be written as

\[
P^c = s^w \rho^w \frac{\delta \mathcal{A}^w}{\delta s^w} \tag{25b}
\]

where \( V^w \) is replaced by \( s^wV \) and \( \mathcal{A}^w \) is \( s^w \rho^w \mathcal{A}^w V \). Later in this work, (25b) will be shown to contain only one of the terms making up the macroscopic thermodynamic relationship for capillary pressure. The important fact is that water in a porous medium does not form a closed system because it exchanges energy with interfaces and other phases. Therefore integration of (23) to obtain (24a) is not permissible.

This fact has been recognized by Morrow [1970], who applied the first law of thermodynamics to a system similar to that considered by Leverett [1941]. Equating the external work done on the porous medium to the change in free energy of the medium, he obtains [Morrow, 1970, equation (67),]

\[
P^c = -d\mathcal{A}/dV^w \tag{26}
\]

where \( \mathcal{A} \) is the Helmholtz energy of all phases and interfaces and \( V^w \) is the volume of water in the porous medium. From the energy balance for the porous medium under isothermal conditions when compression effects are negligible, one obtains [Morrow, 1970]

\[
d\mathcal{A} = \gamma^w d\mathcal{A}^w + \gamma^s d\mathcal{A}^s + \gamma^w s^w d\mathcal{A}^w \tag{27}
\]

where \( d\mathcal{A}^\alpha \) is the total area of \( \alpha \beta \) interface in the porous medium. Note that in this relation, Morrow [1970] does not include any change in free energy of bulk phases. Subsequently, he sets \( d\mathcal{A}^s = -d\mathcal{A}^w \) and \( \gamma^s - \gamma^w = \gamma^w \cos \theta \), to obtain

\[
-\frac{d\mathcal{A}}{dV^w} = \frac{P^c}{s^w} \left( \frac{d\mathcal{A}^{w}}{dV^w} + \frac{d\mathcal{A}^{s}}{dV^w} \cos \theta \right) \tag{28}
\]

Note that the use of the relationship (12b) with the natural state considered to be the equilibrium state, \( \gamma^s - \gamma^w = \gamma^w \cos \theta \), is somewhat inconsistent because of mixing of scales involved. Morrow [1970] points out that these relationships may not be directly applied to a porous medium because the displacement of interfaces and volume changes there, do not take place reversibly. He states "When given volumes of fluid are commingled in a complicated network of nonuniform pores, typical of a porous media, many stable fluid configurations are possible. Unlike many thermodynamic systems which are stable at a single minimum free energy, there will be many local minima of free energy, and the global minimum for the system has no special significance [Morrow, 1970, p. 113]. An important conclusion one
may draw from this observation is that in a given porous medium containing two fluid phases, saturation and interfacial areas are independent variables. That is, many local minima of energy may occur at a given saturation because a range of interfacial areas is possible, depending on the nature and constitution of phases and interfaces. For example, if the w phase spreads indefinitely over the surfaces of soil particles, even at very small saturations, the \( w_n \) interfacial area may be large. Otherwise, the interfacial area may be small at low saturations. In light of these observations, the right side of (28) evidently may be written in terms of partial derivatives only if the energy of the porous medium is kept constant. That is,

\[
P^c = \frac{\gamma^{wn}}{\varepsilon} \left( \frac{\partial a^{wn}}{\partial s^w} \right)_{A^*,A^*\theta,T} - \frac{\gamma^{wn}}{\varepsilon} \left( \frac{\partial a^{wn}}{\partial s^w} \right)_{A^*,A^*\theta,T} \cos \theta_e
\]

(29)

where \( a^{\alpha\beta} \) is the area of \( \alpha\beta \) interfaces per unit volume of the porous medium, and \( A^\alpha \) and \( A^\beta \) are free energy per unit volume of the phases and interfaces of the porous medium, respectively. (Recall, still, the inconsistency involved in (29) due to the presence of a microscopic equilibrium contact angle \( \theta_e \).) Note that (25b) (due to Leverett [1941]) and (29) are mutually exclusive. It will be shown later that a general relationship for macroscopic capillary pressure contains the terms appearing in both (25b) and (29).

Relationships for capillary pressure are also found in mixture theory approaches to describing multiphase flow in porous media. A peculiar aspect of most mixture theory models of a multiphase system is that the system is assumed to be composed of immiscible fluid and solid phases but no account is made for interfaces. In most of these theories, first a relationship is found for thermodynamic pressure of fluid phases, and then capillary pressure is simply defined to be equal to the difference in fluid pressures [e.g., Bowen, 1982; Allen, 1986; Thigpen and Berryman, 1985]. Some typical relationships include the following from Bowen [1982]:

\[
P^c = \frac{-1}{\varepsilon} \frac{\partial A}{\partial s^w} \]

(30a)

where \( A \) is the sum of the Helmholtz free energies of all phases per unit volume of the porous medium, and the expression from Allen [1986]:

\[
P^c = -\sum \sigma^{\alpha} \rho^{\alpha} \frac{\partial A^{\alpha}}{\partial s^{\alpha}} \quad \alpha = w, n
\]

(30b)

A fundamental inconsistency in these works is the fact that no interfaces and no interface properties are included in the underlying theory. These, of course, are necessary if one is to admit the existence of capillary pressure. Interfacial properties do not appear either in conservation laws or in constitutive equations. For example, the (macroscopic) force exerted by phase \( w \) on phase \( n \) is equal to the negative of force exerted by phase \( n \) on phase \( w \), as if there is no surface tension or any other interfacial force present (see Hassanizadeh and Gray [1990] for additional discussion). A more rigorous approach has been developed by Marie [1981, 1982], Kalaydjian [1987], and Pavone [1989, 1990].

Marle [1981] develops a continuum description of the porous medium and, based on a nonequilibrium formulation of entropy production for the system, obtains the following relationship for pressure differences between nonwetting and wetting phases:

\[
(\rho)^n - (\rho)^w = -\gamma^{wn} \tau^{wn} - \varepsilon C \frac{\partial s^w}{\partial t}
\]

(30c)

where \( C \) is a material constant and \( \tau^{wn} \) is the macroscopic curvature of interfaces (some average of the microscopic curvature of interfaces).

An alternative expression has been obtained by Kalaydjian [1987], who also employs Marie’s method

\[
P^c = (\rho)^n - (\rho)^w = \gamma^{wn} \tau^{wn} f - \varepsilon C \frac{\partial s^w}{\partial t}
\]

(31)

where \( f \) is a function characterizing the internal structure of the porous medium, and is defined such that [Kalaydjian, 1987]

\[
f \tau^{wn} = -\frac{\partial a^{wn}}{\partial t} \frac{\varepsilon \delta s^w}{\delta t}
\]

(32a)

where \( a^{wn} \) is the area of \( wn \) interfaces per unit volume of the porous medium.

This definition of \( f \) is undesirable because it relates a medium property to the time rate of change of some state variables. In any case, one may combine (31) and (32a) and write as an approximation:

\[
P^c = \gamma^{wn} \frac{\partial a^{wn}}{\partial s^w} - C \frac{\delta s^w}{\delta t}
\]

(32b)

For \( \partial a^{wn} / \partial s^w \) to be consistent with the capillary pressure versus saturation curve of Figure 5, the dependence of \( a^{wn} \) on \( s^w \) would have to be similar to that depicted in Figure 6. However, as saturation decreases to near residual value, one would expect the \( wn \)-interfacial area per unit volume to also decrease. This is in clear violation of the requirements of (32b). Alternatively, one could suggest that \( P^c \) as defined by (32b) is not the same function depicted in Figure 5.

Pavone [1989], whose approach is based on the work of Marie [1981], provides an extension of (32b) in the form

\[
P^c = \gamma^{wn} \frac{\cos \theta}{\kappa} - \gamma^{wn} \frac{\partial a^{wn}}{\partial (\varepsilon s^w)} - \eta \frac{\delta (\varepsilon s^w)}{\delta t}
\]

(33)
where $R$ is a characteristic length, $\theta$ is the contact angle, the coefficient $\eta$ is bounded by $\eta \geq 0$, and $P^c$ is called the dynamic capillary pressure equal to the pressure difference between the nonwetting and wetting phases. Under equilibrium conditions, where $\delta(\varepsilon_s^w)/\delta t = 0$, (33) resembles relation (28) suggested by Morrow [1970]. The presence of the contact angle, a microscopic quantity, in this macroscopic expression is troublesome. Pavone [1989] identifies the first term on the right side of (33) as the pressure required to move the contact line and identifies the sum of the first two terms as the static capillary pressure. Thus at equilibrium, the static and dynamic capillary pressures will be equal.

At this point, the search for a consistent treatment of macroscopic capillary pressure seemingly has provided some insights but many inconsistencies and contrasting viewpoints. Although the relationships provided in the literature suggest a connection between macroscopic capillary pressure and the change in Helmholtz free energy due to saturation change, they provide conflicting results. One relation contains the work done by (or the change in energy of) only wetting interfaces, whereas another relation includes the work of all interfaces. Examination of other formulations reveals lack of agreement as to whether macroscopic capillary pressure should be related to the change in energy of only the wetting phase, the change in energy of only the fluid phases, or the change in energy of all phases. It will be shown in the next section that these relations are, indeed, all incomplete although they do contain elements of a proper formulation.

**Capillary Pressure at the Macroscale: Proposed Approach**

For progress to be made in the understanding and modeling of multiphase flows, the definition of macroscopic capillary pressure must be developed in the framework of a sound thermodynamic theory rather than being given arbitrarily. One must provide macroscopic balance laws and appropriate constitutive relationships for interfacial as well as phase properties of the porous medium. Capillary pressure must be independent of external forces and should rely on the intrinsic properties of the multiphase system, particularly those of the interfaces. Additionally, constitutive hypotheses must be made consistently and within a framework that will allow expansion of the theory as additional complex and important processes are included.

In a number of recent works, Gray and Hassanizadeh [1989, 1991a, b] and Hassanizadeh and Gray [1990] have produced a thermodynamic theory of two-phase flow in a porous medium which has the aforementioned characteristics. The main constitutive hypothesis in this theory is the dependence of the Helmholtz free energy functions for the phases and interfaces on state variables such as mass density, temperature, saturation, porosity, interfacial area density, and the solid phase strain tensor. The specific forms of the constitutive equations are [Gray and Hassanizadeh, 1991a]

$$
A^n = A^n(p^n, T, a^{nw}, a^{ns}, s^w, \varepsilon) \quad (34a)
$$

$$
A^w = A^w(p^w, T, a^{wn}, a^{ws}, s^w, \varepsilon) \quad (34b)
$$

$$
A^f = A^f(p^s, T, a^{ns}, a^{ws}, E^s, \varepsilon) \quad (34c)
$$

$$
A^{\alpha\beta} = A^{\alpha\beta}(\Gamma^{\alpha\beta}, T, \varepsilon, a^{\alpha\beta}, s^\alpha) \quad \alpha\beta = wn, ws, ns \quad (34d)
$$

where

- $A^\alpha$ Helmholtz free energy of phase $\alpha$ per unit mass of phase $\alpha$;
- $A^{\alpha\beta}$ Helmholtz free energy of interface $\alpha\beta$ per unit mass of interface $\alpha\beta$;
- $p^\alpha$ mass of $\alpha$ phase per unit volume of $\alpha$ phase;
- $T$ temperature;
- $\varepsilon$ porosity;
- $s^\alpha$ saturation of fluid phase $\alpha$;
- $a^{\alpha\beta}$ area of $\alpha\beta$ interface per unit volume of porous medium;
- $E^s$ area solid phase strain tensor;
- $\Gamma^{\alpha\beta}$ excess mass of the $\alpha\beta$ interface per unit area.

The choice of independent variables in the preceding equations is based on the expected behavior of the phases inferred from past experience. For example, the interfacial area of the $\alpha$ phase with the $\beta$ phase per unit volume of $\alpha$ phase, $a^{\alpha\beta}$, is considered to be important to the determination of the state of the system (see, for example, Crawford and Hoover [1966]). Also, it is known that a given volume of a fluid in a porous medium may attain various microscopic distributions in the pores, depending on the energy state of phases and interfaces. Thus one might expect the free energy of a phase to depend on such groups as $a^{\alpha\beta}$, $a^{\alpha\beta}$, $s^\alpha$, $e$, $a^{\alpha\beta}$, and $a^{\alpha\beta}$ separately rather than in these combinations. Therefore it is convenient to formulate the constitutive theory in terms of $e$, $a^{\alpha\beta}$, and $s^\alpha$ separately.

The explicit inclusion of interfaces and interfacial properties in the proposed theory is essential because they are known to have a significant role in determining the thermodynamic state of the whole system. Scheidegger [1974] states that hysteresis (in capillary pressure) seems to be caused by instability of interface configurations. Dussan [1987] remarks that it is somewhat surprising that such a small amount of interfacial material can have such a substantial influence on the state of the entire body of the fluid.

Based on constitutive relations (34a) through (34d) and application of the Coleman and Noll method of exploitation of entropy inequality, Gray and Hassanizadeh [1991a] show that the following combination of terms contributes to the entropy production such that in the absence of other thermodynamic forces, one must have

$$
-3^w \left[ \varepsilon(P^n - P^w) + \left( \varepsilon s^w \rho^w \frac{\partial A^w}{\partial s^w} + \varepsilon s^w \rho^w \frac{\partial A^n}{\partial s^w} \right) \sum_{\alpha\beta} a^{\alpha\beta} \Gamma^{\alpha\beta} \frac{\delta A^{\alpha\beta}}{\delta s^\alpha} \right] \geq 0 \quad (35)
$$

where $s^w$ is the material time derivative of the wetting phase saturation observed when moving with the solid phase, $P^n$ is the macroscopic pressure of the $n$ phase, and $P^w$ is the macroscopic pressure of the $w$ phase. The macroscopic pressures are obtained, not as some averages of microscopic pressures, but directly at the macroscale through the thermodynamic definition [Hassanizadeh and Gray, 1990].
In (35), \(P^n - P^w\) is the resultant of external forces causing the movement of fluids in the porous medium. This movement is opposed (or assisted) by capillary forces. At equilibrium, the capillary forces will balance \(P^n - P^w\). Based on this consideration, (35) clearly suggests that macroscopic capillary pressure be defined thermodynamically by

\[
P^c = -s^w \rho^w \frac{\partial A^n}{\partial s^n} - s^n \rho^n \frac{\partial A^n}{\partial s^n} - \sum_{\alpha \beta} \gamma^{\alpha \beta} \frac{\partial A^{\alpha \beta}}{\partial s^\alpha} \frac{\partial A^{\alpha \beta}}{\partial s^\beta} \tag{37}
\]

According to this definition, macroscopic capillary pressure is related to the change in the free energy of phases and interfaces as a result of change in the saturation. Inequality (35) explains the spontaneity of the imbibition process. According to this equation, the free energy of the system must decrease for the saturation of the wetting phase to increase (i.e., for \(\delta s^w > 0\)); this would be a spontaneous process. On the other hand, to decrease the wetting phase saturation (\(\delta s^w < 0\)), the energy of the system must be increased. This will not be a spontaneous process and will require an increase in \(P^n - P^w\) such that work is done on the system. Note that dependence of \(P^c\) on the solid phase free energy does not appear in (37) because the solid phase free energy is assumed to be independent of saturation in (34c). Furthermore, note that by application of the chain rule to (34d), one obtains

\[
\left(\frac{\partial A^{\alpha \beta}}{\partial s^\alpha}\right)_{\alpha \beta, T, \varepsilon, \Gamma, \delta} = - \left(\frac{\partial A^{\alpha \beta}}{\partial s^\alpha}\right)_{T, \varepsilon, \Gamma, \delta, A, \varepsilon, \delta, A} \tag{38}
\]

so that (37) may also be written as

\[
P^c = -s^w \rho^w \frac{\partial A^n}{\partial s^n} - s^n \rho^n \frac{\partial A^n}{\partial s^n} - \sum_{\alpha \beta} \gamma^{\alpha \beta} \frac{\partial A^{\alpha \beta}}{\partial s^\alpha} \frac{\partial A^{\alpha \beta}}{\partial s^\beta} \tag{39}
\]

where \(\gamma^{\alpha \beta}\) is the macroscopic surface tension of the \(\alpha \beta\) interface defined thermodynamically at the macroscale as [Hassanizadeh and Gray, 1990]

\[
\gamma^{\alpha \beta} = - (\Gamma^{\alpha \beta})^2 \frac{\partial A^{\alpha \beta}}{\partial \Gamma^{\alpha \beta}} = -a^{\alpha \beta} \Gamma^{\alpha \beta} \frac{\partial A^{\alpha \beta}}{\partial a^{\alpha \beta}} \tag{40}
\]

Examination of (37) and (39) clarifies the discrepancies discussed previously concerning the contributions of various energy changes to the capillary pressure function. It appears that none of the relations discussed in the previous section contain all relevant energy changes. In other words, those relations are all special cases of definition (37) or (39) for capillary pressure.

According to the approach advocated here, capillary pressure provides an indication of the tendency of the system to admit a rise in the saturation of the wetting phase when temperature, fluid densities, medium porosity, interfacial mass density, and interface area per unit volume are held constant. Macroscopic capillary pressure is thus defined solely as an intrinsic property of the system, in the same way that \((10b)\) defines microscopic capillary pressure as an intrinsic property of the interface. Relations (34a) through (34d), in conjunction with (37), indicate that macroscopic capillary pressure is a function of fluid densities, temperature, medium porosity, specific interfacial areas, interfacial mass densities, and fluid saturation:

\[
P^c = (\rho^n, \rho^w, T, \Gamma^{nw}, \Gamma^{ns}, \Gamma^{ws}, a^{nw}, a^{ns}, a^{ws}, e, s^w) \tag{41}
\]

Note that \(P^c\) is only a measure of the tendency of the system to undergo a change in saturation. Whether this change will actually occur depends, of course, on the overall state of the system, and in particular, the pressure distribution of the two fluids. This is mathematically stated by the residual entropy inequality (35) which, after substitution of (37), may alternatively be written

\[
-\delta s^w [(P^n - P^w) - P^c] \geq 0 \tag{42}
\]

This inequality requires that if \(P^n - P^w > P^c\) then \(\delta s^w\) must be negative. In other words, if \(P^n - P^w\) is greater than the capillary pressure, the system will undergo drainage. On the other hand, (42) indicates that if \(P^n - P^w > P^c\) then \(\delta s^w\) must be positive. Thus imbibition occurs when \(P^n - P^w\) is less than the capillary pressure. Only at equilibrium, when \(\delta s^w = 0\) and no change in saturation is occurring, will \(P^n - P^w = P^c\).

This discussion suggests that examination of an approximate constitutive equation for \(\delta s^w\) may help provide some additional insight. For a linear theory, the following approximation for \(\delta s^w\) may be written:

\[
\delta s^w = -L^w [(P^n - P^w) - P^c] \tag{43}
\]

where \(L^w\) is a nonnegative material coefficient. Both the general equation (42) and approximation (43) suggest that at a given point in the system and at any given time, saturation will change locally in order to restore equilibrium and the equivalences between \(P^n - P^w\) and \(P^c\). Ample experimental evidence exists that \(P^c - s^w\) curves are also a function of \(s^w\). In an experiment where the drainage is fast, the measured value of \(P^n - P^w\) is larger than the value of \(P^c\) determined under very slow (i.e., near static) drainage experiments [Davidson et al., 1966; Topp et al., 1967; Smiles et al., 1971]. This is in full agreement with (43). The coefficient \(L^w\) may be interpreted as a measure of the speed at which the change in saturation takes place. If \(L^w\) is found to be very large, equivalence between \(P^n - P^w\) and \(P^c\) will be reestablished virtually instantaneously after equilibrium is disturbed. Thus if one uses the commonly employed relation

\[
P^c = P^n - P^w \tag{44}
\]

as the definition of macroscopic capillary pressure, even for a system not at equilibrium, one is intrinsically assuming that any actual disturbances in this equivalence are eliminated almost instantaneously because of the system dynamics (i.e., \(L^w \gg 0\) in the linearized case). System dynamics such as these are probably achieved only for porous media with
good permeability. As permeability decreases, the applicability of (44) will become suspect. In cases where permeability of the medium to the wetting phase is very low, (44) will apply only at equilibrium and one probably needs to employ an equation such as (43) to correctly model system dynamics.

Of additional interest is the fact that the definition (37) or (39) provides a thermodynamic statement of the "heat of wetting." It is known that the decrease in the Helmholtz free energy of a porous medium when entered by a wetting fluid is liberated as heat [Scheidegger, 1974]. Equation (37) indicates that the heat of wetting per unit volume of the porous medium for an infinitesimal change in saturation will be \( \varepsilon \rho C ds_w \). Thus the total heat of wetting for a porous medium with finite volume \( V \) where saturation changes from \( s_1 \) to \( s_2 \) will be

\[
\Delta H = \int_V \left( \int_{s_1}^{s_2} \varepsilon \rho C ds_w \right) dV \quad (45)
\]

Another important result that can be deduced from (37) regards the commonly employed form of the capillary pressure versus saturation curve of Figure 5. As was mentioned earlier, the rise of capillary pressure to infinity at low saturations is physically unacceptable. This statement is supported by (37). The Helmholtz free energies per unit mass of the phases and interfaces are bounded. Thus as the saturation of a phase approaches an irreducible value (or even zero), one would expect terms such as \( s^a \partial A^{a\alpha} / \partial s^a \) and \( a^a \partial A^{\alpha a} / \partial s^w \) to also remain bounded. Other terms, namely, \( s^a \rho_\alpha \) and \( a^a \gamma_{\alpha \beta} \), denote the mass of phase \( a \) and interface \( \alpha \beta \) per unit volume of the porous medium, and they also remain finite. Therefore, (37) shows the concept that capillary pressure may rise to infinity to be invalid.

Equations (37) and (39) deserve further study to reveal information about the properly defined capillary pressure function. In applying (44), one must realize that \( P^a \) and \( P^w \) are the macroscopic pressure values at a given location within the porous medium. They are not always in hydraulic equilibrium with values of pressure applied outside the porous medium. This is especially true for a phase which exists at very low saturations or in very low permeability porous media. It seems reasonable that the slope of the capillary pressure versus saturation curve remains small when a phase becomes microscopically disconnected at low saturations.

"Hysteresis" in Macroscopic Capillary Pressure

An important feature of standard macroscopic capillary pressure curves is the hysteresis loop and scanning curves as discussed in conjunction with Figure 5. Practically speaking, there are virtually an infinite number of hysteretic scanning curves that can be contained within the primary hysteresis loop [Morrow and Harris, 1965]. Hysteresis in the capillary pressure versus saturation relationship is attributed to causes such as the geometric nonuniformity of the individual pores, the hysteresis in contact angle, entrapped air, swelling, shrinkage, and aging phenomena [Hillel, 1980]. However, the most widely discussed explanations of hysteresis are the so-called "ink-bottle effect" and "Haines jumps" [Bear, 1972; Corey, 1977; Bear, 1979; Hillel, 1980; Greenkorn, 1983] which are actually one and the same effect.

According to these explanations, interfaces undergo abrupt jumps during a drainage process, so that a higher capillary pressure will prevail during drainage than imbibition. Whether such abrupt movement of interfaces are, indeed, responsible for the phenomenon of hysteresis is strongly doubtful. Proponents of this explanatory theory have not produced incontrovertible proof of it. On the contrary, careful experiments by Crawford and Hoover [1966] and Morrow [1970] have shown that the abrupt movement of interfaces causes very small fluctuations in capillary pressure with amplitudes much smaller than the difference measured between drainage and imbibition curves of a hysteresis loop at a given saturation. What is more, Haines jumps occur not only during drainage but also during imbibition such that a \( P^c \) versus \( s^w \) graph showing the effect of Haines jumps will look like Figure 7.

Regardless of the mechanisms they employ to explain hysteresis, most researchers agree that hysteresis is related to the configuration and distribution of interfaces. It is widely recognized that many different interface configurations, and thus a range of interfacial areas, are possible for a given saturation. Based on estimates of capillary pressure, surface areas, and pore volume for a simplified porous medium, Crawford and Hoover [1966] find that the ratio of surface area to volume would be an important parameter in determining the energetic state of the system. Furthermore, consideration of the microscale situation, as in Figure 4, indicates that apparent hysteresis may arise because of the choice of \( s^w \) as the only independent variable. It seems that the size of the hysteresis loop is perhaps a measure of the lack of understanding of the processes actually occurring rather than an accurate depiction of multiphase behavior in porous media.

The approach proposed here is to obtain a more appropriate representation of the functional dependence of capillary pressure. Equation (41) indicates that capillary pressure should be represented as a function of 11 independent variables. However, this situation may be simplified for many cases of practical interest. Consider the case where the phase densities, interfacial mass densities, temperature, and matrix porosity may be considered constant. Then (41) simplifies to the form

\[
P^c = \Phi^c(a^{w\alpha}, a^{w\beta}, a^{w\gamma}, s^w) \quad (46)
\]
For many soils, the total specific interfacial area of the solid-fluid interfaces, \( a_{ns} + a_{wn} \), will be a constant. Additionally, except at very low saturations, the wetting phase may be considered to completely coat the solid phase such that \( a_{ns} = 0 \) and thus \( a_{wn} \) will be a constant. This further reduces the functional dependence indicated in (46) such that a reasonably streamlined but still rather general functional form for capillary pressure would be

\[
pc = \phi(a_{wn}, a_{ws})
\]  

(47)

With this functional form, instead of working with a \( P^c \) versus \( S^w \) relationship in the form of a two-dimensional "hysteresis plane," one should model capillarity as a three-dimensional surface. That is to say, capillary pressure must be considered as a function of two independent variables. The hysteresis plane may be interpreted as nothing but the projection of the \( P^c-a^w-a^w \) surface onto the \( P^c-a^w \) plane. Projections of that surface onto \( P^c-a^w \) and \( a^w-s^w \) planes are expected to provide "hysteresis loops" similar to those schematized in Figures 8a and 8b, respectively. Of course, the sizes of the loops in Figures 8a and 8b and the values of ordinates and abscissa where intersection with the axes occurs requires experimental study.

CONCLUSION

Microscopic equations of momentum are employed to describe the movement of a meniscus and a contact line formed in a capillary tube. The fluid-fluid interface is modeled as a Newtonian membrane, while the solid-fluid interfaces are modeled as elastic surfaces. The well-known Young-Laplace equation for an interface \( p^n - p^w = 2\gamma^nn/R \) is derived as the equilibrium equation of momentum for the meniscus. The corresponding equilibrium momentum equation for the contact line is the Young equation, \( \gamma^wn \cos \theta = \gamma^ws - \gamma^wn \). An expression for the microscopic capillary pressure, valid also for nonequilibrium conditions, is given as \( p^c = 2\gamma^wn(\nabla^\sigma \cdot N) \). Evidence is presented that the commonly employed equation relating the capillary pressure to the pressure in the bulk phases, \( p^c = p^n - p^w \), must be viewed as an equilibrium force balance and not as a definition of \( p^c \). Hysteresis in the microscopic capillary pressure and contact angle is shown to be related to the elastic forces developed within the solid-fluid interfaces that act upon the contact line and resist its movement within the tube.

The standard approaches for describing macroscale capillary pressure are reviewed. Some approaches are argued to be simple extensions of microscale concepts and equations. As a result, inconsistencies arise in the functional forms suggested for \( P^c \). Although the relationships provided in the literature suggest a connection between macroscopic capillary pressure and the change in Helmholtz free energy due to saturation change, they provide conflicting results. One relation contains the work done by (or the change in energy of) only fluid-fluid interfaces, whereas another relation includes the work of all interfaces. Still other approaches do not contain any terms related to the change in energy of the interfaces, but instead suggest a dependence on the change in free energy of the bulk phases. An alternative approach to describing macroscale capillary pressure is proposed, and it is found that capillary pressure is related to the change in free energy of the two fluid phases and all three interfaces that accompanies a change in saturation. Capillary pressure is seen to be a function of the specific area of the fluid-fluid interface per unit volume \( a^w \), as well as of saturation \( S^w \). The commonly depicted \( p^c \) versus \( S^w \) hysteresis loop should be seen as a projection of the \( p^c-a^w-a^w \) surface onto the \( p^c-S^w \) plane.

APPENDIX A: Microscopic Momentum Balance Equations for a Surface

A classic presentation of the momentum balance equation for a surface was provided by Scriven [1960]. Additional insights appear in the works by Moeckel [1975] and Slattery [1980]. An alternative derivation of this equation that integrates the three-dimensional momentum equation over an infinitesimal layer of fluid has been presented by Gray et al. [1993]. The microscopic momentum equation for a surface is obtained as

\[
\Gamma \frac{D\sigma U}{Dt} = \Gamma g - \nabla^\sigma \cdot S + N \cdot \left[ \rho(v - U)(v - U) - T \right] = 0
\]

(A1)

where
Fig. A1. Unit normal vector N on $a\beta$ interface.

\[ F_{\text{excess}} = \text{mass of the interface (with units of mass per unit area)}; \]
\[ g = \text{acceleration due to body forces}; \]
\[ U = \text{three-dimensional velocity of the interface}; \]
\[ N = \text{unit vector normal to the interface pointing into the } a \text{ phase as in Figure A1}; \]
\[ \nabla_{\sigma} = \nabla - \nabla \cdot N; \]
\[ S = \text{stress tensor for the interface}; \]
\[ D_{\sigma}/Dt = \text{surface material derivative operator}; \]
\[ V = \text{three-dimensional velocity of the interface}; \]
\[ \tau = \text{stress tensor for the phases adjacent to the interface}; \]
\[ [F] = \text{jump in the quantity } F, [F] = F^a - F^\beta. \]

The last term on the left side of (A1) accounts for momentum transfer to the interface from the adjacent phases.

In the present study, (A1) will be simplified for consideration of the case where the inertial and body force terms are unimportant. Furthermore, mass transfer between the surrounding phases and the interface will be neglected. Thus with reference to Figure A1, the momentum balance for the interface becomes

\[ -\nabla_{\sigma} \cdot S^{a\beta} - N \cdot [T^a - T^\beta] = 0 \quad (A2) \]

where the superscripts $a$ and $\beta$ refer to the phases on each side of the interface, respectively, and the stress tensors for the bulk phases are evaluated at the interface. Constitutive relations are needed for the stress tensors appearing in (A2).

First, consider the bulk fluid phases and the fluid-fluid interface to be isotropic and Newtonian. Thus the stress tensors may be written

\[ S^{wn} = \gamma^{wn} l_{\sigma} + \tau^{wn} \quad (A3a) \]
\[ T^a = -p^a l_{\sigma} + \tau^a, \quad a = w, n \quad (A3b) \]

where
\[ \gamma^{wn} = \text{interfacial tension of the interface between the } w \text{ and } n \text{ phases}; \]
\[ p^a = \text{pressure in the } a \text{ phase}; \]
\[ \tau^a = \text{viscous Newtonian stress tensor for phase } a; \]
\[ \tau^{wn} = \text{viscous Newtonian stress tensor for the } wn \text{ interface}; \]
\[ l_{\sigma} = \text{identity tensor}; \]
\[ l_{\sigma} = \text{projected surficial identity tensor, } l = NN. \]

Substitution of (A3a) and (A3b) into (A2) yields

\[ \nabla_{\sigma} \cdot (\gamma^{wn} l_{\sigma}) + \nabla_{\sigma} \cdot \tau^{wn} - N(p^w - p^n) + N \cdot (\tau^w - \tau^n) = 0 \quad (A4) \]

The main focus of this work is the interface. For convenience, then, the viscous effects of the phases interacting with the interface will be neglected. With this simplification employed in (A4), expansion of the first term provides a form that will be particularly useful in subsequent discussions:

\[ \nabla_{\sigma} \gamma^{wn} - N \gamma^{wn}(\nabla_{\sigma} \cdot N) + \nabla_{\sigma} \cdot \tau^{wn} - N(p^w - p^n) = 0 \quad (A5) \]

This momentum balance equation will be applied to microscale interfaces to explain the concept of capillary pressure. In fact, it is the contention here that the proper definition of microscopic capillary pressure, a definition that holds for both dynamic and equilibrium states, is given as

\[ p^c = \gamma^{wn}(\nabla_{\sigma} \cdot N) \quad (A6) \]

Note that this definition depends only on properties of the interface, its interfacial tension and a geometric factor, such that capillary pressure is an intrinsic property of the interface.

Next, consider the solid-fluid interface and assume it to be isotropic and linearly elastic. Therefore the stress tensor for these interfaces may be written

\[ S^{as} = \gamma^{as} l_{\sigma} + \lambda^{as}[(\nabla_{\sigma} e^{as}) + (\nabla_{\sigma} e^{as})^T] \]
\[ + (\lambda^{as} - \eta^{as})(\nabla_{\sigma} \cdot e^{as}) l_{\sigma} \quad a = w, n \quad (A7) \]

where $e^{as}$ is the surface displacement vector for the $as$ interface, $\gamma^{as}$ is the interfacial tension of the $as$ interface, and $\lambda^{as}$ and $\eta^{as}$ are elastic constants. This stress tensor, along with that of (A3a), will be used in determining the forces acting on a contact line.

**APPENDIX B: MICROSCALE MOMENTUM BALANCE EQUATION FOR A CONTACT LINE**

The momentum balance equation for a curve formed as the locus where three phase interfaces come together in space may be inferred from (A1), may be derived by performing a momentum balance on an element of the curve, or may be obtained by integrating the three-dimensional momentum balance equation using the transport and divergence theorems of Gray et al. [1993]. The equation that results is

\[ D_{\sigma} F^c + v^* \cdot [p(u - U)(u - U) - S]_{\text{edges}} = 0 \quad (B1) \]

where
\[ F^c = \text{excess mass of the contact line (with units of mass per unit length)}; \]
\[ u = \text{three-dimensional velocity of the contact line}; \]
\[ \Lambda = \text{unit vector tangent to the contact line}; \]
\[ \nabla^c = \text{curvilinear divergence operator, equal to } \Lambda \Lambda \cdot V; \]
\[ C = \text{stress tensor for the contact line}; \]
\[ D_{\sigma}/Dt = \text{material derivative operator for the contact line}; \]
\[ v^* = \text{normal to the contact line pointing outward to surfaces interacting with the line along its edges}. \]

The last term on the left side of (B1) accounts for momentum transfer to the contact curve from the adjacent phase interfaces. At a given point on the curve, three different $v^*$ exist, one corresponding to each surface. Note that $\Lambda \cdot v^*$ and $\Lambda \cdot N$, where $N$ has been defined as the normal to the interface intersecting the contact curve, will equal zero. Furthermore, $g$, $U$, and $S$ have been defined in Appendix A.
As with the surface momentum equation, \((B1)\) will be simplified for consideration of the case where the inertial and body force terms are unimportant to the curve movement.

Furthermore, mass transfer between the adjacent interfaces and the contact curve will be neglected. Thus with reference to Figure B1, the momentum balance for the contact line becomes

\[-\nabla \cdot \mathbf{C} - \mathbf{v}_{wn} \cdot \mathbf{S}^{wn} - \mathbf{v}_{ws} \cdot \mathbf{S}^{ws} - \mathbf{v}_{ns} \cdot \mathbf{S}^{ns} = 0\]  

\((B2)\)

Constitutive relations for the interfacial stresses are given by \((A3a)\) and \((A7)\). If the contact line is considered to be isotropic and inviscid, the stress tensor \(\mathbf{C}\) will have the form

\[\mathbf{C} = -\gamma^{wns} \mathbf{A} \mathbf{A}\]  

\((B3)\)

where \(\gamma^{wns}\) is the contact curve compression. As a simplification, the viscous effects of the interfaces interacting with the contact curve under dynamic conditions will be neglected. With this condition employed in \((A3a)\), substitution of \((A3a)\), \((A7)\), and \((B3)\) into \((B2)\) yields

\[-\nabla \cdot (\gamma^{wns} \mathbf{A} \mathbf{A}) = -\mathbf{v}_{wn} \gamma^{wn} - \mathbf{v}_{ws} \gamma^{ws} - \mathbf{v}_{ns} \gamma^{ns} - \mathbf{F} = 0\]  

\((B4)\)

where

\[\mathbf{F} = \lambda^{ws} \mathbf{v}_{ws} \cdot [((\nabla \sigma \cdot w^{ws}) + (\nabla \sigma \cdot e^{ws}) \mathbf{T}] + (\lambda^{ws} - \eta^{ws}) (\nabla \sigma \cdot e^{ws}) \mathbf{v}_{ws} + \lambda^{ns} \mathbf{v}_{ns} \cdot [((\nabla \sigma \cdot e^{ns}) \mathbf{T}] + (\lambda^{ns} - \eta^{ns}) (\nabla \sigma \cdot e^{ns}) \mathbf{v}_{ns}\]  

\((B5)\)

The vector \(\mathbf{F}\) accounts for the elastic deformation of the solid-fluid surfaces as a result of the pull of the meniscus on the contact line. Expansion of the first term in \((B4)\) provides a form for the contact line analogous to \((A5)\) obtained for the \(wn\) surface:

\[-\nabla \gamma^{wns} + \gamma^{wns} \mathbf{A} \cdot \nabla \mathbf{C} - \mathbf{v}_{wn} \gamma^{wn} - \mathbf{v}_{ws} \gamma^{ws} - \mathbf{v}_{ns} \gamma^{ns} = \mathbf{F}\]  

\((B6)\)

After determination of the material coefficients, simultaneous solution of \((B6)\) with \((A5)\) (along with the appropriate equations such that the pressures in the phases can be determined) would be necessary to describe the dynamics and geometry of the interface between the two fluid phases. Additionally, the interactive force between the contact line and the surface \(\mathbf{F}\) would also have to be known. Thus full description of the dynamics of a phase interface is very complex.

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(Received June 29, 1992; revised May 10, 1993; accepted May 20, 1993.)