

MISCONCEPTIONS IN THE USE OF SURFACE TENSION IN CAPILLARITY

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SYNOPSIS

This paper deals with some basic concepts of capillarity. Phenomena of solid-liquid systems are reviewed in order to recapitulate relationships involved in cohesion, adsorption, contact angles, and capillary rise. The acceptance in soil mechanics theory of "surface tension" as a physical reality rather than a convenient analogy is rejected. The attempt is made to supply a mechanism for describing equilibrium in soil-water systems which avoids the inconsistencies arising from surface tension, upon which are postulated tensile strength in water, apparent cohesion, and relations involving pore pressure, hydrodynamic excess, and effective shearing stress as inherent properties distinguished from the total forces of resistance necessary for static equilibrium.

It is recognized that any material in equilibrium involves molecular attraction in combination with equal and opposing forces of molecular repulsion. Difficulties arising from the attempts to describe conditions of equilibrium in terms of one or the other force system separately as an inherent property are discussed. Capillary rise is described as the result of internal pressure in the liquid in combination with molecular attraction.

Experimental data from laboratory experiments extending over several years are presented to clarify and demonstrate the mechanism offered to describe capillary rise.

In the development of modern soil mechanics during the past 25 or 30 years there is no subject of more fundamental importance than the mechanics of the soil-water system. In the concepts which have been used to describe the physical forces involved in such a system it has been difficult for any student of the subject to grasp clearly the relationships among adsorption, molecular attraction, capillarity, and cohesion, to cite only the more important concepts.

The misunderstanding seems to originate in a failure to grasp full implication of the conditions required for a material system to be in a state of rest, or to apply rigorously the laws of static equilibrium. It is assumed in this discussion that there is no question that in such a state there must be an equal and opposite reaction for every force which is acting. Thus for any material, liquid or solid, capable of maintaining form or occupying space even for limited periods of time, there must be a balance between opposing forces.

Unfortunately it has become a custom or habit to formulate concepts of such phenomena in terms of the net effects or only the most obvious results which become evident to the observer in his experience with physical

phenomena. Thus in mass attraction, which is akin to molecular attraction, attention is focused on the attraction itself as an inherent property rather than recognizing that bodies subject only to mass attraction could not maintain a fixed position relative to one another unless such attraction was opposed by equal forces of repulsion of some nature which provided static equilibrium.

Faraday, in discussing gravitation, expressed this viewpoint very well in a letter to Maxwell written in 1857¹

"I have nothing to say against the law of action of gravity. It is against the law which measures its total strength as an inherent force that I venture to oppose my opinion; and I must have expressed myself badly (though I do not find the weak point) or I should not have conveyed any other impression. All I wanted to do was to move men from the unreserved acceptance of a principle of physical action which might be opposed to natural truth. The idea that we may possibly have to connect *repulsion* with the lines of gravitation (which is going far beyond anything my mind would

¹ Campbell and Garnett, "The Life of James Clerk Maxwell," MacMillan & Company, London, 1882.

venture on at present, except in private cogitation) shows how far we may have to depart from the view I oppose."

Difficulties of this character have always handicapped physical concepts of materials which must be dealt with in engineering problems. Thus solids are idealized as materials possessing a high degree of rigidity emphasizing cohesion as the specific product of increased molecular attraction. The essential property of liquids is accepted as the ability to resist a decrease in volume under hydrostatic pressure or balanced pressure in all directions. This is a stress condition which emphasizes only the ability of the individual molecules to reserve a specified volume through the forces of repulsion which they possess.

Confusion arises when the attempt is made to define clearly the difference between solids and liquids and to formulate relations for dealing with the transition from the solid to liquid state which takes place in borderline materials. The same confusion becomes even more acute in the soil-water systems of soil mechanics where it is possible to subdivide the liquid and solid phases of the mass and where one becomes involved with solid particles, adsorbed moisture films and capillary forces. In order to handle such problems in more realistic terms it is first necessary to accept that all materials possess the basic properties of both solids and liquids but to a varying degree.

Thus conditions of equilibrium in a liquid must recognize the role of both forces of molecular attraction and repulsion acting in a balanced state. As stated by Rouse² in discussing forces acting at the surface of liquids,

"... the existence of a resultant force normal to any surface must require an equal and opposite force within the fluid if static equilibrium is to prevail; within every liquid body therefor, it must be realized that there will exist an internal pressure of such magnitude as to counteract the surface forces due to unbalanced molecular attraction."

Likewise the state of stress in solid masses includes not only the cohesive forces of molecular attraction but forces of repulsion resulting in cubical compression directly comparable

to hydrostatic pressure of a fluid. Consequently the behavior of solids and liquids can only be truly portrayed in terms of both sets of forces and the predominance of one over the other.

One of the most frequent sources of misconception in soil mechanics is the attempt to postulate tensile resistance in water as an inherent property derived from molecular attraction. Clarification of this point requires a definition of tension in the structural sense as a phase of the strength of materials accompanied by a recognition that molecular attraction and tensile resistance are not synonymous.

In a liquid the balance between molecular forces of attraction and repulsion is such that a confined mass resists decrease in volume under applied pressure due to forces of repulsion between molecules, but these molecules are not fixed in position and are free to move about at will. In the absence of confining forces on the boundaries of the mass the liquid has complete mobility and no inherent resistance to change in shape. In such a material the forces of repulsion may be said to be predominant. Molecular attraction between molecules serves only to prevent the mass from expanding in volume and is insufficient to provide resistance to change in shape or resistance to being pulled apart which is a characteristic of structural solids.

On the other hand in a solid the molecular attraction has become sufficiently predominant that the molecules become fixed in position forming definite linkage within the mass. Such a mass has rigidity and resistance to change in shape characteristic of structural solids. Cohesion, tensile strength and shearing resistance become physical realities in a material capable of sustaining application of force in static equilibrium without artificial support. In a general sense the transition from the solid to the liquid state provides no sharp dividing line and there are many materials such as plastic solids which supply both characteristic reactions within the ordinary range of observation and practical application.

The following definitions have been written to summarize the viewpoint presented:

Tensile strength is the resistance to being pulled apart in those materials in which the forces of molecular attraction are sufficiently predominant to produce a solid structure with

² Rouse, "Elementary Mechanics of Fluids," John Wiley & Sons Inc., New York, 1946, p. 315-317.

molecules fixed in position in contrast to their mobility in a liquid.

Cohesion is defined as that property of a material which produces resistance to displacement by mutual attraction between particles involving forces of molecular origin characteristic of microscopic and submicroscopic matter. In soil-water systems this definition is intended to include both adhesion and cohesion as ordinarily defined and to imply ability to sustain applied forces in static equilibrium.

Shearing resistance in a purely objective sense may be defined as resistance to tangential displacement under the application of tangential force. Static shearing resistance in solids is the product of molecular attraction which is sufficiently predominant over forces of repulsion to sustain measureable shearing stress in a condition of static equilibrium.

The mechanics of cohesion in the soil-water system as developed by some investigators in the field of soil mechanics has become a rather intricate subject with a number of elusive concepts which require most precise thinking if one is to distinguish between reality and hypothesis and select only those ideas which are fundamentally sound. Terzaghi³ has presented this subject from the viewpoint of soil physics in a series of articles on the principles of soil mechanics published in 1925 which, in his more recent publications, remain substantially unchanged. Every student of soil mechanics should give these articles thoughtful study as they represent the foundation for a general theory of soil behavior which many find hard to accept but difficult to refute.

Apparent Cohesion—Terzaghi summarizes his conceptions of the phenomena of cohesion of clay as follows:⁴

"The cohesion of clay is due to two factors. One of these is the pressure exerted by surface tension of the capillary water, a force whose intensity exceeds all other forces the earthwork engineer has to deal with. It may amount to several hundred atmospheres; it compacts loose, colloidal sediments more thoroughly than can be done by artificial means except in the

laboratory by using a high power testing machine. Swelling of clay is nothing more or less than the purely elastic expansion produced by the elimination of the surface tension of the capillary water. Local evaporation of the capillary water or local flooding of the surface of clay deposits produces secondary stresses the intensity of which is far greater than the weight of the heaviest structures and which were found to be the primary cause of many vast soil displacements known as earth slips.

"The second one of the factors mentioned consists in the fact that the properties of water contained in voids of width less than 0.0001 mm. are no longer identical with those of ordinary water. In such voids, viscosity and surface tension are increased (in inverse proportion to the diameter of the voids) and the water loses its ability to evaporate in contact with the air. Thus the capillary water of the clays is to a certain degree solidified by the influence of the forces exerted by the molecules of the solid matter. Due to this fact the capillary pressure assumes far greater values than it would if the surface tension of the capillary water had its normal value."

Based upon these concepts a theory of the mechanics of cohesion in clay has been fabricated, and enlarged to include a general theory of soil mechanics which represents a path that a student of soil mechanics may follow unless an intimate knowledge of the phenomena involved reveals some fundamental fallacy. In the writer's opinion this path leads to a bog of soil physics from which modern soil mechanics has not yet been extricated and from which the only escape is to turn back and seek more solid ground for further advance.

Surface Tension—In addition to accepting surface tension as a physical reality instead of a mathematical device substituted for the actual forces which give rise to free surface energy, Terzaghi postulates tensile resistance in water while admitting no shearing strength in the accepted sense. On the other hand, authorities in physics and physical chemistry are emphatic in pointing out that there is no contractile skin on liquid surfaces and that in reality there can be no tensile stress. Adam⁵ makes quite clear the character of surface tension as a mathematical device for dealing with problems involving surface energy and

³ Terzaghi, "Principles of Soil Mechanics," *Engineering News-Record*, Vol. 95, 1925.

⁴ Terzaghi, "Principles of Soil Mechanics: Compressive Strength of Clay," *Engineering News-Record*, Vol. 95, p. 796 (1925).

⁵ Adam, "The Physics and Chemistry of Surfaces," Oxford University Press, 1930, p. 4.

points out the danger in mistaking it for a physical reality:

"The great convenience of the hypothesis of surface tension, as the equivalent of free surface energy, combined with the fact that it was in use nearly a century before the conception of energy became definite, has given the words 'surface tension' a predominance in the literature of surfaces, which does not rightly or logically belong to them. The term 'surface tension' has often been strained to imply that liquids have in their surfaces some mechanism like a stretched membrane pulling parallel to the surface. The surface is said to be in a 'state of tension'. This view must not be pushed too far. Any mechanism possessing free energy in the surface will undergo the spontaneous contraction which has led to the idea of surface tension; hence we can gain practically no idea of the actual nature of the mechanisms in the surface, from this fact of spontaneous contraction alone. The view that there is some skin in the surface, pulling parallel to it, leads to great difficulties when the structure of the supposed skin is considered in terms of molecules. Some of these will now be mentioned; others will appear later in the book."

"On molecular theory, positive surface free energy, or surface tension, is due to an inward attractive force, exerted on the surface molecules by the underlying molecules. There is no special force between the surface molecules, pulling parallel to the surface. . . ."

"... the essential mechanism, even in Laplace's theory (which subdivides the liquid indefinitely), of the production of the free surface energy, is the perpendicular inward attraction, exerted on the surface molecules by the underlying ones; there is no need to speculate how this can be transformed into a surface tension parallel to the surface, for the surface tension does not exist as a physical reality, and is only the mathematical equivalent of the free surface energy. The mathematical device will always be available as a substitute for this free energy, whatever the mechanism by which this energy is produced molecularly; it can, therefore, never tell us anything about the mechanisms at the surface."

The literature of modern soil mechanics frequently includes misconceptions which have arisen from the mistake of describing soil behavior in terms of "surface tension" and it is extremely important at the outset to recognize that here is one point where reality and hypothesis lead in different directions. The proper use of this mathematical device, as in

explaining the physical chemistry of surfaces, may not be objectionable, but it certainly would be desirable to find the true mechanism of the actual forces of molecular attraction which operate in liquids and at liquid surfaces. Rouse² states:

"For many years the surface phenomena discussed . . . were explained in terms of an apparent tension in an elastic skin or membrane which was thought to form at every liquid surface. It was, of course, never decided why the stress in such a skin remained constant no matter how much it was stretched, or how the skin could cling tenaciously to a solid boundary and at the same time slide freely along the boundary as the liquid surface was displaced. As a matter of fact, there are so many physical inconsistencies in the surface-tension concept that the continued designation of [surface energy by] the *coefficient of surface tension* is, to say the least, misleading. Oddly enough, however, the quantitative evaluation of surface phenomena by means of the surface-tension concept yields perfectly accurate results, despite the erroneous physical picture upon which it is based. Indeed, the use of the force diagrams involved in this concept still provides the only simple means of deriving many of the fundamental relationships for surface energy."

The necessity for bridging this gap becomes quite apparent when one reviews attempts that have been made to oppose some of the unsound hypotheses that have arisen in modern soil mechanics. Merriman,⁶ in 1925 questioned the validity of the tremendous forces of capillarity postulated by Terzaghi by an appeal to common sense logic. But this opposition passed with little notice because it was not supported by pointing out the fallacy in surface tension. However, the effort is interesting reading for the student of soil mechanics and the correspondence has, therefore, been appended to this discussion. Merriman's arguments could have been much strengthened by pointing out that in a soil-water system subjected to evaporation and shrinkage any increase in molecular attraction accompanying a decrease in moisture content and thickness of moisture films is constantly kept in balance by an equal increase in film pressure due to forces of molecular repulsion. This balanced condition within the mass offers no basis for postulating any external force application on

⁶ See Appendix A.

the boundary of the mass which could subsequently find no reacting force from within to provide equilibrium.

ADSORPTION AND CAPILLARITY

In recapitulating the fundamental concepts of soil-water systems to provide a mechanism for describing true cohesion it is necessary to review briefly the essential elements of adsorption of liquids on solid surfaces, wetting phenomena, and capillarity. The attempt to do this is considerably complicated by the continued and universal use of the mathematical device of "surface tension" even after it was widely accepted that no such tension existed as a physical reality. It is probable that any mechanism offered as a substitute for "surface tension" in an attempt to come closer to the truth will meet with considerable resistance and cause controversy. Nevertheless such an attempt must be made, for to do less would only perpetuate existing misconceptions.

Capillarity is generally measured by the extent of rise in a capillary tube while the free energy of solid and liquid surfaces is measured in terms of a number of adsorption effects which are described in detail in standard texts on physical chemistry. Attention will first be directed to the universal property of solid surfaces of adsorbing substances such as liquids which come into contact with them, producing various wetting phenomena through purely physical adsorption.

Mechanism of Adsorption—Physical adsorption is a reversible process producing layers on the surface of a solid which achieve a state of equilibrium through a balance between condensation and evaporation. These films are generally conceived as monomolecular at least in the adsorption of gases, while in liquids orientation of molecules may extend beyond the surface layer producing films many molecules in thickness. Langmuir has formulated a theory of gaseous adsorption which appears to provide an ideal mechanism for describing wetting phenomena.⁷ In Figure 1(a) is represented the lattice of a solid surface containing elementary spaces each one of which represents the position of an elementary particle to which a molecule in the adsorbed layer may

become attached. In the more complex materials it is not to be expected that all of the elementary spaces are alike, but rather that they may represent different kinds of particles with varying capacities to attach and hold molecules which impinge upon the surface. Depending upon the vapor pressure and temperature, condensation and evaporation are constantly going on at the solid surface, and Langmuir has extended his theory to quantitatively estimate the rate at which molecules come into contact with the surface and the "relative life" or period of attachment to the surface.

Extending the mechanism to the situation in which a liquid and a gas are brought into contact with the solid surface, it is not difficult to conceive how the replacement of one by the other may progress. Assuming that the forces of attraction of the solid surface for the liquid are considerably greater than for the gas, the replacement of adsorbed gas should take place as rapidly as the processes of condensation and evaporation would allow. In other words, unoccupied elementary spaces are filled and those which are vacated by gas molecules are as rapidly replaced by the more highly adsorbed liquid molecules, and not again made available. The preferential adsorption of the liquid would progress until the three-phase system came to some state of equilibrium.

In Figure 1(b) is shown a drop of liquid on a solid surface. Following the reasoning of the previous paragraph, the drop would spread out on the surface until the advancing front of the liquid achieves a state of equilibrium.

As shown at the left-hand drop front, in terms of surface tension the spreading of the drop of liquid is described as if a tensile force T_{sg} were being exerted parallel to the solid surface acting to extend the liquid. Conversely, the attraction of the solid surface for the gas tends to extend the film of adsorbed gas or restrain the liquid from spreading and is represented by an opposing tensile force T_{sl} also parallel to the surface and equal to the free energy of the liquid-solid interface. A third tensile force T_{gl} represents the "surface tension" on the liquid-gas interface and is conceived to be a force acting at the contact angle θ which establishes equilibrium. These are the tensile forces that are substituted for the actual forces of molecular attraction and repulsion which act at the three interfaces.

⁷ Friend, "Textbook of Physical Chemistry," Chas. Griffin & Co., Ltd., London, Vol. 1, p. 427.

The equilibrium of these tensile forces is a special case of Neumann's triangle,⁸ a relationship used in physical chemistry and derived from a force polygon for a drop of liquid floating in another liquid in which it is immiscible. The equilibrium of such a system of forces may be satisfied in the latter case but in the case of a drop of liquid spreading on a plane

the use of surface tension to define the stable contact angle of a drop of liquid resting on a solid surface:

$$T_{SG} = T_{SL} + T_{GL} \cos \theta$$

Recalling that unbalanced forces of molecular attraction acting at liquid surfaces create internal pressure within the liquid, it may be

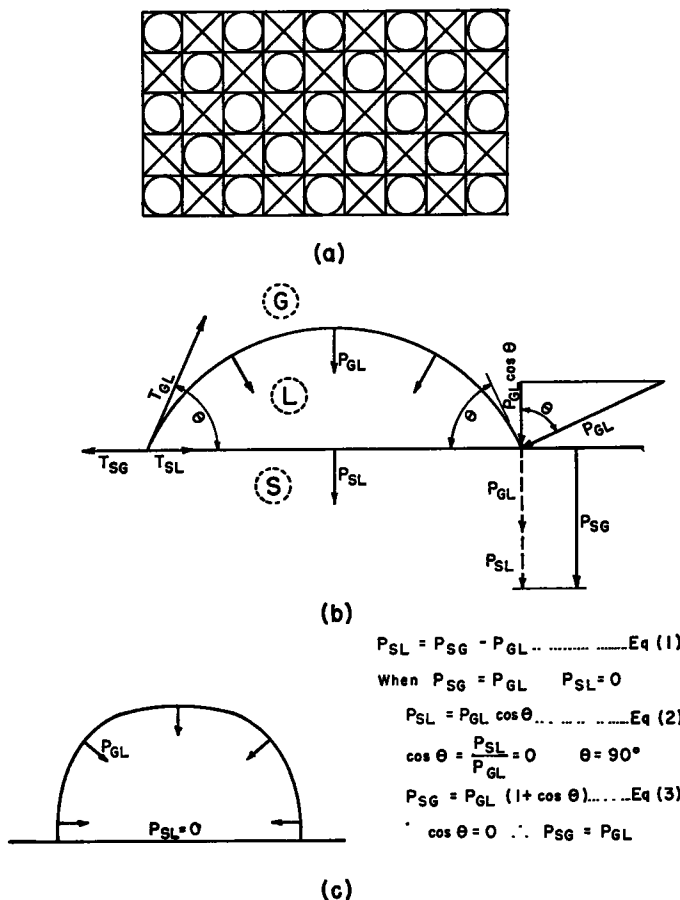


Figure 1. Adsorption on a Solid Surface

solid surface Neumann's triangle violates the well known axiom of statics that when two of three concurrent forces T_{SG} and T_{SL} are colinear, the third force T_{GL} must be zero. In spite of this definite violation of the laws of static equilibrium the following equation is the conventional relationship resulting from

⁸ Adam, *Op. Cit.* p. 255.

more realistic to describe spreading of the drop in terms of internal pressures in the liquid body rather than in terms of hypothetical surface tension. Thus the state of equilibrium may be reached when the internal pressure within the drop is balanced by the adhesion pressure of the solid surface for the gas. If the attraction of the solid surface for the liquid is sufficiently in excess of that for the

gas the contact angle may be zero and the liquid film may spread out until it approaches a monomolecular film and it is said to perfectly wet the solid surface. When the liquid molecules are adsorbed the unbalanced molecular attraction along the solid-gas interface is decreased by an amount equal to the molecular attraction of the liquid for its own molecules.

The unbalanced molecular attraction remaining in the liquid-solid interface is the difference between the adhesion pressure on the solid-gas interface and the unbalanced molecular attraction of the liquid-gas interface. The relationship of the molecular forces of attraction on the two solid interfaces may be expressed by the following equation:

$$P_{SL} = P_{SG} - P_{GL} \quad (1)$$

Thus the actual forces of molecular attraction acting perpendicular to the interfaces of solid, liquid, and gas phases produce equilibrium of the drop at a stable contact angle as shown on the right-hand drop front in Figure 1(b). These forces of molecular attraction create internal pressure or film pressure within the drop which must be equal and opposite in effect. These pressures are shown as the forces per unit area (P) with subscripts designating the respective interface. At the drop front where the gas-liquid interface merges with the solid-liquid interface continuity requires equality of the film pressures within the liquid phase. Considering the directional characteristics of the attraction on the gas-liquid interface, equality of film pressure referred to the horizontal surface is given by:

$$P_{SL} = P_{GL} \cos \theta \quad (2)$$

This equation establishes the stable contact angle θ .

Spreading of the drop may be described in terms of the hydraulic gradient between the internal pressure within the liquid at the drop front and the adhesion pressure or film pressure on the solid-gas interface P_{sg} . Equilibrium between the liquid and gas on the solid surface is given by Eq. (1) and may also be written as follows by combining Eq. (1) and Eq. (2):

$$P_{sg} = P_{GL}(1 + \cos \theta) \quad (3)$$

One check on the validity of Equations (1), (2), and (3) is illustrated by the special condition shown in Figure 1(c) representing a con-

tact angle of 90 deg. In this case there is no unbalanced molecular attraction along the solid-liquid interface so the film pressure reduces to the internal pressure within the drop due to the unbalanced molecular attraction of the gas-liquid surface. Under the internal pressure concept the film of liquid would push off the film of gas as long as the film pressure within the liquid phase exceeds that of the gas phase and vice versa. Such a description of the replacement of one film by the other would seem to be a more realistic concept for formulating in mathematical terms the selective adsorption more minutely portrayed by Langmuir.

The mechanism suggested in the previous discussion is one of hydraulic flow in accordance with principles of fluid mechanics, and would seem to apply more accurately to this situation than static tension which comes from the field of elastic solids. In terms of fluid flow the film pressure exerted at the liquid-solid boundary on the inside of the advancing front of the drop causes a decrease in θ until the internal pressure $P_{GL} + P_{GL} \cos \theta$ becomes equal to the external pressure P_{sg} . At that point under a zero hydraulic gradient, flow ceases and the drop is in equilibrium.

A similar line of reasoning may be applied to liquids which attract their surface molecules more than they are attracted by the solid. The net force at the solid-liquid interface is directed toward the interior of the liquid rather than the solid and the liquid surface is retarded rather than advanced. From the standpoint of soils, however, the interest is largely in the behavior of capillary water which in general wets the solids completely.

Adhesional and Cohesional Work—It may be pointed out that the form of Eq. (3) is identical with the conventional equation for the work of adhesion between two substances except that it was derived by reference only to the forces of molecular attraction and does not involve work. Eq. (3) also reduces to the conventional relation for the work of cohesion when the contact angle becomes zero, representing perfect wetting of a solid by a liquid.

The substitution of work supposedly done in the formation of surfaces within liquids for the free surface energy created when the surfaces are formed is a generally accepted device for avoiding some of the inconsistencies of

surface tension. The work approach may be questioned, however, on the basis that work requires the application of force acting through a finite distance. In the separation of a liquid, the forces of molecular attraction mobilized in opposition reach their full value at the instant of separation before any finite distance

equivalent to the postulated work of cohesion is that the molecular forces of attraction exerted at the solid surface are equal to or greater than twice the molecular attraction of the liquid. When the molecular attraction of the solid was equal to the molecular attraction of the liquid as would be represented in the work of cohesion, the interfacial attraction is zero and the drop assumes a contact angle of 90 deg. without further spreading as shown in Figure 1(c).

Capillary Rise—While the preceding discussion of wetting phenomena and contact angles may aid in selecting a mechanism to describe capillary rise, it is pertinent to cite the views of several writers and investigators who have studied this subject. Leslie in 1802 first introduced the conception of closer packing of molecules near the solid boundary, but later writers have generally discarded this idea in favor of the surface tension mechanism. Other writers including Adam⁹ take the position that there is no need to speculate on the specific mechanism but that "... the energy relations determine the stable contact angle; the fluidity of the liquid permits the molecules to move about until they rest at this stable contact angle; the contact angle and the curvature of the tube curve the liquid surface; the pressure difference follows from the free energy resident in the surface and the liquid then flows up the tube under the hydrostatic pressure."

It is interesting to analyze the latter statement, which actually does not avoid the assumption of a specific mechanism which is in fact the mathematical device of "surface tension". It was stated that free energy relations determine the contact angle and that the contact angle determines the free energy relations because of a pressure difference across the curved surface of the meniscus. This situation is illustrated by a capillary tube of unit cross section in Figure 2(a). The assumption that there is a pressure drop ($p_1 - p_2$) across the meniscus in the capillary can only be true if there actually is a surface with physical tension. Further than this, static equilibrium necessitates that this "skin" be attached to the walls of the capillary so as to provide a reaction external to the water column sufficient

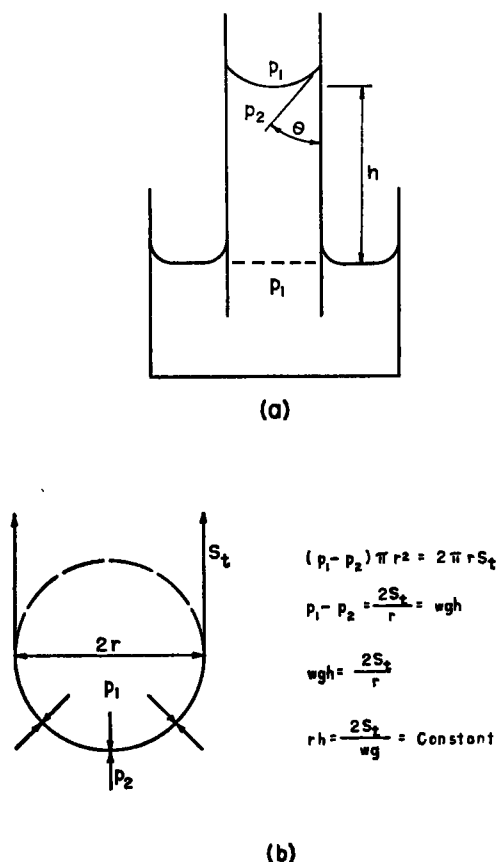


Figure 2. Surface Tension Analogy in Capillary Rise

is involved and under conditions at which the work done approaches zero.

Furthermore it may be pointed out that the force required to separate a column of liquid of unit cross section is only one-half of the unbalanced molecular attraction created. This is true because these unbalanced forces bear the relation to each other of action and reaction and cancel out when the interfaces are brought together leaving a net unbalanced force of zero. The reason that Eq. (3) is

⁹ Adam, *Op. Cit.* p. 17.

to support the net vertical force downward. The pressure differential across the curved surface is the most widely accepted conception, and many writers deny that this necessarily implies physical tension in the surface layer and attachment to the walls of the tube. Such a view cannot, however, be demonstrated by a rigorous application of the principles of static equilibrium.

If "surface tension" were a physical reality and the curved meniscus did transfer the vertical component of the pressure differential which it carries to the walls of the capillary, then the mechanism of capillary rise would become quite simple. The meniscus becomes analogous to the piston in a pump and the liquid is forced up in the tube by hydrostatic pressure until the static head wh is equal to the pressure differential across the meniscus. The capillary rise h would vary inversely as the radius of the tube when the curvature of the meniscus is spherical and the surface tension a constant. These relations are shown in Figure 2(b) and represent the generally accepted idea of capillary rise. Several of the methods devised for measuring surface tension also measure capillary rise and employ the relation that the weight of liquid in the capillary raised above the free surface of the liquid is a measure of the capillary pull of surface tension.

That the product rh of the radius of curvature and the height of capillary rise is a constant was the first fact that was discovered from capillary rise experiments. This product is known as the capillary constant and its value was firmly established by the measurement of capillary rise in small tubes for which the meniscus was assumed as circular so that the radius of curvature could be taken as the radius of the tube. From this it follows that, for any given liquid of density w under standard conditions of temperature, pressure, and type of capillary, the "surface tension" would be constant. Measurements of capillary rise and related phenomena have been universally expressed in terms of "surface tensions" as might be expected from the simplicity of the relations and the apparently consistent manner with which the device fitted the experimental observations. Study of other phenomena having to do with the nature of liquid surfaces led to the view that surface tension was not a physical reality but simply a con-

venient analogy. In this connection it is pertinent to point out that in capillary rise measurements the capillary constant is the factor which has actually been observed and surface tension is an interpretation of that constant. One other experimental fact stands out: the effect of capillarity, whatever the mechanism, is to support a given quantity of liquid above the surface of the free liquid, and it can be measured in those terms.

If surface tension is not a physical reality it appears that the search for a substitute mechanism must recognize three facts firmly established by experiment. In the first place, the product rh known as the capillary constant has been established under specific conditions by what appears to be ample experimental evidence. Second, the weight of any liquid raised above the free surface by capillarity is a measure of the forces of capillarity and these forces must exist in the system whereby static equilibrium can be established. Third, capillarity has its origin in the presence of a solid surface in contact with a liquid and, therefore, must be a boundary effect inseparable from the solid-liquid surface.

Referring again to the discussion of a drop of liquid spreading on a horizontal solid surface as shown in Figure 1(b), it was postulated that spreading took place under an internal pressure in the drop in excess of the adhesion pressure of the gas outside the drop; when the hydraulic gradient at the edge of the drop became zero spreading ceased. It is now proposed to discuss capillary rise from this viewpoint as a problem of fluid mechanics, extending the relations to a liquid in contact with a vertical solid surface. In the case of a drop spreading on a horizontal surface, when the contact angle becomes zero the drop spreads indefinitely, completely wetting the surface because there were no available forces to establish a stable form of the liquid body. This is not true in the case of the vertical surface as the vertical spreading encounters the force of gravity as a reaction when the liquid is elevated above the free surface. Following this approach the contour of the curved liquid surface near the solid boundary should represent the hydraulic gradient from the solid surface to the point at which the curvature becomes tangent to the free liquid surface as shown in Figure 3.

It is first necessary to review the relation

between the forces of molecular attraction available at the various interfaces and the contact angles that may result. These forces of attraction and the equivalent film pressures

solid surface. When the solid attracts the liquid with the same intensity that the liquid attracts its own molecules the net pressure P_{SL} will be zero and the solid has no effect on the free

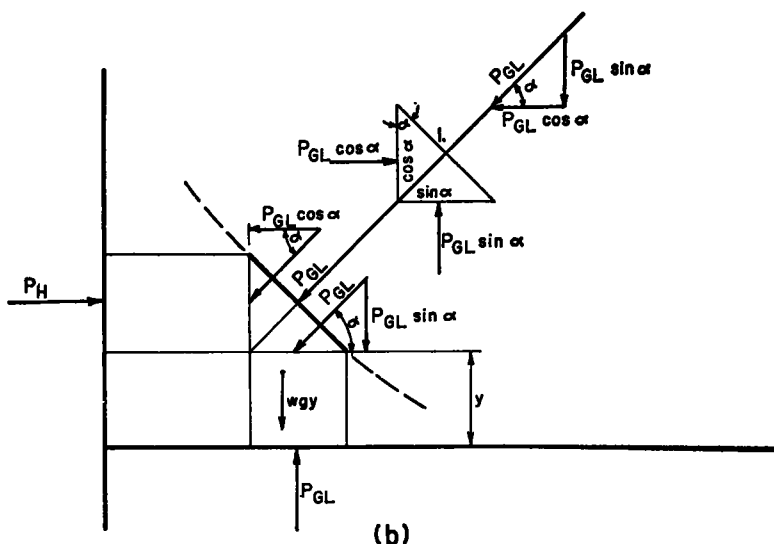
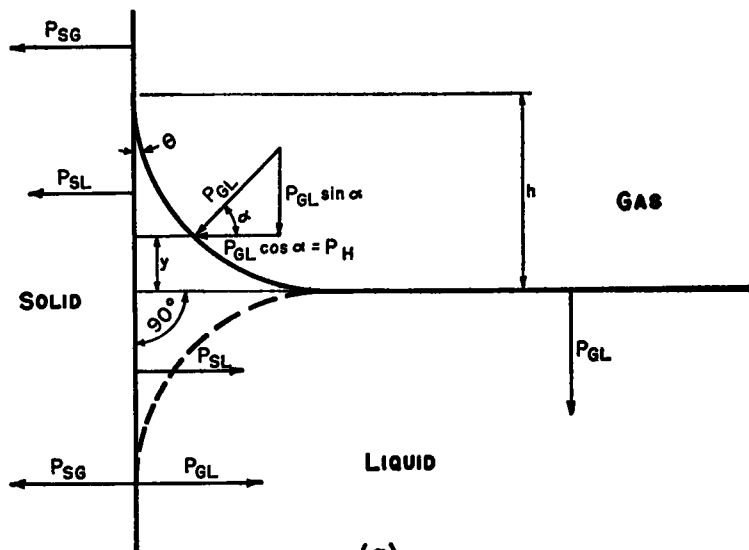


Figure 3. Equilibrium of the Meniscus

are designated by the same letters and subscripts as before. When the liquid is considered as being in contact with the solid surface the algebraic sum or net film pressure P_{SL} will determine the behavior of the liquid at the

liquid, or the contact angle is 90 deg. This is equivalent to saying that the gas is attracted to the solid with the same intensity that the liquid is attracted, or the gas film pressure P_{SG} is equal to the liquid film pressure P_{GL} .

When $P_{sg} = P_{gl}$,

$$P_{sl} = P_{sg} - P_{gl} = 0$$

Substituting in Eq. (2),

$$\cos \theta = \frac{P_{sl}}{P_{gl}} = 0$$

and

$$\theta = 90^\circ$$

When the attraction P_{sg} is greater or less than the attraction of the liquid for itself, the net attraction P_{sl} is exerted on the liquid in the vicinity of the solid causing the liquid to be elevated or depressed from the free liquid surface. In terms of film pressure this situation amounts to the adhesion pressure of the gas P_{sg} being greater or less than P_{gl} by the amount of the added film pressure P_{sl} due to the net attraction available at the solid surface. The curvature of the liquid or the meniscus then takes a form dictated by the equilibrium of forces available at the solid surface. Equations (1) and (2), set up to define the conditions of equilibrium in a drop of fluid on a horizontal solid surface, may be applied as before. When $P_{sg} = 2P_{gl}$,

$$P_{sl} = P_{sg} - P_{gl} = P_{gl}$$

$$\cos \theta = \frac{P_{sl}}{P_{gl}} = 1$$

$$\theta = 0^\circ$$

This is a case of perfect wetting presumably representative of water in contact with glass or possibly soil solids. Values of $\cos \theta$ between zero and unity represent contact angles associated with positive values of capillary rise varying from no wetting to perfect wetting with net attraction or additive film pressures P_{sl} varying from zero to unity.

Cases in which the potential attraction of the solid for the liquid is less than the attraction of the liquid for itself result in depression of the liquid in contact with the solid with the net or resultant force P_{sl} being directed toward the liquid and away from the solid surface. In terms of film pressure this is equivalent to saying that the adhesion pressure of the gas P_{sg} is greater than the film pressure of the liquid itself P_{gl} .

There is, however, one additional case which requires discussion, and that is the effect on capillary rise if the attraction of the solid sur-

face exceeds the value of twice the molecular attraction of the liquid for itself ($P_{sg} > 2P_{gl}$). Authorities differ on whether or not the adhesion pressure in excess of $2P_{gl}$ increases the height of capillary rise or if the value which results in an angle of $\theta = 0^\circ$ is the limiting case of capillarity. Certainly a value of $\cos \theta$ greater than unity has no significance, but it is possible that an adsorbed film of moisture may exist at an angle of zero with the solid surface for a considerable height in excess of the actual capillary rise as determined by the meniscus. In that event, it is sometimes considered that actually the capillary rise takes place as if the walls were lined with water rather than being a solid surface. If this is the case it is not clear how the attraction of water on water can be sufficient in itself to produce the adhesion pressure required for capillary rise. It appears that for the film pressure just inside the fluid body to become equal to the adhesion pressure of the solid surface requires a double interface with additive molecular attractions; in the case of water on water a double film thickness with additive molecular attractions could not exist independent of the solid surface.

Thus it seems logical that capillarity might reflect solid surface adhesion pressures in excess of the value $2P_{gl}$ in a capillary rise greater than the conventional values based on the unbalanced molecular attraction of the liquid-air interface, but limited, however, to the monomolecular film making up the double interface. It also seems reasonable that in the case of capillary openings approaching molecular dimensions, such as may be encountered near contact points between soil particles, adsorbed moisture films become quite independent of gravity effects and capillarity in the usual sense as applied to a meniscus in a capillary tube, which in effect is dependent upon the film pressure in the liquid itself.

Static Equilibrium in Capillary Rise—Attention may now be devoted to the forces in the vicinity of the solid surface under which a body of water within the meniscus is elevated above the free water surface and maintained in static equilibrium. It is postulated that the attraction of the solid surface has a net component P_{sl} in a horizontal direction which serves to rotate the unbalanced molecular

attraction P_{GL} of the liquid-gas interface from its normal vertical direction. This leads to the upward curvature of the liquid-gas interface which then represents the hydraulic gradient within the body of liquid in its stable form. At this point it may be noted that no special curvature is assigned to the hydraulic gradient and the manner in which the angle α may vary between its terminal values is indeterminate. Insofar as this curved surface is concerned its continuity is expressed by the following equation which becomes Eq. (2) at the solid surface where the angle α becomes the contact angle θ and the horizontal component P_H becomes P_{SL} .

$$P_H = P_{GL} \cos \alpha$$

When $\alpha = \theta$, $P_H = P_{SL} = P_{GL} \cos \theta$

At the other extremity of the curved surface where it becomes tangent to the free liquid surface the angle of inclination α is 90 deg. and the horizontal component disappears. Here some attention should be given to the generally accepted evidence in physical chemistry that the molecular attraction P_{SL} of the solid for the liquid does not extend much beyond a monomolecular layer in contact with the solid surface. In the above discussion and as shown in Figure 3 the horizontal component P_H originates in the molecular attraction P_{GL} of the liquid itself and does not include the additive molecular attraction P_{SL} until the liquid-gas interface comes in contact with the solid surface. This situation and the relation between the forces acting perpendicular to the various interfaces has already been defined by Equations (1) and (2). Continuity within the liquid body is expressed by Eq. (2) where coincidence of the liquid-gas interface and liquid-solid interface requires equal film pressures referred to the vertical surface. Equality of film pressure within the liquid and adhesion pressure of the gas is expressed by Eq. (3).

Admitting no additional molecular attraction from the solid surface as acting on the body of liquid within the meniscus necessitates a further search for the mechanism by which this weight of liquid is sustained above the free liquid surface. The conditions of equilibrium within the meniscus are shown in Figure 3(b). It is postulated that due to the directional characteristics of the molecular

attraction of the liquid-gas interface, the force intensity P_{GL} may be projected along its line of action to a horizontal plane on which surface its influence in a vertical direction is represented by the downward component $P_{GL} \sin \alpha$.

If y is the distance to which the water is elevated above the free liquid surface, g the acceleration of gravity, and w the density of the water, then the following equilibrium equation may be written for the element of water involved translated into force units.

$$\begin{aligned} wgy &= P_{GL} - P_{GL} \sin \alpha \\ y &= \frac{P_{GL}(1 - \sin \alpha)}{wg} \end{aligned} \quad \text{Eq. (4a)}$$

When $\alpha = \theta$, $y = h$,

$$h = \frac{P_{GL}(1 - \sin \theta)}{wg} \quad \text{Eq. (4)}$$

Similarly the force intensity, P_{GL} projected onto a vertical plane produces a horizontal component $P_{GL} \cos \alpha$ balanced by horizontal reacting pressure P_H which becomes a film pressure P_{SL} when α is equal to the contact angle θ at the solid surface. This provides another approach to Eq. (2).

At the same time it should be noted that equilibrium of the triangular element involved in the segment of the curved surface may be satisfied in terms of the total forces acting on that element as shown in Figure 3(b). Thus it is seen that the internal pressure P_{GL} is acting on all planes in the liquid, a condition necessary to equilibrium in a body incapable of sustaining any shearing stress. It should be emphasized that this unusual relationship of force intensity or pressure and total forces is peculiar to a solid-liquid system involved in capillary rise. This relationship is predicated on the concept that the molecular attraction in the gas-liquid surface has distinctive directional characteristics which limits its influence in a vertical direction in opposition to the internal pressure in the liquid. This may be due to the fact that a portion of its total thrust is dissipated in building up a horizontal pressure component against the solid surface.

In this connection it may be pointed out that if capillary rise were related to the horizontal component of the molecular attraction

of the liquid surface, Eq. (4) would be written as follows:

$$h = \frac{P_{GL} \cos \theta}{wg}$$

This form of the expression for capillary rise corresponds to the conventional equation. Considering now the discussion concerning the significance of values of $\cos \theta$ greater than unity, in Eq. (4) it is apparent that $(1 - \sin \theta)$ avoids this uncertainty, for Eq. (4) sets the limiting value of capillary rise as being proportional to the molecular attraction of the liquid-gas interface P_{GL} .

The object of the discussion so far has been to provide a mechanism for describing capillary rise to replace hypothetical surface tension, and to demonstrate its validity as satisfying the laws of static equilibrium. When both molecular attraction and repulsion are recognized as necessary to equilibrium in a stable solid-liquid system the phenomenon of capillarity seems to be more accurately described as a push rather than a pull. In other words, in capillary rise the liquid is elevated above the free liquid surface by the internal pressure of the liquid rather than being pulled up and supported by tension in the water.

The internal pressure referred to in this concept is that created by the unbalanced molecular attraction of the free liquid surface quite independent of the hydrostatic pressure which increases with the depth. This internal pressure is a constant within the liquid body above and below the free liquid surface. The conventional hydrostatic pressure, which is a function of the depth below the free liquid surface, is then limited to the body of liquid below that free surface. Within the capillary column the pressure remains constant, rather than being represented by a negative hydrostatic pressure which is sometimes superficially used to avoid the hypothetical tension.

The manner in which static equilibrium in capillary rise is achieved is represented in Figure 4. In part (a) is shown the pressures acting on the body of liquid above the free liquid surface. For purpose of illustration the size of capillary has been selected so that the meniscus is tangent to the free liquid surface at the center where the capillary rise would be zero.

In part (b) are shown the equivalent pressures on the body of liquid, consisting of the internal pressure of the liquid P_{GL} acting upward and undiminished over the full cross section, and the projected pressure from the unbalanced molecular attraction on the liquid surface of the meniscus acting downward. Due to the directional characteristics of the molecular attraction at the liquid surface, the projected pressure on a horizontal plane is diminished to the vertical component of the inclined pressure, which varies from maximum at the center to minimum at the solid boundary.

The meniscus is then curved upward in the vicinity of the solid boundary with vertical ordinates above the free liquid surface as prescribed by Eq. (4a). This ordinate becomes a maximum at the solid boundary. The area under this curve above the free liquid surface shown cross-hatched in Figure 4 represents the ability of the system of forces originating in the presence of the solid boundary to sustain or support a volume of liquid in static equilibrium above the free liquid surface. In circular capillary tubes this area is a cross-section of a volume of revolution representing the total volume of liquid sustained above the free liquid surface. If Figure 4 were considered as two plates of indefinite length perpendicular to the section shown, the area referred to would be directly equivalent to the volume of liquid above the free liquid surface per unit length of solid boundary.

In such terms the capillary rise may be described as shown in part (c) of Figure 4 in which the volume of liquid supported by the internal pressure is represented as a boundary effect characteristic of the solid surface for the given liquid. It should be emphasized that the boundary effect, W_e if expressed as g. per cm. or F_e if expressed in dynes per cm., is a function of the integrated volume of supported liquid, which is a constant for any given combination of liquid and solid. It includes the integrated effect of both the internal pressure arising from the unbalanced molecular attraction P_{GL} and the contact angle θ in Eq. (4).

When this effect is applied to the closed boundary or circumference of a capillary tube the total weight raised above the free surface may be equated to an equivalent capillary

pressure. Expressing this relation in force units leads to the following equation:

$$P_{GL} \pi r^2 = W_c g 2\pi r = F_c 2\pi r$$

$$P_{GL} = \frac{2F_c}{r} \quad (5)$$

In capillary tubes of small diameter the capillary pressure created by the attraction of the solid walls of the tube may be equated to hydrostatic pressure wgh where the radius of curvature is negligible with respect to the capillary rise h .

$$P_{GL} = wgh = \frac{2W_c g}{r} = \frac{2F_c}{r}$$

$$rh = \frac{2W_c}{w} = \frac{2F_c}{wg}$$

The relationship in Eq. (5) is similar to that derived from the surface tension analogy in Figure 2 except that the boundary effect F_c has replaced the surface tension S_L .

The quantity rh is known as the capillary constant (sometimes called "specific cohesion") and has the dimensions of an area. For water and glass at standard temperature it has a value of 14.88 sq. mm. There has always been some speculation as to why the capillary constant has the dimensions of an area. Adam states that "... this rather oddly defined quantity has been widely used for over a century; it arose because the first law of capillarity known was that product of the height of rise and the radius of the tube is approximately constant. ..." That the dimensions of the capillary constant are those of an area does not seem so strange when the effect of the solid surface is considered as shown in Figures 3 and 4. The total weight of water per unit length of perimeter under the hydraulic gradient curve is, naturally enough, represented by an area obtained by dividing that weight by the weight per unit volume of the liquid. It is felt that these facts lend support to the concept of capillary rise presented in this discussion.

Regardless of the mechanism through which these forces operate the effect of capillarity may be measured experimentally. Even if the postulates presented in the preceding discussion are found difficult to accept, it is believed that quantitative relations involved in experimental observations of capillary rise may be

considerably clarified. If the liquid is taken as water having unit density, this boundary effect may be evaluated in g. per cm. of perimeter W_c or in force units of dynes per cm. (F_c) as is usually the case.

$$W_c = \frac{rhw}{2} = \frac{0.1488 \times 1}{2} = 0.0744 \text{ g. per cm.}$$

$$F_c = W_c g = \frac{rhwg}{2} = 0.0744 \times 980$$

$$= 72.8 \text{ dynes per cm.}$$

Another method which evaluates the boundary effect as the area under the hydraulic gradient curve in the case of the plane solid boundary may assist in clarifying this interpretation of the capillary constant. Referring to Figure 4 the section shown may be taken as a section of a cylindrical surface representing capillary rise between two plates rather than a section of a circular capillary tube. The cross-hatched area under the curved surface on either side of the center may be used to evaluate the weight of water elevated above the free surface. When $\theta = 0$,

$$W = w \left(r^2 - \frac{\pi r^2}{4} \right) = 0.2146 wr^2$$

$$r^2 = rh = 0.1488 \text{ sq. cm.}$$

$$\text{Since } w = 1 \text{ and } g = 980,$$

$$F = Wg = 0.2146 \times 1 \times 980 \times 0.1488$$

$$= 31.3 \text{ dynes per cm.}$$

Using the same analogy for the cylindrical capillary surface between two glass plates as employed for the spherical surface, the hydrostatic uplift per unit length of boundary may be expressed in terms of an equivalent pressure P_{GL} :

$$P_{GL} \times 2r = 2Wg = 2F$$

$$P_{GL} = \frac{F}{r} \quad \text{Eq. (6)}$$

Comparing Equations (5) and (6), it is apparent that the boundary effect F for the straight solid boundary is only one half of the boundary effect F_c of the circular capillary tube for which the capillary constant is ordinarily measured. From this it follows that if capillary rise is to be measured in terms of

circular tubes the boundary effect computed for the straight boundary must be multiplied by a factor of two, inasmuch as the perimeter-area ratio (wetted perimeter divided by cross-

sumption only applies to small capillary tubes where the radius of curvature is negligible with respect to the height of capillary rise. While this approximation does not apply for

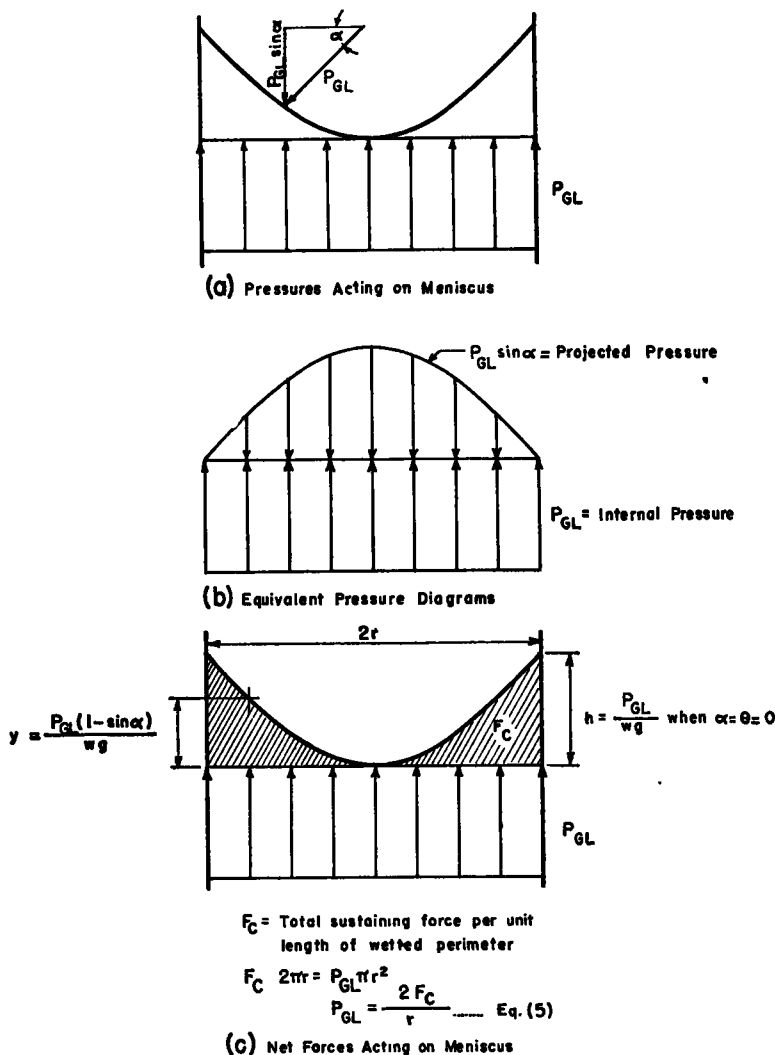


Figure 4. Static Equilibrium in Capillary Rise

sectional area) is $\frac{2}{r}$ and $\frac{1}{r}$ respectively. So F_c = 62.6 dynes per cm.

The approximation which has been used that the curvature of the meniscus is circular has in the last evaluation lead to a considerable error. It is well recognized that this as-

tubes of the size used in Figure 4 it is most convenient to use it and later apply corrections to compensate for the error introduced. Adam¹⁰ describes several methods for correcting measurements of so-called surface tension when the assumption that $rh = r^2$ introduces

¹⁰ Adam, *Op. cit.*, p. 318.

considerable error. One of these methods, known as the ring method, employs the principle that the weight of water raised above the free surface of the liquid is a measure of the surface tension effect. Harkins, Young and Cheng¹¹ have standardized this method and determined the correction factor k , which ranges from 0.75 to 1.1. Expressed in the terms the author has used, the correction factor would be applied as follows:

$$F_c = \frac{2F}{k} = \frac{62.6}{k} = 72.8$$

$$k = \frac{62.6}{72.8} = 0.865 > 0.75$$

$$< 1.10$$

It may be seen then that the error involved in computing the effect of the solid boundary as the area under the circular meniscus is well within the range of error introduced by the approximation involved.

With a mechanism described by which water may be supported above the free water level without use of the surface tension analogy, there remains only to express the final relationships in a formula for capillary rise, which follows directly from Eq. (5).

$$h = \frac{2F_c}{rgw} = \frac{2W_c}{rw} \quad \text{Eq. (7)}$$

As previously pointed out the relations are exactly the same numerically as derived in terms of a hypothetical surface tension. In practical application for water and solid materials with a contact angle of zero and a standard temperature of 20 deg. C., F_c may be taken as 72.8 dynes per cm. for circular tubes and the density of water may be taken as unity.

EXPERIMENTAL INVESTIGATION

Having formulated a concept of capillarity departing substantially from conventional use of surface tension, laboratory experiments were undertaken to further clarify and perhaps confirm the treatment of the subject that has been presented. These experiments consisted of a series of measurements of capillary forces using glass rods and tubes of varying diameter. A considerable range of diameters or

perimeter-area ratios was used in an attempt to evaluate dimensional effects and isolate the boundary effect associated with the solid surfaces in contact with the water.

In most of the experiments described herein solid glass rods were used as it was felt that the dimensional effects would be less involved than in the case of capillary tubes. However, one series of tests was conducted with tubes to test the general applicability of quantitative relations developed.

Capillary Weight Differential—These experiments were performed with an analytical balance sensitive to 0.1 mg., using two general

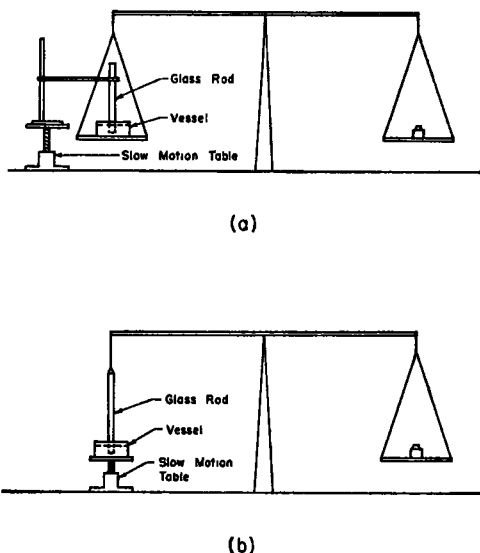


Figure 5. Methods of Measurement

procedures illustrated schematically in Figure 5. The first experiments, Test Series No. 1, were made as shown in Figure 5(a) by measuring the decrease in weight of the vessel of water as the glass rod was withdrawn from the liquid body. It was found that evaporation of water in the vessel affected the results unless the observations were made quite rapidly. Subsequently observations were then made as indicated in Figure 5(b) by measuring the pull on the glass rod as the vessel of water was lowered away from the rod.

Two sets of observations were made to determine the accuracy with which the results could be duplicated and are shown in Table 1,

¹¹ Harkins, Young and Cheng, "The Ring Method for Determination of Surface Tension," *Science*, Vol. 64, p. 333 (1926).

Test Series No. 1 and No. 2. Test Series No. 3 and No. 4 are also parallel sets of observations but were made for the purpose of measuring the height at which separation of the glass rod from the liquid took place. It was noted that the weight difference varied as the glass rod was withdrawn approaching a maximum at the point of impending separation of the rod from the water. These maximum values are the ones recorded in Table 1.

which were more carefully cut and ground and similar variations occurred depending on the care used to clean and polish the glass rods. In the test series reported distilled water was used and glass rods were ground and polished with reasonable care but scarcely with the precision which would apparently be required for exact results.

In Figure 6 the total weight difference as measured is plotted against the perimeter-

TABLE 1
RESULTS OF EXPERIMENTS PERFORMED WITH GLASS RODS

Diameter <i>D</i>	Perimeter <i>P</i>	Area <i>A</i>	Perimeter-Area Ratio, <i>P/A</i>	Height of Separation	Weight Difference, <i>W_p</i>		Deviation
					Measured	Computed	
TEST SERIES NO. 1							
Constants in Eq. (8): <i>W_c</i> = 7.51 mg/mm., <i>K_n</i> = 2.28 mg/sq. mm.							
mm.	mm.	mm. ²	mm./sq. mm.	mm.	mg.	mg.	%
1.02	3.20	0.81	3.92		25.6	25.9	-1.2
2.77	8.70	6.02	1.44		90.2	79.1	+1.4
4.78	15.02	17.95	0.837		148.0	153.7	-3.9
7.77	24.41	47.41	0.515		292.0	291.4	+0.2
10.36	32.55	84.30	0.386		453.1	436.7	+3.6
TEST SERIES NO. 2							
Constants in Eq. (8): <i>W_c</i> = 5.08 mg/mm., <i>K_n</i> = 3.53 mg/sq. mm.							
1.02	3.20	0.81	3.92		22.1	22.3	-0.9
2.77	8.70	6.02	1.44		73.2	74.2	-1.4
4.78	15.02	17.95	0.837		154.1	154.7	-0.4
7.77	24.41	47.41	0.515		316.7	315.8	+0.3
10.36	32.55	84.30	0.386		505.1	495.5	+1.9
TEST SERIES NO. 3							
Constants in Eq. (8): <i>W_c</i> = 5.79 mg/mm., <i>K_n</i> = 3.34 mg/sq. mm.							
1.02	3.20	0.81	3.92	1.92	21.1	21.2	-0.5
2.77	8.70	6.02	1.44	2.23	70.0	70.5	-0.7
4.78	15.02	17.95	0.837	2.31	145.1	146.9	-1.2
7.77	24.41	47.41	0.515	3.02	299.9	299.7	+0.1
10.36	32.55	84.30	0.386	3.29	491.9	470.0	+4.7
TEST SERIES NO. 4							
Constants in Eq. (8): <i>W_c</i> = 5.05 mg/mm., <i>K_n</i> = 3.68 mg/sq. mm.							
1.02	3.20	0.81	3.92	1.15	19.0	19.1	-0.5
2.77	8.70	6.02	1.44	2.22	64.5	66.1	-2.5
4.78	15.02	17.95	0.837	2.68	142.4	141.9	+0.4
7.77	24.41	47.41	0.515	3.22	297.8	297.7	0.0
10.36	32.55	84.30	0.386	3.32	492.6	474.6	+3.8

The agreement in all series of tests is considered quite satisfactory considering the type of apparatus and procedure used and certain experimental difficulties that were encountered. Tests were conducted at fairly constant laboratory temperature but without precise temperature control. In early trial experiments it was found that wide variations resulted depending on whether tap water or distilled water was used. Rods with the irregular or jagged edges also differed widely from those

area ratio for each of the five rods of varying diameter for all of the four series of tests mentioned above. The next step was to determine the factors involved in this total weight difference in terms of the dimensional properties of the glass rods used. It was found that when the weight difference per unit area (the total weight difference divided by the cross-sectional area of the rod) was plotted against the respective perimeter-area ratios, a straight line relationship existed as shown in Figure 7.

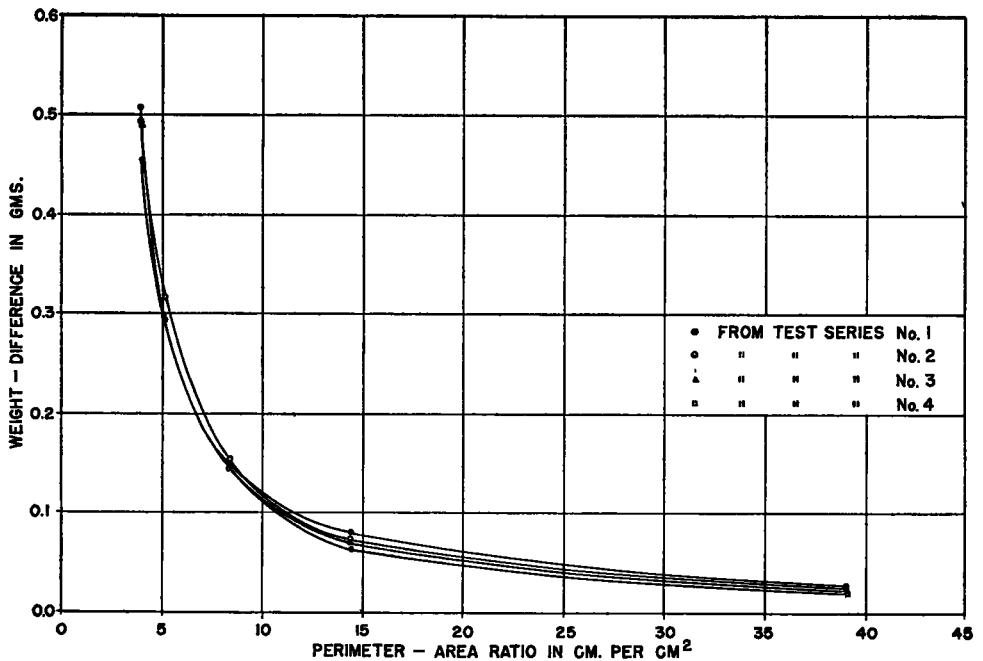


Figure 6. Total Capillary Weight vs. Perimeter Area Ratio

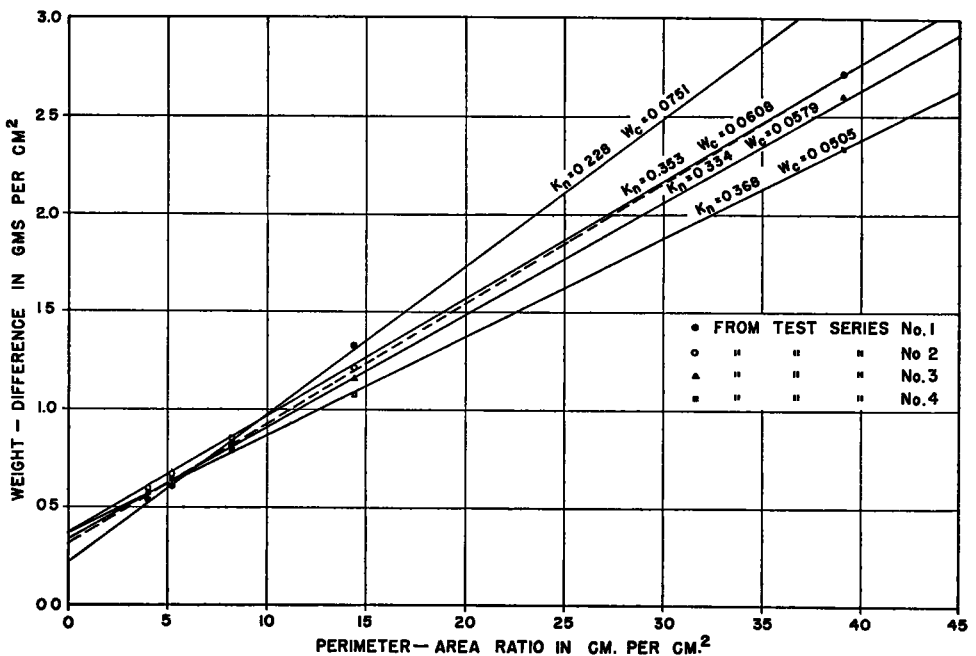


Figure 7. Linear Equation for Capillary Weight

This relationship may be expressed by a linear equation having two constants, one of which is connected to the surface boundary (perimeter of the rod) and the other a force per

unit of cross-sectional area of the rod. This equation is written as follows:

$$C_p = W_e \frac{P}{A} + K_n \quad \text{Eq. (8)}$$

where C_p = weight difference per unit area in g. per sq. cm.; W_e = weight carried as a function of perimeter, in g. per cm., P/A = the perimeter-area ratio in cm. per sq. cm.; and K_n = weight carried as a function of the cross-sectional area in g. per sq. cm.

Figure 7 shows the straight line relationship determined as the statistical average by the method of least squares for all observations in each of four test series presented. The individual points plotted are the original test values and the dashed line is the mathematical average for all four test series. The values of W_e and K_n for each series are shown in

accuracy with which the linear equation represents the data is very much closer than the average deviation shown.

In order to further check the validity of the linear equation for both form and value of constants a series of tests was conducted using glass tubes of varying diameter. The results of these tests are presented in Table 2. If the equation and the constants obtained are a true expression of the attraction between water and glass they also should be applicable to glass tubes. In Table 2 under the column headed "Computed Weight Difference" are shown the values obtained from the linear equation using the average constants from the four series of tests on glass rods. Under Table 2 is shown the method of computing this weight difference and the equation as applied to the glass tubes. It may be noted that the

TABLE 2
RESULTS OF EXPERIMENTS PERFORMED WITH GLASS TUBES

Diameter		Area		Perimeter		Weight Difference W_p		Deviation
D_1 Outside	D_2 Inside	A_1 Outside	A_2 Inside	P_1 Outside	P_2 Inside	Measured	Computed ^a	
mm.	mm.	sq. mm.	sq. mm.	mm.	mm.	mg.	mg.	%
18.80	16.41	277.59	211.50	59.06	51.55	911.6	888.0	+2.6
11.86	9.47	110.47	70.43	37.26	29.75	514.7	505.9	-1.7
6.86	4.62	36.96	21.34	21.55	14.51	280.0	270.5	+3.4

^a Method of computing weight difference, W_p , for tubes: $W_p = W_e (P_1 + P_2) + K_n (A_1 - A_2) = \pi W_e (D_1 + D_2) + \frac{\pi K_n}{4} (D_1^2 - D_2^2)$, where $W_e = 6.11$ mg. per mm. and $K_n = 3.21$ mg. per sq. cm. (These values are the average of those shown in Table 1.)

Table 1 and in Figure 7 on the respective straight lines. The values of the perimeter factor, W_e , ranged from 0.0505 to 0.0751 g. per cm. with an average value of 0.0611 for all test series. The values of molecular attraction, K_n , ranged from 0.368 to 0.228 g. per sq. cm. respectively, with an average value for all tests of 0.321 g. per sq. cm.

In order to determine the accuracy with which the straight line equations represented the observations, the total weight difference was computed for the five rods using the above equations and the constants determined for the respective test series. These values were tabulated under the column entitled "Computed Weight Difference". The maximum deviation from the straight line relationship is 4.7 percent and the average is 1.5 percent. It may be noted, however, that deviations greater than the average occurred in only five out of 20 observations and in general the

boundary factor W_e acts on the total perimeter which is the sum of the inside and outside perimeters of the tube. The molecular attraction K_n acts on the actual glass cross section only, an area which is quite small as compared to the glass rods. Particular attention is directed to the fact that this molecular attraction does not act over the area of the capillary column inside the tube. The maximum deviation in the computed values from the measured weight difference is 3.4 percent and the average deviation only 2.6 percent even though the constants used are the average of the four series of tests, which showed considerable variation between the separate series.

It may be noted that the values of W_e as measured in these tests are in substantial agreement with the accepted value of 0.0744 g. per cm. calculated from the capillary constant rh . The range of observed values from

psi.! The proof of such a proposition requires neither argument nor elaborate apparatus; so simple a device as the chimney of an old-time student lamp will serve the purpose.

THADDEUS MERRIMAN,
Chief Engineer,
Board of Water Supply.

New York City,
Nov. 18, 1925

(Replying to Mr. Merriman's letter the author writes as follows.—EDITOR)

Sir—Mr. Merriman's reaction on my papers, "Cohesion of Clays" and "Compressive Strength of Clay," is not surprising, inasmuch as the facts communicated in these papers certainly are apt to strike the unprepared mind.

Freed from the non-essential, Mr. Merriman's argument is this: The internal pressure in the clay is supposed to amount to 3,000 psi., hence the tensile strength of the clay ought to be 3,000 psi. This statement is theoretically correct. It is analogous to the following statement: According to the results of independent experiments, the internal pressure of iron—which means the force with which the iron particles are pulled together by molecular forces and cohere to each other—amounts to 4,000,000 psi., hence the tensile strength of iron ought to be equal to 4,000,000 psi. The proof of this proposition, too, requires neither argument nor elaborate apparatus, not even the old-time student lamp; yet the tensile strength of iron is not more than about 57,000 psi. or equal to about 1.4 per cent of the internal pressure. So far as metals are concerned, the cause of this apparent contradiction has been studied, chiefly in England, for many

years, and has recently been explained by A. A. Griffith and others. For clays in a dry state, there exists a similar discrepancy between internal pressure and tensile strength. With increasing moisture content the discrepancy between internal pressure and strength rapidly decreases.

Mr. Merriman is correct, also, in stating: "To postulate a force of this magnitude (3,000 psi.) is a severe test for the native credulity of the uninitiated."

The postulate which Mr. Merriman tries to disprove by an appeal to "common sense" and nothing else was first passed by the board for Mathematics and Physics of the Academy of Sciences in Vienna and was published in the proceedings of the Academy in 1923.

In June, 1924, the same postulate was set forth in a paper before the International Congress for Applied Mechanics in Delft, Holland, a congress in which 250 of the leading experts of Europe participated; the paper is published in the proceedings of that congress, 1925. The physical essence of the postulate which strikes Mr. Merriman was almost instantaneously grasped by those engaged for years in the study of plastic materials, and after the lecture one of the leading experts in mathematical physics made the remark, "It is incredible that this almost self-evident fact was not realized years ago."

It may be fair to point out that, as my articles in *Engineering News-Record* represent an exceedingly brief summary of my experiments and conclusions, the proof of my statements is, necessarily, fragmentary.

CHARLES TERZAGHI

Cambridge, Mass.,
Nov. 19, 1925.

DISCUSSION

JAMES S. HOLDHUSEN, *University of Minnesota*
—The author is to be commended for his willingness to search for a new mechanism to describe capillarity, especially since the mechanical analysis of the problem seems to be so baffling. The paper ought to stimulate new thinking on this important phase of soil mechanics even though the theories presented are not entirely successful.

The author begins his paper by pointing to three apparent fallacies in the surface tension

concept of capillarity. First, he finds it impossible to accept the idea that there might be an actual physical tension in a liquid-gas interface. Indeed, his definition (*sic*) of tension rules out this possibility altogether. It can be demonstrated that surface tension may exist as a physical reality by considering a soap bubble. The pressure within a soap bubble is greater than the surrounding atmospheric pressure and the bubble accordingly assumes a spherical shape. A simple analysis of the

force balance on one-half of the bubble will show that there is a force tending to tear the soap bubble apart; this force is apparently successfully resisted by the membrane tension in the soap film. Since bubbles can also be formed with distilled water, surface tension is evidently a real physical force.

If the argument of actual surface tension is pursued in order to explain shrinkage and cohesive strength in soils, another apparent fallacy is encountered since it must be assumed that water has a tensile strength of about 15 atmospheres (15,000 g. per sq. cm.). This assumption is not lacking in experimental proof; several experimenters have shown that water can withstand very appreciable tension.¹² The highest recorded tensile strength is about 60 atmospheres but it was concluded that this was not the maximum tensile strength. The weakest link in the solid-water structure used in the tests ruptured at this stress; if the solid surface had been sufficiently hydrophylic and if the water had been clean enough, it is conjectured that much higher tensile strengths could have been attained.

The balance of surface tension forces as presented by Prof. Housel (Fig. 1b) omits one force which acts at the junction of the three phases. According to the surface tension concept, the tensioned skin of the liquid attaches itself to the solid surface, and the reaction of the solid to the surface tension in the interface should be included. Since this reaction has a component normal to the solid surface, the apparent fallacy in the balance of forces is eliminated.

Prof. Housel's new approach to the capillary rise phenomenon leaves much to be explained. The main difficulties in the theory stem from a refusal to admit that there is a pressure drop across the curved interface. If Eq. (4a) is accepted, it follows that there is no such thing as capillary rise in the ordinary sense. Since $\sin \alpha = 1$ at the center of the tube, the liquid at the center of the tube could never be raised above its original height by capillary action. In order that capillary rise occur in the usual sense, the author's reasoning indicates that the interface must have the

shape of an inverted cone. By the irrefutable law of hydrostatics, the static pressure head on opposite sides of the meniscus in Fig. 2a must differ by the height of the capillary rise. In this connection, it is interesting to note the author's statement: "The assumption that there is a pressure drop ($p_1 - p_2$) across the meniscus in the capillary can only be true if there actually is a surface with physical tension."

The author is willing to violate the law of hydrostatics in the special case which he analyzes in Fig. 4; this evidently means that the liquid in the meniscus is thought to be capable of supporting shearing stresses since the liquid undeniably has weight. Another misconception is introduced when the author states: "Within the capillary column the pressure remains constant rather than being represented by a negative hydrostatic pressure which is sometimes superficially used to avoid the hypothetical tension." The hydrostatic pressure is only negative with respect to atmospheric pressure so that the column of water is nowhere in a state of tension unless the capillary rise becomes somewhat greater than 30 feet.

The experimental work presented does not lend credibility to the author's viewpoints; the results could have been just as readily explained by the surface tension concept. Again in the words of the author, "The relationship in Eq. (5) is similar to that derived from the surface tension analogy except that the boundary effect F_e has replaced the surface tension S_L ." In the opinion of this writer, Prof. Housel's boundary effect is based on reasoning which leads to results at variance with experiment. It is difficult to see how this quantity can be used to explain cohesive strength in soils.

HAMILTON GRAY, *University of Maine*—The author's desire and attempt to establish rational explanations of capillarity and various aspects of soil behavior which do not require an appeal to the concept of surface tension appear to pose two important questions: (1) Does surface tension actually exist or is it only a convenient fiction which is useful in expressing the observed result of obscure forces or properties in or between liquids, gases and solids? (2) Will the proposed theory of capillarity be compatible with known facts?

¹² H. N. V. Temperly and L. G. Chambers, "The Behaviour of Water under Hydrostatic Tension," *Proc. Phys. Soc. London*, Vol. 58, pp. 420-36 (1946).

The concept of surface tension has been accepted widely because of its simple mechanical nature and its usefulness in the analysis of certain problems. Many profess to believe that surface tension is a manifestation of surface energy, while others consider it merely a convenient mechanism for treating problems in which surface energy is involved.

While water, and other liquids possessing low viscosity, are commonly viewed as being incapable of sustaining tensile stresses, it should also be remembered that these liquids cannot carry compressive stresses either *unless they are confined*. Confinement restricts the mobility of the component parts of a liquid so that changes in shape are prevented and compressive stresses may be resisted. It appears pertinent to inquire whether liquids may not support tensile stresses of considerable magnitude if changes in shape are prevented by appropriate means. A U-shaped sealed glass tube containing only water and vapor, and referred to as a "water hammer", was formerly used in classes in physics to demonstrate that a column of water could be supported by adhesion and cohesion (or molecular attraction) to a higher elevation on one side of the tube than on the other. Tensile stresses presumably existed in the water in this tube. The author knows of no evidence demonstrating that tensile stresses may not be borne by a pure liquid if its mobility is properly restrained.¹³

When a body of pure water is agitated, bubbles tend to form on its surface. These bubbles possess the shape of a zone of a sphere. Dispersion of glycerin or soap facilitates the formation of such bubbles. It can scarcely be contended that soapy water is not a liquid. Soap bubbles may be blown in such a manner that there is no doubt that they contain gas under pressure in excess of that of the surrounding atmosphere and the wall of liquid

which forms the bubbles then would most certainly appear to be in a state of tension. Whether the stress is borne by the surfaces of this wall or film or whether it is borne by the portion of the film which is remote from the surfaces appears immaterial to this discussion.

If a flexible membrane in a gravitational field is constrained to assume a curved shape by contact with a frictionless substance (gas or an ideal liquid), the principles of statics require that tensile stresses exist in the membrane. This is analogous to the compressive stresses which must exist in an arch or dome which is subject to normal pressures acting on its surface.

It appears, therefore, that there is evidence, as above described, pointing to the existence of tension both in thin films and in large masses of liquids and the literature of the subject contains other examples. Consequently it may not be erroneous to postulate surface tension as a fact rather than as a useful mechanism.

Newton's law of gravitation has certain limits but Einstein's introduction of another and more general concept has not required a revision of ordinary engineering computations. As long as Newton's concept does not contradict reliable observations and at the same time is useful, it seems unnecessary to use a substitute in engineering work.

The author states that pressures within a capillary column remain constant rather than varying according to hydrostatic law. If we imagine a capillary column several inches high standing in a vertical tube the lower end of which touches a free water surface, and if in addition the fluid pressure in this capillary moisture is the same at all elevations, it necessarily follows that the hydraulic head at the lower portion of the capillary column is less than the hydraulic head at the upper end in the vicinity of the capillary meniscus. Therefore, if the principles of hydraulics are valid, since there exists a loss of head, the water should move downward out of the capillary tube. On the contrary, it is observed that when the lower end of an empty capillary tube is brought in contact with a free water surface the water rises at a varying rate. This can only occur if there is a difference in head between the upper portion of the capillary column and the free water surface and the head must of

¹³ We cannot form a free-standing prism of water (unless we freeze it) which can be subjected to a compression test, as is concrete. Water, therefore, may be said to possess no compressive strength. By virtue of analogous considerations, water may also be said to possess no tensile strength. However, this does not mean that water cannot sustain compressive and tensile stresses if deformations are prevented by proper confinement of the substance.

necessity be lower at the upper portion of the capillary column. If the author's development forces him to conclude that the pressure in the capillary column is constant and consequently that the head increases with elevation above the free water surface, it is apparent that the new concept violates an accepted principle of hydraulics.

As a final illustration one may point to the differences in supporting power exhibited by a sand near the edge of a pond. The supporting power is least when the sand is submerged. It is greatest when the sand is saturated by capillarity, and has an intermediate value

when the sand is dry. The supporting capacity depends upon the intergranular pressures in the sand and these in turn are influenced by the presence and state of stress in the water occupying its voids. Equilibrium requires that the intergranular pressure be greatest when the supporting power is greatest. This is believed to imply that the void water is in tension when the intergranular stresses are high.

In consideration of the foregoing remarks the writer is unable to perceive that the author has clarified or simplified in a satisfactory manner the subject of surface tension or capillarity.

LIME-FLY ASH COMPOSITIONS FOR USE IN HIGHWAY CONSTRUCTION

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SYNOPSIS

A study has been made relating to the use of a group of lime-fly ash compositions in highway base construction. The use of small amounts of lime together with fly ash and aggregate materials including New Jersey Type A-3 soil, boiler slag, and crushed stone was considered. By carefully controlling the percentages of the ingredients, compositions have been produced which develop high compressive strength after aging for periods of one week or longer. Specimens subjected to wetting and drying and freezing and thawing tests indicate excellent performance when optimum quantities of lime and fly ash are employed. Field tests which have been started on the compositions developed in the laboratory indicate that the use of these materials in the construction of the base course of highways may give superior results at low cost.

The literature (1)¹ gives many references to the use of fly ash (produced by the combustion of pulverized fuel) as a pozzolan in compositions in which lime or another alkali is present. For example, when fly ash is used in concrete (2), the calcium hydroxide produced by the hydrolysis of the portland cement combines with the fly ash forming cementitious silicates which appreciably increase the strength of the concrete. Various structural products are reported (3) which utilize the reaction of hydrated lime with fly ash during their manufacture and further demonstrate the pozzolanic nature of fly ash when used in these compositions.

Some years ago Havelin and Kahn (4), Philadelphia Electric Company engineers,

made the discovery that when small amounts of hydrated lime are added to fly ash in the presence of water and aggregates, such as sand, in carefully controlled amounts, a very surprising product is produced showing the property of high compressive strength when aged for a period of 28 days or longer. Typical data representing results of this early work are shown in Figure 1. It is to be noted in this graph that a critical range of compositions exists wherein high strengths are obtained and that the use of either smaller or greater amounts of lime result in compositions of much lower compressive strength.

The investigation reported in this paper covers an adaptation of this discovery to the field of base course construction of roads and was financed by the Philadelphia Electric Company. The study involves the use of lime

¹ Italicized figures in parentheses refer to the list of references at the end of the paper.