Physics of Water Movement in Porous Solids

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Introductory Remarks by Chairman

Water movement in porous systems is perhaps the most consequential phenomenon with respect to the life and activities of the human race. The movement of water to the plant roots and hence through the plant to the leaves enables the latter to utilize the sun's rays and the carbon dioxide of the air for the synthesis of the basic food materials for animal life. Proper irrigation of deserts and drainage of swamps adds to the areas available for food production and sites of habitation, while adequate drainage has been called justly the first principle of highway and airport engineering. Water may move out of saturated clay and silt layers underneath the foundations of heavy structures and cause their settlement; it may move into and through porous building materials and cause wet walls and cellars. On the other hand, porous building material may conduct water vapor created by human and animal life activity out of rooms and cells and help to keep their atmosphere comfortable and healthy. These are only a few of the myriad and multifarious examples that could be adduced about the importance of water movement in porous systems even if we should exclude such vital processes as the movement of water and of aqueous solutions into, through and out of all living systems. Water has been called the friend and enemy of the engineer and to do its friendly or hostile act, it moves largely through porous systems.

Considering this wide and vital importance in many different areas of human endeavor, it is to be expected that the phenomenon of water movement through porous solids has been studied from many different points of view and that since the dawn of humanity, specific problems deriving from this phenomenon have been solved more or less adequately by methods ranging from the crudely empirical to the most refined theoretical. Because of their specific nature, it is often difficult to apply the solutions thus found to analogous cases in other fields. The situation calls for a general theoretical structure from which specific solutions can be derived for specific conditions. The time has come when it is possible to establish such a theoretical structure at least for that large portion of the total problem which is predominantly physical in nature and in which physicochemical and chemical interactions between the water and the pore walls are sufficiently small to permit their exclusion from the theoretical treatment. In the light of this, we are extremely grateful to Dr. Philip of Australia for giving a comprehensive and most excellent survey on the Physics of Water Movement in Porous Solids.

THE FIRST part of the paper treats the connections between the mechanics of fluids in saturated porous solids and classical hydrodynamics. It is shown that the permeability tensor may be expressed in terms of precise integrals of the internal geometry of the solid. Methods of using the Navier-Stokes equation to compute the permeability of a porous solid in this way are outlined. The limits to Darcy's law arising from the "inertia terms," and from variation in time of the applied potential, are discussed.

The remainder of the paper reviews recent studies of water movement (liquid and vapor phases) in unsaturated porous solids under the influence of gravity, and moisture and temperature gradients. Some attention is also given to the adsorbed phase, and to heat transfer in the solid. A coherent mathematical-physical theoretical framework has been developed, which is amenable to analysis. In the context in which it was con-
structured, it has proved in good agreement with experimental observations of a diversity of phenomena. The theory is incomplete, in the sense that it does not deal adequately with all aspects of water movement in soils of high colloid content.

The aim of this paper is to review some recent developments in the study of water movement in porous solids. Much of this work has been done by soil physicists primarily concerned with microhydrological problems arising in connection with dry and irrigated agriculture. It may not, therefore, be well known to soil mechanicians and foundation engineers, who are equally interested in water movement in soils, though for rather different practical reasons.

Theoretical structure to be presented here has developed, and proved fruitful, in this agro-hydrologic context, and it is emphasized that there are limits to its applicability, as it stands, to foundation problems. In the sense that it does not deal adequately with all aspects of water movement in soils of high colloid content, the theory is incomplete. Nevertheless, it would seem that any more complete quantitative theory must incorporate within it many, if not all, features of the present theory.

Water in the soil and other porous materials may be present in three phases—liquid, vapor, and adsorbed phase. (Attention is restricted to unfrozen materials; ice does not therefore enter into consideration.) Concern in this case is with the transfer of moisture via all three phases, although treatment of the adsorbed phase is cursory. The liquid phase is considered initially and it is useful to introduce the concept of permeability (hydraulic conductivity) by first considering flow through a saturated system.

**FLUID FLOW IN SATURATED SOLIDS**

There is no need for an elaborate treatment of fluid flow in saturated solids here, as many recent reviews of this topic are available (e.g., Carman, 1956, Scheiddegger, 1957). These works, however, do not seem to recognize clearly the connections between the mechanics of fluids in saturated media and classical hydrodynamics. This is the aspect stressed in this compressed treatment. For the purposes of the later sections, however, all that is really required is that there should exist, in a given medium, a linear relationship between applied potential gradient and macroscopic flow velocity. In this sense the theoretical structure outlined in the succeeding sections is independent of this section.

**Darcy's Law.** From his experiments on water flow through filter beds, Darcy (1856) deduced

\[ Q = KA(h+L)/L \]

where \( Q \) is the discharge through filter in unit time, \( A \) is the area of the filter, \( L \) is the thickness of the sand, \( h \) the water depth over the sand, and \( K \) "un coefficient dependant de la nature du sable." Later investigators have applied the equation to the flow of water in homogeneous isotropic media in forms such as

\[ Q/A = u = KS \]

where \( u \) is the macroscopic flow velocity, and \( S \) the magnitude of the potential gradient. An extension of Eq. 2 to apply to any fluid may be made, provided the medium remains stable and does not react with the fluid:

\[ u = (K/\nu)S \]

\( \nu \) is the kinematic viscosity. \( K \), now the permeability, is a characteristic of the geometry of the medium, and is independent of the fluid. A vectorial form of Eq. 3 is

\[ \mathbf{U} = -(\nu/\nu) \nabla \phi \]

where \( \mathbf{U} \) is the vector macroscopic velocity, and \( \phi \) is the potential defined by

\[ \phi = P/\rho + \Omega \]

Here \( P \) is the pressure, \( \rho \) the density, and \( \Omega \) the potential of the external or body forces.
Eq. 4 holds for homogeneous isotropic media, the extension to anisotropic media being

$$\vec{U} = - (1/\nu) \, \vec{K} \, \vec{\nabla} \phi$$

where \( \vec{K} \) is the permeability tensor. In this general case vectors \( \vec{U} \) and \( \vec{\nabla} \phi \) differ in direction except for certain special directions in the medium.

The Capillary Bundle Model, and Its Limitations. Clearly, collections of capillary tubes can be constructed which form a special case of the porous solid. Naturally, these special media belong to the general class of porous solids, and, if the equations exhibited above are valid, they will, of course, hold for these special media. However, theoretical deductions based on this special model are not necessarily valid in the general case. Yet nearly all theoretical studies of porous media have been based on capillary models.

Some workers (e.g., Adzumi, 1937, 1939; Childs and Collis-George, 1950a; Flood, Tomlinson and Leger, 1952) have used quite complicated variants of the simple capillary bundle which involve series- or series-parallel-connected systems treated essentially as pipe networks with laminar axial flow in the pipes (with no allowance for the transitions at bends and changes of section). Even the sophisticated treatments of Scheidegger (1954, 1957) and Fatt (1956a, b, c) depend on the capillary model.

The objections to the capillary bundle model, and its variants, relate both directly to the failure of tube flow to bear much physical resemblance to flow in porous solids in general (hereafter called "medium flow"), and to the fact that, in any case, capillary models cannot give information on some aspects of the flow process which are quite important both to theory and practice.

The difference in character between tube and medium flow will be seen if the fate of a small parcel of fluid moving through each system is considered. In the tube the parcel possesses a constant linear velocity throughout, while in the medium it is subject to forces which continuously change not only the magnitude but also the direction of its velocity. This important difference finds quantitative expression in the \( 1,000 \) to \( 1 \) ratio of the critical Reynolds numbers of the two systems (cf. Muskat, 1937, p. 56; Goldstein, 1938, p. 319).

Obviously, many aspects of medium flow (e.g., effects of particle shape and spacing on permeability; the effect of particle orientation on the directional properties of permeability; the question of identity or non-identity of hydrodynamic and electrical "tortuosity") are unlikely to receive meaningful treatment when the actual medium geometry is discarded at the outset, as it is in the capillary bundle approach. However, it is possible to use classical hydrodynamics to study these questions in a precise way.

The Navier-Stokes Equation in a Porous Solid.

$$\frac{\partial \vec{U}}{\partial t} - \vec{U} \times (\vec{\nabla} \times \vec{U}) + \frac{1}{2} \, \nabla |\vec{U}|^2 = - \nabla \phi + \nu \, \nabla^2 \vec{U}$$

is the Navier-Stokes equation for an incompressible fluid. \( \vec{U} \) is the microscopic vector velocity (as distinct from the macroscopic \( \vec{U} \) introduced earlier) and \( \vec{\nabla} \phi \) has a somewhat different significance than it had in the earlier macroscopic equations. There it was a smoothed potential gradient; here it denotes a vector point function which will generally vary in magnitude and direction from point to point. Textbooks (e.g., Lamb, 1932, p. 576) give the derivation of Eq. 7 from simple considerations about the mechanics of a fluid in motion. Essentially, the equation is established by relating the forces and accelerations on a small element of the fluid on the supposition (rigorous for Newtonian fluids) that the shearing stress sustained by the fluid is proportional to the velocity gradient normal to the plane of shear. The (constant) ratio of the shearing stress to the velocity gradient is the dynamic viscosity of the fluid, \( \mu \), which is equal to \( \rho \nu \).

Navier obtained Eq. 7 as early as 1822, the theoretical basis being improved by Saint-Venant in 1843. Curiously enough, this general analysis of the motion of a viscous fluid preceded the much less general, but better known, studies of Poiseuille and Darcy. Apparently, it was not recognized that their results represented simple special cases of Eq. 7.

When

$$\vec{U} \times (\vec{\nabla} \times \vec{U}) - \frac{1}{2} \, \nabla |\vec{U}|^2 = 0$$

(8)
and the motion is steady in time, Eq. 7 reduces to
\[ \nabla \cdot \mathbf{U} = 0 \]  \hspace{1cm} (10)

For certain special motions and media (e.g., flow parallel to the generators of the generalized tube) Eq. 9 will hold exactly. However, in most media, and certainly in the porous solids which are of interest here, the validity of Eq. 9 depends on the reduction of Re, the Reynolds number of the motion, to sufficiently low values for the inertia terms (i.e., the terms of second degree in \( U \)) to be negligible. Both analysis (Lamb, 1932, p. 599) and experiment (Muskat, 1937, p. 56) suggest an upper limit of Re of order of magnitude unity, below which Eq. 9 holds to sufficient accuracy. Thus Eq. 9 is found to apply to almost all fluid motions in the porous solids of nature and technology, and certainly to all where the concept of permeability is valid.

Use of the continuity requirement
\[ \nabla \cdot \mathbf{U} = 0 \]  \hspace{1cm} (10)
in Eq. 9 yields
\[ \nabla^2 \Phi = 0 \]  \hspace{1cm} (11)
The motions must satisfy Eq. 9 and Eq. 10 (or Eq. 11), together with appropriate boundary conditions. These will include the requirement that at all fluid-solid interfaces the fluid velocity is zero, i.e.
\[ U = 0 \]  \hspace{1cm} (12)

The remaining boundary conditions are now noted. It is well known that in anisotropic porous solids the directions of the (macroscopic) potential gradient and the (macroscopic) flow velocity do not necessarily coincide. It follows that a permeameter test of a specimen may be erroneous if the axis of the specimen does not coincide with a principal axis of the permeability tensor; i.e., if the impermeable side walls exert an artificial restraint on the flow pattern which would not occur if the specimen were subjected to the same potential difference, but were surrounded by a large mass of the medium.

The same difficulty arises in deriving the permeability properties of a given medium from the Navier-Stokes equation, and it can be resolved exactly only when suitable planes of (reflective) symmetry exist in the medium. This may seem to limit the value of this approach. However, certain artificially constructed media do exhibit such symmetry, and most other media can be represented to a good approximation by the repetition in each dimension of some basic solid configuration. (There is, in principle, no need for the geometry of the basic configuration to be simple.) The degree of idealization is evidently very much less than that involved in the capillary bundle model, and it can be fairly claimed that most of the physical characteristics of the real system are retained.

The mathematical permeability test (for this is essentially what is being undertaken) shall be carried out for the case \( v = 1 \) and unit potential difference across the basic cell. These special values may be employed without loss of generality, since the linearity of Eq. 9 and the governing conditions ensure that flow velocities are directly proportional to the applied potential difference, and inversely proportional to \( v \). (Essentially, the linear form of Eq. 9 and the governing conditions comprise a derivation of Eq. 6, and the other forms of Darcy's law, via classical hydrodynamics. Strictly speaking, however, a statistical assumption concerning the uniformity of the medium in the large is also needed; but this is implicit in Eq. 6, etc., in any case.) Therefore, specification of the problem is completed by imposing the boundary conditions:

\[ \Phi = 1 \text{ at plane } 1; \quad \Phi = 0 \text{ at plane } 2. \]
Velocity gradient at planes 1 and 2 is zero.
Velocity components parallel to planes 1 and 2 are zero at these planes.
Velocity and potential gradients normal to planes 3, 4, 5, 6 are zero at these planes.  \hspace{1cm} (13)
Here planes 1 and 2, 3 and 4, 5 and 6, denote pairs of opposite planes of symmetry. It will be understood that the equations hold only in the region of fluid occupancy, and that conditions need be satisfied only on those parts of the planes of symmetry occupied by fluid.

The solution of Eq. 9 subject to these various conditions may be found in the form

$$U = U_{12}(x, y, z)$$

where $x$, $y$, $z$ are Cartesian co-ordinates specifying position within the basic cell, the $x$-direction being normal to plane 1, the $y$-direction normal to plane 3 and $z$-direction normal to plane 5.

Similarly, by replacing Eq. 13 by corresponding boundary conditions for unit applied potential differences between planes 3 and 4, and between planes 5 and 6, two further solutions may be obtained

$$U = U_m(x, y, z); \quad U = U_9(x, y, z)$$

Then, if $K_x, K_y, K_z$ denote scalar permeabilities in the three respective principal directions,

$$K_x = \frac{l_x}{A_x} \int U_{sd} dA; \quad K_y = \frac{l_y}{A_y} \int U_{sd} dA$$

$$K_z = \frac{l_z}{A_z} \int U_{sd} dA$$

Here, $A_x, A_y, A_z$ denote (any) cross-sections of the basic cell normal to the $x$, $y$, and $z$ directions respectively; $l_x, l_y, l_z$ denote the lengths of the basic cell in these same directions and $i$, $j$, $k$ denote the corresponding unit vectors. The permeability tensor is then

$$K = K_x \textbf{i}i + K_y \textbf{j}j + K_z \textbf{k}k$$

Solution of Equation 9. In principle, solution of Eq. 9 subject to these conditions can be obtained by relaxation. For two-dimensional media, a stream-function may be introduced and the problem reduced to solution of a bi-harmonic equation (Shaw, 1953, p. 196, Allen, 1954, p. 105; Southwell, 1956, p. 251). An alternative procedure involving relaxation solution of Laplace's equation and Poisson's equation is needed in three-dimensional problems, and may be better in two-dimensional cases also. Three-dimensional relaxation is a formidable process, and real progress here will probably require use of a high-speed computer. Nevertheless, although real media are threedimensional, the more tractable two-dimensional problem retains many of the physical aspects of interest, and is worthy of some study. Some two-dimensional solutions have been obtained (Philip, 1957g), and illustrate such facts as the non-identity of hydrodynamic and electrical "tortuosities" in porous solids.

It is not likely that this hydrodynamic approach can be applied in detail to a specific field problem. The internal geometry of the solid is unlikely to be known sufficiently accurately, or, if it is known, it will almost certainly be so complicated that the computations become very intricate.

It has been seen, however, that this approach enables fitting the mechanics of fluids in porous solids into the theoretical framework of classical hydrodynamics, and expressing permeability in terms of precise integrals of the internal geometry of the solid. Furthermore, the study of flow through simple configurations by the methods outlined here can do much to fill out understanding of permeability—in particular its relationship to the shape, size, and orientation of pores and particles.

It will be noted that this method of analysis does not resolve the differences between
the "particle" approach to permeability, as exemplified by the Kozeny-Carman equation, and presented in the work of Kozeny (1927), Carman (1937, 1938, 1956), Wyllie (undated; Wyllie and Gregory, 1954) and others, and the "pore" approach of Childs and Collis-George (1950), Purcell (1949) and others. Both are based on the capillary bundle model, and claims for the superiority of one approach or the other within some defined range of technological application must depend primarily on appeal to experiment. However, the methods outlined here can provide soundly based checks on such matters as the supposed constancy of the Kozeny-Carman "constant," and the validity of the "tortuosity" concept in structured solids.

The Limits to Darcy's Law. (a) The "inertia terms." It has been shown that Eq. 9 depends on the validity of Eq. 8. For tube flow Eq. 8 is exact, and Eq. 9 holds until Re is about 2,000, when the laminar flow develops instability, and the flow becomes turbulent. On the other hand, the inertia terms Eq. 8 cannot be neglected in general medium flow above some "critical" value of Re, usually in the range 1 to 5. Often one finds in the literature the suggestion that the failure of Darcy's law with increasing Re is due to the onset of turbulence. It is clear that this is incorrect, and that the non-linearity which signals the failure of Darcy's law arises, in the general medium, from the inertia terms. The recent computations of Tamada and Fujikawa (1957) of drag on an array of cylinders demonstrate this very well, and similar results would apply to the case of flow through a porous solid.

This effect was recognized by Lindquist in 1932. It is emphasized here because, even in very recent publications, the mistaken idea persists that turbulence determines the upper limit of validity of Darcy's law. (Note that, as the flow rate is increased, turbulence may ultimately develop. The point is that there exists, between the Darcy and the turbulent regimes, a non-linear but laminar regime.)

(b) Flow unsteady in time. Darcy's law, and the hydrodynamic analysis given above, are for motions steady in time. Darcy's law has often been applied to problems in which the flows and the potential gradients are not steady in time. Philip (1957b, I) has examined the problem of unsteady flows, applying the Navier-Stokes equation in some simple cases, and developing an approximate analysis in general media. The general result is that, when the applied potential, S, is a function of time, Eq. 3 must be replaced by

\[ u = u_0 e^{-\beta t} + \left( \frac{\beta K}{\gamma} \right) e^{-\beta t} \int_0^t S(T)e^{-\beta T} dT \]  

(18)

Here \( u_0 \) is the value of \( u \) at \( t = 0 \), and

\[ \beta = \frac{p^3 \nu}{\gamma K} \]  

(19)

where \( p \) is the porosity and \( \gamma \) is a numerical constant dependent on the internal geometry. Usually it will be about 1.25.

Eq. 18 may be regarded as the appropriate generalization of Darcy's law. For the case \( u_0 = 0 \), and \( S \) suddenly changed from zero to a constant non-zero value at \( t = 0 \), Eq. 18 yields the result that the instantaneous "permeability" at time \( t \), \( K_t \), is given by

\[ K_t = K(1 - e^{-\beta t}) \]  

(20)

It is seen that the error produced by using the unmodified Darcy's law will be negligible in most practical applications. In periodic systems, however, the differences can be important (Philip, 1957b). It is also possible that perceptible deviations from Darcy's law may occur during the very early stages of absorption or infiltration into unsaturated systems (Philip, 1957h).

MOVEMENT OF THE LIQUID PHASE IN UNSATURATED SOLIDS

Hydraulic Conductivity in Unsaturated Solids. When the solid is not saturated with the liquid, a gaseous phase is also present. In the case which is of interest here the liquid is water, and the gas is air containing water vapor in equilibrium with the liquid
water. (In the petroleum industry other multiphase systems arise—e.g. oil-gas, oil-brine, oil-gas-brine. The physical problem is rather similar to that treated in this and following sections. However, there are some important differences, which cannot be discussed here.)

It has long been assumed (cf. Richards, 1931), and was confirmed experimentally by Childs and Collis-George (1950), that Darcy's law may hold in unsaturated systems in a more general form in which the permeability is now a function of the moisture content of the solid. Analytical proof of this generalized form of the law depends on the assumption that the drag between the phases is negligibly small (Philip, 1957). This is certainly true of the systems to be considered here.

Since water is the only concern, it is now convenient to introduce the term "hydraulic conductivity" (Richards, 1952), K', to denote the quantity K/v, which appears in equations such as Eq. 4. Anticipating the next sub-section, express ϕ in units of length, so that K' has the dimension (length x time^−1). The unit cm sec^−1 is commonly used for K'.

This and the following sections are limited to isotropic solids.

Introduced here is the volumetric moisture content, θ. This is the fractional volume of the solid which would be occupied by the water it contains, if all this water were in the liquid phase. This is almost exactly the volume fraction occupied by liquid water, but the definition takes care of ambiguities which might arise concerning the vapor phase.

Except at the dry end of the moisture range, where the experimental difficulties are great, the general behavior of the K'(θ) function is now well established, thanks to the work of Richards, Moore (1939), Childs and Collis-George, other soil physicists, and a number of investigators in the petroleum industry. K' is found to decrease very rapidly as θ decreases from its saturation value. This is not surprising since:

1. The total cross-section available for flow decreases with θ.
2. The largest pores are emptied first as θ decreases. Since the contribution to permeability per unit area varies roughly as the square of the pore radius, K' may be expected to decrease much more rapidly than θ. (This is an instance where argument from the capillary model is probably permissible.)
3. As θ decreases, the chance of water occurring in pores or wedges isolated from the general three-dimensional network of water films and channels increases. Once continuity fails, there can be no flow in the liquid phase, apart from flow through liquid "islands" in series-parallel with the vapor system (Philip and de Vries, 1957). The latter type of flow is more appropriately treated as "vapor flow" for reasons indicated below.

It is difficult to locate the maximum value of θ at which K' is zero for a given soil. An experiment in which (isothermal) liquid and vapor transfer in dry media are distinguished unequivocally is needed, but does not seem to have yet been made.

"Moisture Potential" and Total Potential of Water in an Unsaturated Porous Solid. The water in unsaturated porous solids is not "free" in the thermodynamic sense, due to capillarity (dominant in moist media) and adsorption (dominant in "dry" media) (Edlefsen and Anderson, 1943). The energy state of the water is commonly expressed by the quantity Ψ (variously known as the "moisture potential," "capillary potential," "moisture tension," "moisture suction," "negative pressure," etc.; see, for example, Richards, 1949, 1953; Childs and Collis-George, 1950b; Croney et al., 1952). It is often convenient to express this quantity as a length, rather analogous to the concept of head in hydraulics. Specifying Ψ in centimeters here, so that g Ψ, where g cm sec^−2 is the acceleration due to gravity, may be identified with the differential specific Gibbs function of the soil water. It follows that the liquid and vapor systems are connected by the relationship

\[ h = \exp \left[ \frac{g \Psi}{RT} \right] \]  

where h is the relative humidity, R (erg gm^−1 deg. C^−1) is the gas constant for water vapor (≈ 4.6.5 x10^8), and T deg. K is the absolute temperature. Note that in unsaturated solids Ψ is negative.

The total potential ϕ may be regarded as comprising Ψ and the gravitational component z, where z is the height above some datum. That is

\[ \phi = \Psi + z \]
rather than \( \psi \), should enter Eq. 21 when \( h \) is expressed in terms of saturated vapor density at the datum level \( z = 0 \), instead of that at elevation \( z \). However, on the occasions when it is necessary to use Eq. 21, there will be very little numerical difference between the two results.

At any fixed temperature, \( \psi \) is a well-defined function of \( \theta \) for any given porous solid. The variation of \( \psi \) with \( T \) is not so well established. It appears that, to a fair approximation, the \( h(\theta) \) relationship is independent of \( T \) in the region where adsorption is dominant (\( h < 0.6 \)) (McBain, 1932; Carman and Raal, 1951; Carman, 1953; Philip and de Vries, 1957). In the region where capillary condensation is dominant it has sometimes been provisionally assumed that \( \psi \) at a given value of \( \theta \) is proportional to the surface tension \( \sigma \) (cf. Philip and de Vries, 1957). However, the experimental data (Richards et al., 1938; Gardner, 1955) suggests that, in rather moist soils, the temperature coefficient of \( \psi \) exceeds that of \( \sigma \). The explanation seems to be that, as \( T \) increases, the volume of totally entrapped air bubbles expands, leading to an altered configuration of the meniscal surface between the liquid water in the medium and the external atmosphere. Experimental study of this effect is in progress in the Australian C.S.I.R.O. Division of Plant Industry.

(The presence of soluble salts somewhat complicates this picture of the energetics of water in a porous solid. Gradients of solute concentration can be expected to have a more important influence on vapor transfer than on liquid transfer. This matter will not be considered further here.)

**The General Equation Describing Liquid Flow of Water in a Porous Solid.** Many of the concepts of the two previous sub-sections were largely implicit in the work of Buckingham (1907). The following half-century saw first neglect, and then gradual rediscovery and exploration of the implications of his study. In 1931 Richards developed a general partial differential equation describing isothermal liquid flow in porous media, but he took as the dependent variable \( \psi \), though he recognized the possibility of an alternative formulation in terms of \( \theta \). This was unfortunate, since the equation in \( \theta \) is somewhat more tractable than that in \( \psi \). In 1936 Childs suggested that moisture movement in porous solids was a diffusion phenomenon, but he confined his attention to the case of constant diffusivity, which does not accord well with observation (cf. Kirkham and Feng, 1949). In 1948, however, Childs and George applied Darcy's law to the isothermal movement of water down a potential gradient produced by a moisture gradient, and deduced a concentration-dependent diffusivity. This work implied the existence of a general partial differential equation describing isothermal liquid flow in porous media, when \( \psi \) was a single valued function of \( \theta \). Klute (1952a, b) derived this equation explicitly. As it shall be shown here it has subsequently been possible to incorporate in this approach moisture transfer in the vapor and adsorbed phases, and the effects of temperature gradients. Also of importance has been the development of numerical methods of solving equations of the diffusion type in which the diffusivity is concentration-dependent.

Eq. 4 may then be written in the form appropriate to unsaturated solids:

\[
q_{\text{liq}}/\rho_w = -K' \nabla \phi \quad (23)
\]

Here \( q_{\text{liq}} \) is the vector flux density in the liquid phase (\( \text{gm cm}^{-2} \text{sec}^{-1} \)) and \( \rho_w \), \( \text{gm cm}^{-3} \) is the density of liquid water. Then, combining the continuity requirement

\[
\frac{\partial \theta}{\partial t} = \frac{1}{\rho_w} \nabla \cdot q_{\text{liq}} \quad (24)
\]

and Eq. 23 yields

\[
\frac{\partial \theta}{\partial t} = \nabla \cdot (K' \nabla \phi) \quad (25)
\]

Eq. 24 neglects vapor (and any adsorbed phase) transfer. (This is quite unimportant in many applications. However, it will be shown later how the other phases may be included in a more precise formulation.) Use of Eq. 22 in Eq. 25 yields
\[ \frac{\partial \theta}{\partial t} = \nabla \cdot (K' \nabla \Psi) + \frac{\partial K'}{\partial z} \]  
\[ (26) \]

When the motion is isothermal, and \( \Psi \) is a unique function of \( \theta \), Eq. 26 reduces to

\[ \frac{\partial \theta}{\partial t} = \nabla \cdot (D_\theta \text{liq} \nabla \Psi) + \frac{\partial K'}{\partial \theta} \cdot \frac{\partial \theta}{\partial z} \]  
\[ (27) \]

where

\[ D_\theta \text{liq} = K' \frac{d \Psi}{d \theta} \]  
\[ (28) \]

This is essentially the equation derived by Klute (1952).

Where temperature gradients exist, and \( \Psi \) depends on both \( \theta \) and \( T \), Eq. 26 may be written as

\[ \frac{\partial \theta}{\partial t} = \nabla \cdot (D_\theta \text{liq} \nabla \theta) + \nabla \cdot (D_T \text{liq} \nabla T) + \frac{\partial K'}{\partial \theta} \cdot \frac{\partial \theta}{\partial z} \]  
\[ (29) \]

(cf. Philip and de Vries, 1957). Here \( D_T \text{liq} \) is given by

\[ D_T \text{liq} = K' \frac{\partial T}{\partial T} \]  
\[ (30) \]

\( D_\theta \text{liq} \) again has the value given in Eq. 28, though now one should write the differential as partial, not total.

In this way the right hand side of Eq. 25 is split into three components—that due to moisture gradient, that due to temperature gradient, and that due to gravity. \( D_\theta \text{liq} \) and \( D_T \text{liq} \) are called the liquid moisture diffusivity and the thermal liquid diffusivity of the medium. Both these quantities vary markedly with \( \theta \). Strictly, they vary also with \( T \), but the variation with \( T \) is relatively slow, and in most practical applications it will suffice to treat \( D_\theta \text{liq} \) and \( D_T \text{liq} \) as purely \( \theta \)-dependent.

The Variation of \( D_\theta \text{liq} \) with \( \theta \). It has already been remarked that \( K' \) decreases rapidly as \( \theta \) decreases from its saturation value. On the other hand, \( d \Psi/d\theta \) increases fairly markedly as \( \theta \) decreases. The net effect is that \( D_\theta \text{liq} \) tends to decrease as \( \theta \) decreases, though not so rapidly as does \( K' \). \( D_\theta \text{liq} \) is of course zero in solids so dry that \( K' \) is zero. Typical \( D_\theta \text{liq}(\theta) \) functions will be found in Childs and Collis-George (1950a), Klute (1952a, b), Staple and Lehane (1954), and Philip (1955b, 1957f). Maximum values of \( D_\theta \text{liq} \) may range from \( 10^{-3} \) cm\(^2\) sec\(^{-1}\) or more for sandy soil down to \( 10^{-7} \) cm\(^2\) sec\(^{-1}\) or less for fine-textured soils. The shape of the curve can also be expected to vary with the texture of the solid.

The Variation of \( D_T \text{liq} \) with \( \theta \). As is noted above, there is some uncertainty as to the precise behavior of \( d^2 \Psi/dT^2 \), especially for values of \( \theta \) close to saturation. Philip and de Vries (1957) computed \( D_T \text{liq} \) for a fine-valued soil, and found a marked peak close to saturation. It is possible that for the reasons noted earlier, the peak should be even more pronounced. In this particular work the maximum value of \( D_T \text{liq} \) was about \( 2 \times 10^{-7} \) cm\(^2\) sec\(^{-1}\) C\(^{-1}\). Both at saturation and in solids so dry that \( K' = 0 \), \( D_T \text{liq} \) will be zero.

MOVEMENT OF THE VAPOR PHASE IN UNSATURATED SOLIDS

Simple Theory of Vapor Transfer. The simplest way to treat the recent developments in understanding of vapor transfer in porous solids is to first present what is, essentially, the classical theory, and then to indicate where the assumptions of the classical theory fail. Then consider a modified theory, recently put forward, which is based on more real assumptions than the classical theory, and which gives quantitative agreement with observed transfer under temperature gradients. The simple theory gives values for the transfer which are only about one-tenth to one-fifth of the observed values.

The classical equation of vapor diffusion, modified so as to apply in porous solids
\[ q_{vap} = -D_{atm} \ m \ a \ a \ \nabla \rho \]  

(31)

where

- \( q_{vap} \) is the vector vapor flux density (gm cm^{-2} sec^{-1})
- \( D_{atm} \) is the molecular diffusivity of water vapor in air (cm^{-2} sec^{-1})
- \( a \) is a tortuosity factor allowing for the additional path length
- \( m \) is the density of water vapor (gm cm^{-3})
- \( \rho \) is the volumetric air content of the medium (cm^3 of air/cm^3)
- \( m \) is the "mass flow factor" introduced to allow for the mass flow of vapor arising from the difference in boundary conditions governing the air and vapor components of the diffusion system (\( m \) may be taken as very close to unity in the systems of interest here.)

Now

\[ \rho = \rho_0 h \]  

(32)

where \( \rho_0 \) is the density of saturated water vapor (gm cm^{-3}). It follows that

\[ \nabla \rho = \rho_0 \nabla h + h \nabla \rho_0 \]  

(33)

If the approximation mentioned earlier is now made, and justified in more detail in Philip and de Vries (1957), that \( h \) is a function of \( \theta \) only, Eq. 33 may be rewritten

\[ \nabla \rho = \rho_0 \frac{dh}{d\theta} \nabla \theta + h \frac{d\rho_0}{dT} \nabla T \]  

(34)

Using Eq. 34 in Eq. 31 gives

\[ \frac{q_{vap}}{\rho_W} = -D_\theta \frac{d\theta}{d\rho} \nabla \theta - D_T \nabla \frac{d\theta}{d\rho} \nabla T \]  

(35)

where

\[ D_\theta \frac{d\theta}{d\rho} = \frac{D_{atm} m a a \rho_0}{\rho_W} \frac{dh}{d\theta} = \frac{D_{atm} m a a g p}{\rho_W RT} \frac{d\psi}{d\theta} \]  

(36)

\[ D_T \frac{d\theta}{d\rho} = \frac{D_{atm} m a a h \beta}{\rho_W} \]  

(37)

Here the final expression for \( D_\theta \frac{d\theta}{d\rho} \) depends on Eq. 21. \( \beta \) in Eq. 37 denotes \( d\rho_0/dT \). \( \rho \) is, of course, temperature dependent, but a value of \( 10^{-4} \) gm cm^{-3} C^{-1} is typical for temperatures occurring naturally in soils.

Isothermal Water Vapor Transfer. Observations in the field (Staple and Lehane, 1954) and the laboratory (Philip, 1955b) suggest that this theory is adequate in the comparatively unimportant case of isothermal vapor transfer. That is, values of \( D_\theta \frac{d\theta}{d\rho} \) computed from Eq. 36 appear to be fairly reliable. Just why the simple theory should be adequate for isothermal transfer, but fails badly for transfer under thermal gradients is a question which will be returned to later.

Water Vapor Transfer Under Thermal Gradients. Quantitative determinations of vapor transfer under temperature gradients (e.g. Gurr et al. 1952; Taylor and Cavazza, 1954; Rollins et al., 1954) have shown that the transfer rates are of the order of five to ten times that predicted by the simple theory. Furthermore, the moisture content at which the maximum vapor transfer is observed to occur is somewhat greater than the simple theory predicts.

Philip and de Vries (1957) have pointed out that the simple theory neglects the interaction of the water vapor with the liquid and solid phases in the medium, and takes no account of the difference between the temperature gradients in the air-filled pores and of the medium as a whole.

They put forward the concept that in a medium in which liquid continuity has failed,
the transfer occurs as a series-parallel process of flow through regions of vapor and liquid. They show that, whereas the classical theory treats the liquid "islands" as obstacles blocking the passage of diffusing vapor, these are in fact regions of very rapid transport of water. Condensation at the upstream end of the island and evaporation at the downstream end produce changes in the curvature of the meniscus at each end, which result in a virtually zero resistance to liquid flow through the island.

Furthermore, when the heat transfer through the various phases of the medium (solid, liquid and gaseous) was examined in detail by methods due to de Vries (1952 a, b), it was found that the temperature gradients across air-filled pores could be of the order of twice the mean temperature gradient in the medium as a whole.

The combined effect of these two considerations is to yield a modified theory which predicts values of $\Delta T_{vap}$ varying from about eight times that predicted by Eq. 36 in wet soils to about three times the value predicted by Eq. 36 in very dry soils. As it stands, the theory is admittedly approximate, especially in the moisture region where liquid continuity is established. Nevertheless, it appears to clarify the understanding of this phenomenon.

Similar complicating factors do not enter the case of isothermal vapor transfer, since: (a) the vapor pressure gradient is now due solely to gradients of moisture content, so that, in general, even very small changes of meniscus curvature produced by condensation and evaporation would be sufficient to reverse the direction of vapor transfer; and (b) the whole matter of differential temperature gradients in different phases does not arise.

One interesting implication of this work concerns the detection and definition of "vapor transfer." The usual experimental means of separating liquid and vapor flow has been to use a soluble "tracer." It is now obvious that such methods cannot distinguish between pure vapor transfer and vapor transfer in series-parallel with transfer through a discontinuous liquid phase in the form of "islands." Clearly, any solute would remain anchored in a particular island; there could be no net transfer of solute even if considerable liquid transport through the islands were taking place. Methods using air gaps are even more obviously fallacious.

Since one of the main practical reasons for distinguishing between liquid and vapor transfer is to gain insight into solute transfer problems in soils, there is a good case for the operational definition of "vapor transfer," proposed by Philip and de Vries (1957), as describing all flows in which there is no liquid continuity. A consequence of this definition is that transfer distinguished as "vapor" by soluble tracer methods would continue to be called "vapor" transfer, even though it is not so in the sense of the classical theory.

The recently published work of Kuzmak and Sereda (1957 a, b) lends further substantiation to the view of thermally induced moisture transfer outlined here.

**POLYPHASE TRANSFER IN POROUS SOLIDS**

**Adsorbed Phase.** It seems probable that, in soils, moisture transfer in the adsorbed phase can be significant only under rather special conditions, such as where the soil is very dry and possesses a large specific surface. Here this matter cannot be dealt with adequately. Theoretical studies such as that of Babbit (1950) and Philip (1955 b, 1957 c) indicate that transfer in the adsorbed phase is also a concentration-dependent diffusion phenomenon, which may be represented by the equation

$$ q_{ads} / \rho_w = - D_{ads} \nabla \theta $$

(38)

(Here $q_{ads}$ is the vector flux density in the adsorbed phase (gm$^{-2}$ sec$^{-1}$) and $D_{ads}$ is a function of $\theta$.) Possibly a second, thermal, term should be added on the right hand side of Eq. 38, but its neglect is consistent with the approximation that $h$ is a function of $\theta$ only.

**General Equation of Polyphase Transfer.** Using Eq. 22 in 23, and adding Eqs. 35 and 38, the following is obtained

$$ q / \rho_w = - D_\theta \nabla \theta - D_T \nabla T - K'k $$

(39)
where

\[ q = q_{\text{liq}} + q_{\text{vap}} + q_{\text{ads}} \]  

(40)

\[ D_\theta = D_{\theta \text{ liq}} + D_{\theta \text{ vap}} + D_{\theta \text{ ads}} \]  

(41)

\[ D_T = D_{T \text{ liq}} + D_{T \text{ vap}} \]  

(42)

It will be recalled that \( k \) is the unit vector in the \( z \)-direction. Combining the continuity requirement in its more exact form (cf. Eq. 24)

\[ \frac{\partial \theta}{\partial t} = - \frac{1}{\rho_w} \nabla \cdot q \]  

(43)

with Eq. 39 the following is obtained

\[ \frac{\partial \theta}{\partial t} = \nabla \cdot (D_\theta \nabla \theta) + \nabla \cdot (D_T \nabla T) + \frac{dK'}{d\theta} \cdot \frac{\partial \theta}{\partial z} \]  

(44)

Comparing this equation with Eq. 29, it can be seen that, in this way, it is possible to incorporate vapor and adsorbed phase transfer into the formulation without complicating the mathematical form. \( D_\theta \) and \( D_T \) may be taken as functions of \( \theta \). Note that the \( D_{T \text{ vap}} \) appearing in Eq. 42 should be the value given by the modified (Philip and de Vries, 1957) theory, not the value found from Eq. 36.

HEAT TRANSFER IN POROUS SOLIDS

Adequate study of the simultaneous heat and moisture fields in porous solids requires some attention also to the matter of heat transfer in such solids. The general heat-conduction equation for this case may be written (Philip and de Vries, 1957; Philip, 1957f):

\[ C \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) + \rho_w L \nabla \cdot (D_\theta \text{ vap} \nabla \theta) \]  

(45)

\( \lambda \), the thermal conductivity (cal \( \text{sec}^{-1} \text{ cm}^{-1} \text{ C}^{-1} \)), includes the contribution to apparent conductivity arising from transport of latent heat by thermally induced vapor transfer (de Vries, 1952a). Both \( \lambda \) and the volumetric heat capacity, \( C \) (cal \( \text{cm}^{-2} \text{ C}^{-1} \)), may vary with \( \theta \). \( L \text{ cal gm}^{-1} \) is the latent heat of vaporization of water. It will be noted that Eqs. 44 and 45, both equations of the diffusion type involving \( \theta \) - and, strictly, \( T \) - dependent diffusivities and conductivities as well as gradients of \( \theta \) and \( T \), together govern the simultaneous moisture and heat fields in the soil. De Vries (1958) has recently developed a more refined analysis of simultaneous heat and moisture transfer, which avoids certain simplifications in the formulation which leads to Eq. 45. The more precise approach promises, unfortunately, to be very complicated.

DISCUSSION

The preceding outlined results would be of limited interest if it were not possible to solve the equations developed. Fortunately, the equations can be solved in the cases of a number of phenomena of fundamental interest in microhydrology. The solutions are in conformity with experimental observations, and have proved serviceable in providing insight into the physics of such diverse phenomena as absorption (Klute, 1952a, b; Philip, 1957c, h, k, 1958a, b), infiltration (Philip, 1954, a, b, 1957c, d, e, h, 1, k, 1958a, b), capillary rise (Philip, 1957c, 1958a), evaporation from soils (Philip, 1954b, 1957d, f), drainage and water retention by soils (Staple and Lehane, 1954; Day and Luthin, 1956, Philip, 1957d) and extraction of soil-water by plants (Philip, 1957d).
Typical results of this approach include the prediction of the various zones of the moisture profile during infiltration observed in the classical work of Bodman and Colman (1944; Colman and Bodman, 1945), prediction of the (experimentally well-established) "falling-rate" and "constant-rate" phases of evaporation from an initially saturated porous solid in a constant environment [and of a final phase of the drying process in which the heat flux in the solid influences the evaporation rate, which explains certain observations of Penman (1941)], and quantitative explanation of data of Richards and Moore (1952) on the effect of the quantity of water applied to a soil on the subsequent drainage and retention of the water. These matters cannot be elaborated here, and the reader is referred to the original papers. Youngs (1957) has recently published work which provides more detailed experimental confirmation of this approach, as applied to the problem of infiltration.

It will be noted that the \( D, K', \) and other \( \theta \)-dependent functions entering the preceding analysis are experimentally determined, and are not readily or reliably represented as analytical functions of \( \theta \). Even if they were, the equations will usually be so complicated that numerical methods of solution would still be required. This has meant that appropriate numerical methods have been needed. Rapid and accurate methods of solving concentration-dependent diffusion equations have been developed in this connection (Philip 1955 a, 1957 a, e).

The analysis of unsteady state phenomena by this means has been limited to problems which are one-dimensional (or exhibit radial symmetry) and in which the initial and boundary conditions are relatively simple. The study of more complicated cases will not be as readily accomplished, and there is definite scope for applying a simpler approximate model of moisture transfer. In cases where water is made available at the surface of a solid, and information is desired on its rate of entry (i.e. problems of absorption or infiltration) such a simple model is available (Philip, 1954a). The connection between the simple model and the detailed diffusion theory has been explored (Philip, 1957 i,k, 1958b) and it is found that the model corresponds to the limiting case (approximated in coarse-textured or dry media) where \( D_\theta \) and \( K' \) assume very large values close to saturation, and are virtually zero throughout the rest of the moisture range. The approximate model has been used to illustrate the magnitude of the effects on infiltration dynamics of vertical heterogeneity of initial moisture content and of permeability characteristics (Philip, 1958c).

An important aspect of the theoretical structure outlined in prior sections is that it provides a coherent scheme which connects an (apparent) diversity of phenomena. Even quite recently each of these phenomena received its own empirical explanation, but now they can be regarded as particular solutions of the general equation 44 (plus Eq. 45, in cases where heat flux is important). This appears to be a definite step towards the establishment of the study of moisture transfer in porous solids as a quantitative physical science.

A limitation in the present approach is that many of the equations, including those which may be usefully solved, depend on the assumption that such characteristics of the soil as \( K', \psi \), and \( D_\theta \) are unique functions of \( \theta \). Many of the difficulties arising in this connection are more apparent than real (Philip 1957h, 1958 a, b). However, some matters are beyond the scope of the analysis in the present form. For example, the variation of \( K' \) with electrolyte concentration in soils of high colloid content (Quirk and Schofield, 1955) means that such soils cannot be adequately dealt with when gradients of electrolyte concentration are present. Again, in deep soils of high colloid content, the \( \psi (\theta) \) relationship may well be influenced by overburden pressures, and the problem falls outside the field of the present approach. For all that, there remains a wide range of agricultural soils for which this theoretical framework is relevant.

It is scarcely necessary to point out that this approach does not depend on any special geometrical model of the solid (e.g. capillary tubes, packings of spheres). Clearly, the theory, in its isothermal form, holds for any solid which can be characterized by a moisture-potential- and a conductivity-function. The more general theory requires additional characteristics to be uniquely determined by \( \theta \) and \( T \), but this is no more restrictive.

The task of integrating into this structure the additional complications of colloidal
behavior, and of mechanical effects such as the influence of surface and foundation loads remains largely untouched. This seems to be the major theoretical problem yet to be faced in modern soil water studies. It demands an intimate combination of the skills of many disciplines—mathematical physics, thermodynamics of irreversible processes, physical chemistry of colloids, soil mechanics, and rheology—to name but the most obvious ones.

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