

Correction of the Buckingham–Darcy Law for flow of high strength salts in variably saturated porous media

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Abstract

The Buckingham–Darcy Law is used to describe fluid flow in unsaturated porous media at low Reynolds number. In order to provide a priori corrections to this law, a process thermodynamic approach is utilized to ascertain the functional dependence. Using this knowledge, corrections to the hydraulic conductivity coefficient are proposed and compared with available data. The proposed corrections substantially predict the observed behavior of flow of high concentration (saturated) sodium chloride solutions in porous media. During the derivation, physical principles consistent with the thermodynamics of the system were utilized. A review of these principles and their results provides an alternative form of the generalized Gibbs–Duhem Relation for continuous processes, indicating that the identical equivalence to zero is unlikely to occur for dissipative processes. Further, the postulated Gibbs and Gibbs–Duhem Relations indicate that special differential operators need to be used for continuous processes rather than the usual use of a generic differential. © 2006 Elsevier Ltd. All rights reserved.

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1. Introduction

The goal of this paper is to place the Buckingham–Darcy Law into the proper context with respect to process thermodynamics. Then, using this context, the proper corrections to the Buckingham–Darcy Law coefficient are postulated for high salt strength aqueous solutions in unsaturated porous media. Finally, the postulated corrections are tested against data collected by Scotter [22].

Darcy's Law is an empirical linear relationship that has been shown to describe the flow (at sufficiently low Reynolds number) of liquid in saturated porous media. Buckingham subsequently extended Darcy's Law to the case of unsaturated flows in porous media [4]. Since this time, other important gradients have been examined for their effects on liquid flow. These include gradients in salt concentration (cf., [15,16]) and temperature (cf., [17,21,24]). Approaches to handle salt gradients include postulation of an osmotic pressure for incorporation into a Darcy-like law (cf., [16]) and the use of Onsager Relations in process thermodynamic formulations of the flow problem and subsequent experimental determination of osmotic efficiency (cf., [15]). The following uses a process thermodynamic approach, but rather than assuming that formulation of

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Notation

Variables and parameters

$\vec{x} = \begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$	position vector
t	time
ρ	mass density
m	mass
ϕ	volume fraction
X	mass fraction
V	volume
\overline{B}	surface (boundary) of V
\vec{n}	unit normal vector to a surface S pointing outward from V
n	porosity
$\vec{w} = \vec{x}_t$	average velocity of center of mass
\vec{v}	true velocity within a phase (e.g., at the pore scale)
$\tilde{v} = \vec{v} - \vec{w}$	velocity variation
Φ	kinetic energy functional
\vec{j}	non-advective flux
\vec{g}	gravitational acceleration constant
g	magnitude of gravitational acceleration constant
\hat{M}	source–sink term of mass
\hat{H}	source/sink term of entropy
H	entropy in the reversible thermodynamics formulation
e	specific total energy (i.e., energy per mass)
T	temperature
P	pressure
K	hydraulic conductivity
k	permeability
S	saturation
D	diffusivity
u	internal energy

η	<i>two meanings</i> : specific entropy or the Brooks and Corey fitting parameter when written as a superscript. These are the commonly used standard symbols
μ	<i>two meanings</i> : chemical potential of constituent β in phase α ($\mu^{\beta\alpha}$) or viscosity of the liquid (μ^L). These are the commonly used standard symbols
σ	<i>two meanings</i> : entropy production terms in the energy equations (e.g., $\sigma^{\alpha\rightarrow\gamma}$ or σ^α) or interfacial tension between the liquid gas interface (σ^{LG}) in the diffusion correction equations. These are the commonly used standard symbols

Superscripts and subscripts

α	index over a consistent set of phases
β	index over a consistent set of constituents
$\beta\alpha$	denotes property of β in α (e.g., $\rho^{\beta\alpha}$ is density of constituent β in phase α)
S	solid phase of a mixture
L	liquid phase of a mixture
G	gaseous phase of a mixture
s	saturated with water (e.g., used for saturated hydraulic conductivity)
ss	non-reactive structural solid constituent of a mixture (e.g., silica sand upon which salt precipitates)
h	precipitated salt (anhydrous) constituent of a mixture (h is for halite or table salt)
w	pure water or H ₂ O constituent of a mixture
a	dry air constituent of a mixture
0	zero-salt reference condition
η	Brooks and Corey fitting parameter when written as a superscript
D	non-advective (e.g., diffusion)
HD	non-advective heat flux (e.g., conduction)

the problem in terms of Onsager coefficients is a sufficient endpoint, the Onsager system of equations is examined to extract the functional dependence of the hydraulic conductivity. Subsequently, the dependence is made explicit, and the theory is compared with data. In the discussion section, the current results are placed in proper context with the literature above. Also, the general thermodynamic derivation conducted herein provides insight for the use of the Gibbs–Duhem Relation for dissipative systems. A substantial discussion of the implications is completed.

2. Principles used in the following derivation

In the following derivation, as in most contemporary thermodynamics papers, a set of mathematical tools are used. These tools are often applied for the sake of brevity,

but unfortunately at the cost of clarity of the derivation. This is further complicated by the necessary use of poorly (physically) understood terms such as entropy and entropy production. While these terms may be well-defined mathematically, a physical understanding of entropy terms involves understanding interrelated dissipative fluxes in complex systems. In an attempt to clarify the following derivation, a short summary of governing physical principles applied to the problem is provided here (listed in the general order in which they are applied).

2.1. Governing principles

- (A) A conservation equation may be written for every localized extensive (i.e., depends on the amount) variable. The localized extensive variables are those that

are associated with the extensive variables from equilibrium thermodynamics (cf., [7]). Here, a more general notion of conservation equation is utilized. For example, in a viscous flow system, momentum is not conserved (due to frictional losses), but a conservation equation for momentum may be written that accounts for the loss of momentum.

- (B) The specific entropy (a localized extensive variable) in the heat flow conservation equation may (reasonably) be associated with the heat of formation (per unit temperature). This allows use of physical intuition when writing a heat conservation equation and is consistent with the historical formulation of heat flow (as noted below in the derivation).
- (C) Each thermodynamic flux has a *natural* primary thermodynamic force associated with it, and the flux–force “pairs” should be written in their *natural* form (i.e., coupled) in the energy conservation equation. This principle embodies a physical notion, namely, that fluxes directly arise from the gradients in certain potentials and indirectly from others. For example, a gradient in the mechanical potential, given by pressure and gravity, *directly* results in liquid phase flow; whereas, a gradient in temperature must cause expansion resulting in a gradient in pressure to *indirectly* cause fluid flow. This principle is not always true or precise, though it shall be shown to be useful when looking for motivation. An immediate counter-example is the case of advective transport of heat which depends on both gradients in mechanical potential and temperature.
- (D) Energy fluxes associated with fluxes of conserved quantities (i.e., those quantities described in A) have fluxes associated with *all* movement of the conserved quantity. This principle is utilized when postulating the poorly defined energy exchange terms, and its use becomes apparent in the derivation.
- (E) The entropy production term in the energy conservation equation may be thought of as an accounting tool. It will become apparent that the entropy production (as it is traditionally used) is associated with the energy conservation equation and *not* the heat flow equation. It is used to account for non-negligible energy fluxes that are not accounted for in the energy conservation equations (i.e., there is an apparent loss of energy that obeys the entropy maximization principle). The physical principle utilized here is that energy must be conserved, and that entropy may be produced by dissipations or by not considering all of the important processes. This principle allows for dissipative losses other than heat flow to contribute to entropy production.

These five physically derived principles are used to motivate development of appropriate energy equations from which the Buckingham–Darcy Law for high salt strength aqueous solutions will be derived.

3. Basic conservation laws

For the sake of completeness, and so that the following derivation is as clear as possible, the derivation begins with a brief discussion of the implicit assumptions underlying the methods to be used, followed by a detailed derivation of the first conservation laws developed for subsequent use. However, in the interest of brevity, since the procedure used is identical in principle for subsequent derivations, derivations are streamlined, and in some cases, the reasonableness of a particular form is noted. This is not due to a lack of ability to derive the equations rigorously, but rather, it is presumed that such digression does not add significantly to the identified goal of developing corrections to Darcy’s Law. In this way, a proper motivation for implementing corrections to Darcy’s Law is developed. Variables and other notation used for the following derivations are defined in the “Notation” section.

The continuum approach and mixture theory are used to derive a set of equations that describe multi-phase flow in porous media. The continuum approach assumes that super-REV (cf., [1]) parameters such as mass density of phase α (ρ^α) and volume fraction of phase α (ϕ^α) are well-defined mathematically. Mixture theory assumes that each component of a mixture is well-defined in terms of these parameters, and that the sum of all of the components represents the total material in an arbitrary volume (V). Mixture theory also assumes that the phases and constituents co-exist at all points in space. This assumption of co-existence allows the definition of a density in the mathematical sense, which in turn allows the use of differential and integral calculus in problem solving. However, “smearing” the properties into well-defined densities precipitates the need to develop effective parameters that represent the average behavior of the mixture (e.g., porosity, permeability, etc. [1]). One approach to develop flow parameters is through the use of process thermodynamics (cf. [8]) and the Onsager Relations [18,19].

For the purposes of this manuscript, a *component* is a very general term defined as any sub-part of a mixture for which the previous notions hold. *Constituents* are defined as the simplest components that it is *necessary* to divide a mixture into (e.g., H₂O and a homogeneous mixture of dry air might be a typical choice of constituents used to describe moist air for a given problem). *Phases* are defined as components of the mixture that may be delineated from other phases by a distinct (i.e., sudden) change in one or more of the densities in the system to be modeled (e.g., liquid water containing dissolved air and moist gaseous air, or oil and water). In a mixture, phases are assumed to be collocated (i.e., multiple phases may be present at exactly the same point), and exchanges between phases are treated as source/sink terms. Each phase is made up of one or more constituents. Normally, different phases have different equations of motion and/or energy, though sometimes, energy equations for the

entire mixture of phases are written to simplify the mathematics of the system.

Using the previous ideas, flow in a porous media may be divided into immiscible flows (describing the relation between the phases) and miscible flow (describing flow within a phase). When considering the volume fractions (ϕ) of the phases and the mass fractions (X) of the constituents in each phase, by definition,

$$\sum_{\alpha=1,\dots,N} \phi^\alpha = 1 \tag{1}$$

$$\sum_{\beta=1,\dots,N^\alpha} X^{\beta\alpha} = 1 \tag{2}$$

where N is the total number of consistent phases into which a substance may be divided, and N^α is the total number of consistent constituents in an arbitrary phase α . *Consistency* of the components means that no component is a sub-component of another component. This ensures that there is no double-counting of components. In order to provide clarity to the derivation and to allow the reader to use their intuition, it may be assumed that $\alpha = S, L, G$ (i.e., solid, liquid, and gas phases) and $\beta = ss, h, w, a$ (i.e., non-reactive solid, salt, pure water, and dry air constituents) are consistent sets of components for the same system.

The Gauss Divergence Theorem (Eq. (3)) and the Reynolds Transport Theorem (Eq. (4)) are used during the following derivation, so they are stated here for completeness. The Gauss Divergence Theorem allows conversion of surface integrals to volume integrals. When taking the time derivative of an integral, the Reynolds Transport Theorem allows for the fact that the volume of integration may be a function of time. Let f be an arbitrary function, and let \vec{z} be an arbitrary vector of sufficient smoothness (different sufficient conditions are given by Kellogg [13], but most commonly, the condition of continuous differentiability is used).

$$\int_V (\nabla \cdot \vec{z}) dV = \oint_B (\vec{z} \cdot \vec{n}) dB \tag{3}$$

$$\begin{aligned} \frac{d}{dt} \int_{V(t)} f(\vec{x}, t) dV &= \int_{V(t)} \frac{\partial f(\vec{x}, t)}{\partial t} dV + \oint_{B(t)} f(\vec{x}, t) \vec{w} \cdot \vec{n} dB \\ &= \int_{V(t)} \left[\frac{\partial f(\vec{x}, t)}{\partial t} + \nabla \cdot (f(\vec{x}, t) \vec{w}) \right] dV \end{aligned} \tag{4}$$

The vector \vec{w} arises naturally as the velocity of the boundary during the derivation of (4), but use of the Gauss Divergence Theorem converts this velocity to the localized velocity at each point (e.g., this will be the average linear velocity for groundwater flow). Also, for ease of notation, the so-called material derivative or substantial derivative of an arbitrary function f is defined as

$$\frac{Df}{Dt} \equiv \frac{\partial f}{\partial t} + \vec{w}^\alpha \cdot \nabla f \tag{5}$$

3.1. Conservation of mass

Define the mass of constituent β in phase α as

$$\begin{aligned} [\text{mass of constituent } \beta \text{ in phase } \alpha] \\ = \int_V \phi^\alpha \rho^{\beta\alpha} dV = \int_V \phi^\alpha X^{\beta\alpha} \rho^\alpha dV \end{aligned} \tag{6}$$

Before the time-dependent mass conservation equation can be derived, it is advantageous to choose a volume, $V(t)$, such that the resulting equations are in terms of the barycentric (center of mass) velocity of the phase. This is desired because the conservation of energy equation requires the barycentric velocity for computation of the kinetic energy. Denote $V(t=0) = V_0$, an arbitrary initial volume. Using the methods of continuum mechanics, it is assumed that at some arbitrarily small time after $t=0$, all particles initially inside V_0 will be arbitrarily close to their initial positions. This means that it is possible to define a new volume, $V(t)$, such that only particles of β initially inside V_0 are still in $V(t)$ (minus any particles lost to sources or sinks). At the molecular level, certainly this is false, but since only the macroscopic level is considered, this is unimportant as long as the same net amount of mass of β remains inside the volume (minus sources/sinks) and that the deformation of the volume corresponds to the *effective* motion of β . Choosing this mass-conserving volume, there is no movement of constituent β (in phase α) across the surface $B(t)$ of $V(t)$; and movement of constituent β between phases looks like a source/sink term because all phases coexist by the mixture theory assumptions. The resulting mathematical description of the mass conservation law is

$$\frac{d}{dt} \int_{V(t)} \phi^\alpha X^{\beta\alpha} \rho^\alpha dV = \int_{V(t)} \hat{M}^{\beta\alpha} dV \tag{7}$$

where $\hat{M}^{\beta\alpha}$ is the source/sink term. Since the volume possibly encompasses other phases of the mixture, sources/sinks include exchange between the phases, exchanges between the constituents in a phase (e.g., chemical uptake by organic colloids suspended in the liquid phase), as well as any other possible sources. Application of the Reynolds Transport Theorem to Eq. (7), and subsequent rearranging yields

$$\int_{V(t)} \left[\frac{\partial}{\partial t} (\phi^\alpha X^{\beta\alpha} \rho^\alpha) + \nabla \cdot (\phi^\alpha X^{\beta\alpha} \rho^\alpha \vec{w}^{\beta\alpha}) - \hat{M}^{\beta\alpha} \right] dV = 0 \tag{8}$$

Since $V(t)$ is arbitrary in size and location, the integrand must be identically zero, giving us the local form of the conservation of mass equation.

$$\frac{\partial}{\partial t} (\phi^\alpha X^{\beta\alpha} \rho^\alpha) + \nabla \cdot (\phi^\alpha X^{\beta\alpha} \rho^\alpha \vec{w}^{\beta\alpha}) - \hat{M}^{\beta\alpha} = 0 \tag{9}$$

Summing Eq. (9) over the constituents yields

$$\frac{\partial}{\partial t} (\phi^\alpha \rho^\alpha) + \nabla \cdot \left(\sum_\beta \phi^\alpha X^{\beta\alpha} \rho^\alpha \vec{w}^{\beta\alpha} \right) - \hat{M}^\alpha = 0 \tag{10}$$

where the term \hat{M}^α is the source/sink term that describes exchange between the phases. The above procedure may be followed for the phase, rather than the constituent, and Eq. (10) is reproduced except the term in parentheses is replaced by $\phi^\alpha \rho^\alpha \vec{w}^\alpha$, which implies that the phase velocity is

$$\vec{w}^\alpha = \frac{\sum_\beta \phi^\alpha X^{\beta\alpha} \rho^\alpha \vec{w}^{\beta\alpha}}{\sum_\beta \phi^\alpha X^{\beta\alpha} \rho^\alpha} \quad (11)$$

Noticing that

$$\sum_\beta \phi^\alpha X^{\beta\alpha} \rho^\alpha (\vec{w}^{\beta\alpha} - \vec{w}^\alpha) = 0 \quad (12)$$

the non-advective velocity of a constituent is defined as $\vec{w}^{\beta\alpha D} \equiv \vec{w}^{\beta\alpha} - \vec{w}^\alpha$. By these choices of velocities, \vec{w}^α is the barycentric velocity of the phase, and $\vec{w}^{\beta\alpha D}$ is the diffusion/dispersion velocity (i.e., the velocity relative to the barycentric phase velocity). As a result of the above, the mass conservation equation for the phase is

$$\frac{\partial}{\partial t} (\phi^\alpha \rho^\alpha) + \nabla \cdot (\phi^\alpha \rho^\alpha \vec{w}^\alpha) - \hat{M}^\alpha = 0 \quad (13)$$

and the mass conservation for each constituent is

$$\frac{\partial}{\partial t} (\phi^\alpha X^{\beta\alpha} \rho^\alpha) + \nabla \cdot (\phi^\alpha X^{\beta\alpha} \rho^\alpha \vec{w}^\alpha + \phi^\alpha X^{\beta\alpha} \rho^\alpha \vec{w}^{\beta\alpha D}) - \hat{M}^{\beta\alpha} = 0 \quad (14)$$

where the divergence operator is operating on the *net* flux of the constituent within the phase (i.e., advective flux plus the diffusive/dispersive flux). Notice that $\phi^\alpha X^{\beta\alpha} \rho^\alpha$ is the volumetric concentration of β in phase α , so (14) is the transport equation associated with the flow Eq. (13).

Using principles A and B above, a similar equation may be derived using the same method for heat flow, yielding

$$T^\alpha \left[\frac{\partial}{\partial t} (\phi^\alpha \rho^\alpha \eta^\alpha) + \nabla \cdot (\phi^\alpha \rho^\alpha \eta^\alpha \vec{w}^\alpha + \phi^\alpha \rho^\alpha \eta^\alpha \vec{w}^{\alpha HD}) - \hat{H}^\alpha - \eta^\alpha \hat{M}^\alpha \right] = 0 \quad (15)$$

where T^α is the temperature, and η^α is commonly referred to as the specific entropy of phase α (i.e., $\phi^\alpha \rho^\alpha \eta^\alpha$ is the entropy density). The second to the last term is the heat exchange via conduction between the phases, the last term is the heat energy exchanged as mass changes phases, and the fluxes inside the divergence operator are the advective heat flux and the conductive and dispersive heat flux. Recalling that η^α is a localized extensive variable, that T^α is its associated intensive variable, and that TdH (H is a capital η) is the heat flow in equilibrium thermodynamics [7], it becomes apparent that the above equation is derived by developing a conservation equation for the localized extensive variable. The above equation merely states that the localized extensive variable entropy may be advected, conducted intra-phase (i.e., diffused), dispersed due to pore-scale velocity variations, and exchanged either by conduction between the phases or when mass is exchanged (e.g., heat of formation). Any number of non-advective

fluxes or exchange terms may be added without impacting the derivation below, and it is only critical that a law of this form may be written in order to proceed.

4. Conservation of energy

The specific energy (e^α) of phase α may be written in the usual form (cf., [8]):

$$e^\alpha = T^\alpha \eta^\alpha + \frac{P^\alpha}{\rho^\alpha} + \sum_\beta \mu^{\beta\alpha} X^{\beta\alpha} + \frac{1}{2} \vec{v}^\alpha \cdot \vec{v}^\alpha + \vec{g} \cdot \vec{x} \quad (16)$$

P^α is the pressure in the α phase, $\mu^{\beta\alpha}$ is the chemical potential of constituent β in the α phase, $\frac{1}{2} \vec{v}^\alpha \cdot \vec{v}^\alpha$ is the specific kinetic energy of the fluid, and $\vec{g} \cdot \vec{x}$ is the specific energy associated with gravity (i.e., gravitational acceleration vector dotted with the position vector; this equals gx_3 in the regular Cartesian coordinate system).

Notice that \vec{v}^α is the true barycentric velocity of the phase at each point (i.e., no longer treated as a mixture), whereas \vec{w}^α is the “smeared” effective barycentric velocity of the phase defined for the mixture. \vec{w}^α is related to \vec{v}^α in that \vec{w}^α is a type of volume average of \vec{v}^α . For non-zero velocities, this implies that \vec{v}^α is more variable than \vec{w}^α , which in turn implies that the integral of the true specific kinetic energy term represented by $\frac{1}{2} \vec{v}^\alpha \cdot \vec{v}^\alpha$ will be different from, and likely greater than, the kinetic energy described by $\frac{1}{2} \vec{w}^\alpha \cdot \vec{w}^\alpha$. The precise relationship between \vec{v}^α and \vec{w}^α may be established by taking the volume average of each (cf., [25]). In this process, the integrand containing \vec{w}^α also must contain the “smeared” function ϕ^α so that the integrand is a proper density, while the volume average of \vec{v}^α is constrained to be zero within all other phases (easily obtained through the use of an indicator function). But, this represents a level of complexity that is unnecessary for the following derivation for the following reason. Since the velocity \vec{v}^α is not continuously differentiable in porous media, then neither is $\frac{1}{2} \vec{v}^\alpha \cdot \vec{v}^\alpha$. So for the same reason we developed the notion of the smoothed variable ϕ^α , a smooth variable representing the specific kinetic energy (which corresponds to the mass density in the mixture formulation) is needed. Since this variable is implicitly related to ϕ^α , the notation used here for this variable is $\Phi(\vec{w}^\alpha, \vec{v}^\alpha)$, where $\Phi(\vec{w}^\alpha, \vec{v}^\alpha)$ is a *functional* (i.e., an integral) that represents the smoothed specific kinetic energy. Fortunately, the only property of $\Phi(\vec{w}^\alpha, \vec{v}^\alpha)$ that is needed for the derivation below is that it goes to zero as velocity goes to zero. Since this is true, this precludes the lengthy digression of establishing the exact relationship between \vec{v}^α and \vec{w}^α (i.e., rigorously defining $\Phi(\vec{w}^\alpha, \vec{v}^\alpha)$) for the purposes of this paper. Now, Eq. (16) implies that the energy density may be written as

$$\phi^\alpha \rho^\alpha e^\alpha = \phi^\alpha \rho^\alpha \left(T^\alpha \eta^\alpha + \frac{P^\alpha}{\rho^\alpha} + \sum_\beta \mu^{\beta\alpha} X^{\beta\alpha} + \Phi(\vec{w}^\alpha, \vec{v}^\alpha) + \vec{g} \cdot \vec{x} \right) \quad (17)$$

In (17), the specific kinetic energy term was the only term requiring alteration. This is true because subsystems are additive in thermodynamics. The kinetic energy term required alteration only because of postulation of a smooth *volume* fraction function, and specific kinetic energy is a function of *volumetric* flow rate. No other specific energies depend on the volumetric properties.

Using principle A, and performing essentially the same conservation procedure as above, but assuming that the volume of integration is that which yields the advective velocity \vec{w}^α , yields the local form of the energy equation:

$$\frac{\partial}{\partial t}(\phi^\alpha \rho^\alpha e^\alpha) + \nabla \cdot (\phi^\alpha \rho^\alpha e^\alpha \vec{w}^\alpha) = - \sum_k \nabla \cdot \vec{j}_k^\alpha + \hat{E}^\alpha \quad (18)$$

The first term is the accumulation of energy, the second term is the divergence of the advected energy flux, the third term is the sum of an arbitrary number of (non-advective) fluxes across the volume boundary $B(t)$, and the last term is the sources/sinks. The above may be rewritten as

$$\begin{aligned} & \left(\frac{P^\alpha}{\rho^\alpha} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\alpha, \tilde{v}^\alpha) \right) \left[\frac{\partial}{\partial t}(\phi^\alpha \rho^\alpha) + \nabla \cdot (\phi^\alpha \rho^\alpha \vec{w}^\alpha) \right] \\ & + \sum_\beta \mu^{\beta\alpha} \left[\frac{\partial}{\partial t}(\phi^\alpha \rho^\alpha X^{\beta\alpha}) + \nabla \cdot (\phi^\alpha \rho^\alpha X^{\beta\alpha} \vec{w}^\alpha) \right] \\ & + T^\alpha \left[\frac{\partial}{\partial t}(\phi^\alpha \rho^\alpha \eta^\alpha) + \nabla \cdot (\phi^\alpha \rho^\alpha \eta^\alpha \vec{w}^\alpha) \right] \\ & + \phi^\alpha \rho^\alpha \frac{D}{Dt} \left(\frac{P^\alpha}{\rho^\alpha} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\alpha, \tilde{v}^\alpha) \right) + \sum_\beta \phi^\alpha \rho^\alpha X^{\beta\alpha} \frac{D\mu^{\beta\alpha}}{Dt} \\ & + \phi^\alpha \rho^\alpha \eta^\alpha \frac{DT^\alpha}{Dt} = - \sum_k \nabla \cdot \vec{j}_k^\alpha + \hat{E}^\alpha \end{aligned} \quad (19)$$

The equation above has been written employing principle C from above to obtain an equation in terms of *natural* variable couples. The first three terms are written as intensive variables multiplied by the differentials of the *corresponding* localized extensive variables, the second set of three terms are the localized extensive variables multiplied by differentials of the *corresponding* intensive variables, and the remaining terms (on the right-hand side of the equation) are associated with energy exchanges relative to the barycentric velocity of the α phase, between the phases, and production of entropy. The three terms inside the first set of parentheses are the specific energies associated with the center of mass (i.e., they *correspond* to the center of mass). In equilibrium thermodynamics, the pressure is normally associated with the extensive variable volume rather than mass. Here, there has been a special choice of volume that conserves mass by design, so mass and volume are not separable in this formulation. This requires that pressure is also related to mass, and the relationship is seen explicitly through inclusion of the phase density (which equals one over the specific volume) in the pressure term in (19). In general, the specific energies associated with the center of mass may be viewed as the compressional (elastic) energy, the gravitational (potential) energy, and the kinetic energy.

Each of these energies is a potential that may result in (or perpetuate) flow of the phase. In this way, the first term of the equation is associated with the conservative work. In a very natural extension of equilibrium thermodynamics, the above reasoning results in the conclusion that the third term is related to the conservative heat flow (though heat conduction has not been accounted for yet); and analogously, the second term is related to the conservative chemical energy flux (without the chemical diffusion term). Next, the observation that these are “almost” the conservative heat and chemical energy fluxes is helpful when defining the right-hand side of (19).

In general, it is desired to allow energy to be exchanged via: mass exchange between the phases; conduction between the phases; intra-phase conduction and dispersion of heat; and intra-phase transfer of constituents resulting from chemical potential gradients (e.g., chemical diffusion). Description of fluxes and exchanges are defined by the scientist developing the governing equations. These fluxes and exchanges must satisfy principle D from above, and in fact, principle D may be used to check that no fluxes are forgotten. Here, the possibility that chemical energy and heat may move non-advectively is considered (i.e., heat or chemical energy may be transferred by other mechanisms such as diffusion, dispersion, conduction, etc.). This is accomplished by writing the very general form of the intra-phase energy fluxes on the right-hand side of the energy conservation equation as

$$\begin{aligned} - \sum_k \nabla \cdot \vec{j}_k^\alpha &= - \sum_\beta \nabla \cdot (\phi^\alpha \rho^\alpha X^{\beta\alpha} \mu^{\beta\alpha} \vec{w}^{\beta\alpha D}) \\ &\quad - \nabla \cdot (\phi^\alpha \rho^\alpha T^\alpha \eta^\alpha \vec{w}^{\alpha HD}) \end{aligned} \quad (20)$$

Divergence terms of this form may be derived using the integral methods above by assuming each of the terms in parentheses are fluxes passing the boundary $B(t)$ (which is deforming with velocity \vec{w}^α) associated with $V(t)$. The first term is the sum of the chemical energy fluxes resulting from diffusion/dispersion, and the second term are the conductive and dispersive heat fluxes.

During mass exchange, it is necessary that the exchanged mass go from the energy state of the one phase to the energy state of the other phase. Considering the energy exchanges associated with heat conduction and exchange of mass between two arbitrary phases gives the following exchange term:

$$\begin{aligned} \hat{E}^{\alpha \rightarrow \gamma} &= \sigma^{\alpha \rightarrow \gamma} + \hat{H}^{\alpha \rightarrow \gamma} (T^\alpha - T^\gamma) + \sum_\beta \hat{M}^{\beta\alpha \rightarrow \beta\gamma} (\mu^{\beta\alpha} - \mu^{\beta\gamma}) \\ &\quad + \hat{M}^{\alpha \rightarrow \gamma} \left[\left(\frac{P^\alpha}{\rho^\alpha} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\alpha, \tilde{v}^\alpha) + T^\alpha \eta^\alpha \right) \right. \\ &\quad \left. - \left(\frac{P^\gamma}{\rho^\gamma} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\gamma, \tilde{v}^\gamma) + T^\gamma \eta^\gamma \right) \right] \end{aligned} \quad (21)$$

The last terms (i.e., all terms associated with mass exchange) are the change in energy that must accompany a change in state due to mass exchange between the phases. They represent the energy required to form α phase mass

at a particular state (as uniquely defined by the specific energies) from γ phase mass in another state. The second term is the analogous heat exchange due to conduction. The first term on the right-hand side is related to the entropy production (cf., [8]). It represents those energy exchanges/uses/losses that have not been quantified. Its use here is as an accounting tool that ensures equality is preserved in the event that representation of the right-hand side of the energy equation is inadequate to describe all energy exchanges, conversions, or losses (i.e., principle E from above). Notice that summing over the phases yields
$$Y^\alpha = \sum_\gamma Y^{\alpha \rightarrow \gamma} \quad \text{for } Y^\alpha = \hat{E}^\alpha, \sigma^\alpha, \hat{H}^\alpha, \hat{M}^\alpha, \hat{M}^{\beta\alpha} \quad (22)$$

Also, conservation of localized extensive quantities also requires that

$$Y^{\alpha \rightarrow \gamma} = -Y^{\gamma \rightarrow \alpha} \quad \text{for } Y = \hat{E}, \sigma, \hat{H}, \hat{M} \quad (23)$$

Substituting (20) and (21) into the energy conservation equation, and cancellation of terms associated with the other conservation equations, yields

$$\begin{aligned} & \phi^\alpha \rho^\alpha \frac{D}{Dt} \left(\frac{P^\alpha}{\rho^\alpha} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\alpha, \tilde{v}^\alpha) \right) + \sum_\beta \phi^\alpha \rho^\alpha X^{\beta\alpha} \frac{D\mu^{\beta\alpha}}{Dt} \\ & + \phi^\alpha \rho^\alpha \eta^\alpha \frac{DT^\alpha}{Dt} + \sum_\beta \phi^\alpha \rho^\alpha X^{\beta\alpha} \vec{w}^{\beta\alpha D} \cdot \nabla \mu^{\beta\alpha} \\ & + \phi^\alpha \rho^\alpha \eta^\alpha \vec{w}^{\alpha HD} \cdot \nabla T^\alpha \\ & = \sigma^\alpha - \sum_\gamma \left(\hat{H}^{\alpha \rightarrow \gamma} T^\gamma + \sum_\beta \hat{M}^{\beta\alpha \rightarrow \beta\gamma} \mu^{\beta\gamma} \right. \\ & \left. + \hat{M}^{\alpha \rightarrow \gamma} \left(\frac{P^\gamma}{\rho^\gamma} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\gamma, \tilde{v}^\gamma) + T^\gamma \eta^\gamma \right) \right) \end{aligned} \quad (24)$$

In general for the following, it is sufficient that the right-hand side behaves as a source/sink term (i.e., it is a point-wise exchange of energy), because this implies that the left-hand side includes only the differential terms. Defining the right-hand side as the source/sink term, $\tilde{\sigma}^\alpha$, the above may be rewritten as

$$\begin{aligned} & \phi^\alpha \rho^\alpha \frac{\partial}{\partial t} \left(\frac{P^\alpha}{\rho^\alpha} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\alpha, \tilde{v}^\alpha) \right) + \sum_\beta \phi^\alpha \rho^\alpha X^{\beta\alpha} \frac{\partial \mu^{\beta\alpha}}{\partial t} \\ & + \phi^\alpha \rho^\alpha \eta^\alpha \frac{\partial T^\alpha}{\partial t} + \phi^\alpha \rho^\alpha \vec{w}^\alpha \cdot \nabla \left(\frac{P^\alpha}{\rho^\alpha} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\alpha, \tilde{v}^\alpha) \right) \\ & + \sum_\beta (\phi^\alpha \rho^\alpha X^{\beta\alpha} \vec{w}^\alpha + \phi^\alpha \rho^\alpha X^{\beta\alpha} \vec{w}^{\beta\alpha D}) \cdot \nabla \mu^{\beta\alpha} \\ & + (\phi^\alpha \rho^\alpha \eta^\alpha \vec{w}^\alpha + \phi^\alpha \rho^\alpha \eta^\alpha \vec{w}^{\alpha HD}) \cdot \nabla T^\alpha = \tilde{\sigma}^\alpha \end{aligned} \quad (25)$$

The above equation is written as a sum of the accumulations plus the sum of the flux terms is equal to a source/sink term (which is related to entropy production). In accordance with process thermodynamics and the Onsager Reciprocal Relations, the fluxes may be written in terms of the associated thermodynamic “forces” as follows:

$$\begin{aligned} \phi^\alpha \rho^\alpha \vec{w}^\alpha & = L_{11} \nabla \left(\frac{P^\alpha}{\rho^\alpha} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\alpha, \tilde{v}^\alpha) \right) + L_{12} \nabla T^\alpha \\ & + \sum_\beta L_{1(\beta+2)} \nabla \mu^{\beta\alpha} \end{aligned} \quad (26a)$$

$$\begin{aligned} & \phi^\alpha \rho^\alpha \eta^\alpha \vec{w}^\alpha + \phi^\alpha \rho^\alpha \eta^\alpha \vec{w}^{\alpha HD} \\ & = L_{21} \nabla \left(\frac{P^\alpha}{\rho^\alpha} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\alpha, \tilde{v}^\alpha) \right) + L_{22} \nabla T^\alpha \\ & + \sum_\beta L_{2(\beta+2)} \nabla \mu^{\beta\alpha} \end{aligned} \quad (26b)$$

$$\begin{aligned} & \phi^\alpha \rho^\alpha X^{\xi\alpha} \vec{w}^\alpha + \phi^\alpha \rho^\alpha X^{\xi\alpha} \vec{w}^{\xi\alpha D} \\ & = L_{(\xi+2)1} \nabla \left(\frac{P^\alpha}{\rho^\alpha} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\alpha, \tilde{v}^\alpha) \right) + L_{(\xi+2)2} \nabla T^\alpha \\ & + \sum_\beta L_{(\xi+2)(\beta+2)} \nabla \mu^{\beta\alpha} \quad \text{for all } \xi \end{aligned} \quad (26c)$$

where the L are the Onsager Coefficients. Some formulations of process thermodynamic problems suggest that $\tilde{\sigma}^\alpha$ should be written $T^\alpha \tilde{\sigma}^\alpha$, requiring that temperature be divided through each term (cf., [8]). Since we will only consider the isothermal case in the example below, this reduces to inclusion of a constant which is readily absorbed into the Darcy coefficient. It also may be argued that instead of (25), the proper equation to consider is the equation that results from a summation over the phases (and interfaces when these are important to the energy balance), and in general, this is likely correct. This would result in the need to include additional Onsager coefficients that are coupled with gradients of the localized extensive variables in the other phases (and interfaces). But, since the purpose of this derivation is motivation for the Darcy Law correction, and since the principles applied below may also extend to accounting for these additional terms, this level of detail is avoided here.

Notice that (26a)–(26c) are flux laws. Rather than substituting back into (25), the common practice is to substitute the flux laws into the appropriate conservation equation (e.g., (26a) corresponds to (13)). Eq. (25) is not used after this, because the entropy production is not known. Eq. (26a) is the mass flux law, and it is equivalent to stating that the mass flux is a function of all of the forces (or by the previous discussion, may include gradients in the other phases or interfaces):

$$\begin{aligned} \phi^\alpha \rho^\alpha \vec{w}^\alpha & = \tilde{q}^\alpha = \tilde{q}^\alpha(\nabla \psi^\alpha, \nabla T^\alpha, \nabla \mu^{\beta_1\alpha}, \dots, \nabla \mu^{\beta_N\alpha}) \quad \text{with} \\ \psi^\alpha & = \frac{P^\alpha}{\rho^\alpha} + \vec{g} \cdot \vec{x} + \Phi(\vec{w}^\alpha, \tilde{v}^\alpha) \end{aligned} \quad (27)$$

Taking the differential of the above yields

$$\begin{aligned} d\tilde{q}^\alpha & = \left(\frac{\delta \tilde{q}^\alpha}{\delta(\nabla \psi^\alpha)} \right) d(\nabla \psi^\alpha) + \left(\frac{\delta \tilde{q}^\alpha}{\delta(\nabla T^\alpha)} \right) d(\nabla T^\alpha) \\ & + \left(\frac{\delta \tilde{q}^\alpha}{\delta(\nabla \mu^{\beta_1\alpha})} \right) d(\nabla \mu^{\beta_1\alpha}) + \dots \\ & + \left(\frac{\delta \tilde{q}^\alpha}{\delta(\nabla \mu^{\beta_N\alpha})} \right) d(\nabla \mu^{\beta_N\alpha}) \end{aligned} \quad (28)$$

where the partial differential operator δ is a convenient notation that only implies that the differential makes sense as defined. In general, this differential operator returns the outer product of the two partial differential vectors. So, each coefficient is a tensor, though this level of complexity

is unnecessary in the following, because only the homogeneous isotropic case of Darcy’s Law will be considered. Assuming that the flux is homogeneous first order in the “forces” (i.e., a doubling of all of the forces results in a doubling of the flux), it can be shown that

$$\tilde{q}^z = \left(\frac{\delta \tilde{q}^z}{\delta(\nabla \psi^z)} \right) \nabla \psi^z + \left(\frac{\delta \tilde{q}^z}{\delta(\nabla T^z)} \right) \nabla T^z + \left(\frac{\delta \tilde{q}^z}{\delta(\nabla \mu^{\beta_{1z}})} \right) \nabla \mu^{\beta_{1z}} + \dots + \left(\frac{\delta \tilde{q}^z}{\delta(\nabla \mu^{\beta_{Nz}})} \right) \nabla \mu^{\beta_{Nz}} \quad (29)$$

As a result, it is now clear what the Onsager Coefficients represent. For example, the first coefficient is

$$L_{11} = \left(\frac{\delta \tilde{q}^z}{\delta(\nabla \psi^z)} \right)_{\nabla T^z=0, \nabla \mu^{\beta z}=0} \quad \text{for all } \beta \quad (30)$$

where the subscripts indicate the fixed values of the gradients. Since the gradients are equal to zero, this implies that the temperature and chemical potential are constant. So, this coefficient is determined experimentally by evaluating the change in mass flux that occurs under a gradient in the specific energy associated with the mass density under isothermal conditions in the absence of intra-phase gradients in chemical potential. For the liquid phase this coefficient is related to Darcy’s hydraulic conductivity, and like the hydraulic conductivity, it may assume the form of a tensor. It is now possible to incorporate thermodynamic corrections to Darcy’s law. Since gravity is a constant, under isothermal conditions with no gradients in concentration of the constituents, the mass flux law may be written as

$$\phi^L \rho^L \bar{w}^L = \left(\frac{\delta(\phi^L \rho^L \bar{w}^L)}{\delta\left(\nabla\left(\frac{P^L}{\rho^L g} + x_3 + \frac{\Phi(\bar{w}^L, \bar{v}^L)}{g}\right)\right)} \right)_{T^L, \mu^{\beta L}} \times \nabla\left(\frac{P^L}{\rho^L g} + x_3 + \frac{\Phi(\bar{w}^L, \bar{v}^L)}{g}\right) \quad (31)$$

Considering creeping flows, the kinetic term is negligible [12], because $\Phi(\bar{w}^L, \bar{v}^L)$ must go to zero as velocity goes to zero. Also, it is noted that within the coefficient (i.e., the differential term), temperature and concentration are constant within the phase. Under such conditions, for both saturated and unsaturated flows, it is reasonable to assume that $\delta(\phi^L \rho^L \bar{w}^L) = \rho^L \delta(\phi^L \bar{w}^L)$. This results in

$$\phi^L \bar{w}^L = \left(\frac{\delta(\phi^L \bar{w}^L)}{\delta\left(\nabla\left(\frac{P^L}{\rho^L g} + x_3\right)\right)} \right)_{T^L, \mu^{\beta L}} \nabla\left(\frac{P^L}{\rho^L g} + x_3\right) \quad (32)$$

Since the flux on the left is the Darcy flux, and the “force” is the one commonly associated with Darcy’s Law, the precise thermodynamic meaning of the hydraulic conductivity is

$$K^L = - \left(\frac{\delta(\phi^L \bar{w}^L)}{\delta\left(\nabla\left(\frac{P^L}{\rho^L g} + x_3\right)\right)} \right)_{T^L, \mu^{\beta L}} \quad (33)$$

The thermodynamic derivation above ensures that all relevant variables are accounted for when correcting Darcy’s coefficient. If there are other important energy fluxes (e.g., electrostatic energy), then the energy conservation equation must necessarily include these terms, thereby ensuring that the Darcy coefficient is also a function of the intensive variables associated with these energies a priori. So, it remains to derive the appropriate corrections for the hydraulic conductivity, and in general, it is assumed that the coefficient may be written as a product of functions that are dependent upon only one variable (i.e., the corrections are independent). In this paper, only the corrections associated with changes in sodium chloride content (from zero to saturation) are illustrated, and an example is completed to illustrate the results.

In addition to the parameters noted by the subscripts in (33), the hydraulic conductivity is implicitly a function of the specific energy associated with the mass density in the porous medium (i.e., $\phi^L \rho^L$). It has already been noted that for a liquid, the phase density is a constant in the coefficient, leaving a functional dependence on the phase volume fraction which can be directly related to the saturation in an approximately incompressible porous media.

This is the extent to which the above thermodynamic derivation aids in the development of governing equations. This is largely the result of the fact that the Onsager coefficients are phenomenological coefficients that operate on the scale of interest, and assumption of the validity of equations (26a)–(26c) disconnects the derivation from the first principles derivation of (25). If the local equilibrium assumption is made, then equilibrium thermodynamics may be used to develop corrections based on pore-scale physics, alternately empirical relations describing the functional dependence upon the primary variables may be used. Here, it is assumed that previously established corrections to the Darcy’s Law coefficient may be used to infer the proper form of corrections resulting from changes in salt concentration. It is only necessary to properly interpret how the change in salt will affect each type of correction. In this way, sequential corrections to the standard zero-salt concentration, saturated system Darcy coefficient may be established for the addition of salt. Examine the approximate relation given by Brooks and Corey [3] to describe the saturation relation:

$$K^L = K_s^L \cdot (S^L)^\eta \quad (34)$$

where the subscript s refers to the saturated reference condition, S^L is the saturation of the pore spaces with liquid, and η is a fitting parameter. Also consider the common approximate relation given by

$$\frac{K_s^L}{\rho^L g} = \frac{k_s^L}{\mu^L} \quad (35)$$

where k is the permeability and μ^L is the liquid viscosity. Since the role of the density term is apparent in the above relation, it remains to correct the coefficient for viscosity and liquid saturation. Since viscosity is implicitly contained

in K_s^L , it becomes necessary to choose a reference salt condition under which the hydraulic conductivity will be measured. Here, the zero-salt reference condition is chosen, yielding the corrected form:

$$K^L = K_0^L \left(\frac{\mu_0^L}{\mu^L} \right) \left(\frac{S^L}{S_0^L} \right)^\eta \quad \text{where } K_0^L = K_{s_0}^L (S_0^L)^\eta \quad (36)$$

4.1. Testing the theory: salinity correction to hydraulic diffusivity

In a series of papers by Scotter and Raats [23], Parlange [20], and Scotter [22], the phenomenon of water condensation near salt (NaCl) crystals in a relatively dry porous media is experimentally and mathematically analyzed. All of Scotter’s experiments published in 1974 were conducted at 25 °C. Among these experiments, soil water diffusivity experiments were conducted at multiple water contents using dilute salt-strength water, but one experiment was performed using a saturated salt solution (Fig. 2). Also, a soil moisture characteristic curve was generated for dilute strength water (Fig. 1). The data in both figures have been converted to volumetric water contents, instead of the gravimetric water contents reported, using Scotter’s reported values of bulk density. Since Scotter was concerned with measuring net water diffusivity, Fig. 2 represents both vapor and liquid flow (i.e., total water diffusivity). It is assumed that vapor flow dominates below ~8% volumetric content, and above this, liquid flow dominates [22]. The liquid water diffusivity data in Fig. 2 may be fit by a curve of the form:

$$D_0^L = a \cdot (\phi_0^L - \phi_{\min}^L)^b \quad (37)$$

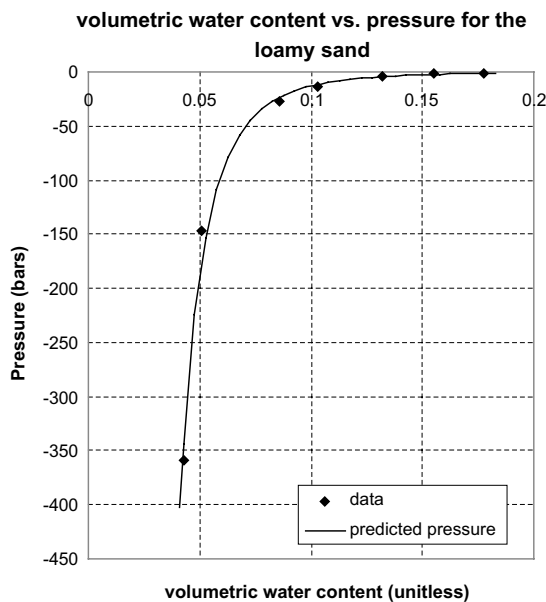


Fig. 1. Data from Scotter [22] converted from gravimetric water content to volumetric water content. The predicted pressure is computed using the Brooks and Corey model (Eq. (44)) with $P_{cr}^L = 0.90684$ and $\lambda = 0.26$.

where a and b are fitting parameters. The fit of the curve to the data is shown in Fig. 3, where the liquid water volume and diffusivity data have been transformed to liquid volume and diffusivity. In this figure, all of the zero-salt data is unchanged, and only the saturated salt solution data moves. This is because the volume occupied by the salt solution is different than the volume that would be occupied by only the water if the salt were removed. It is the goal of the following derivation to compute the salt correction for this curve. In order to estimate the diffusivity in the region where liquid water flux dominates, Scotter assumed an equation of the following form holds:

$$\rho^L \phi^L \bar{w}^L = -D^L \nabla (\rho^L \phi^L) \quad (38)$$

The left-hand side of this equation is merely the Darcy flux times the density, and the right-hand side is the diffusive mass flux. For each of the experiments, the salt concentration was constant, which implies the density is also constant. Therefore, the above equation reduces to

$$\phi^L \bar{w}^L = -D^L \nabla \phi^L \quad (39)$$

For Scotter’s experiments, it is assumed that the pressure terms dominate the gravitational terms. This is reasonable in fine textured porous media at relatively low saturations (which is what Scotter was considering during subsequent 1-D horizontal experiments). Under these conditions, in a homogeneous, isotropic medium, with constant density liquid, (32), (33), and (39) yield the following approximate relation:

$$D^L \nabla \phi^L \cong \frac{K^L}{\rho^L g} \nabla P^L \quad (40)$$

which indicates that the following is true:

$$D^L \cong \frac{K^L}{\rho^L g} \frac{\partial P^L}{\partial \phi^L} \quad (41)$$

So, to compare the theory above with Scotter’s data, and in general, to be able to provide the proper thermodynamic correction of salt to the liquid diffusion coefficient (as defined here), it remains to evaluate the differential term in the above equation. Assuming that porosity is constant, and recognizing that a constant salt-strength implies a constant saturation ratio (S^L/S_0^L) (i.e., the ratio of salty water volume to the volume occupied by the same amount of zero-salt water is constant), it is true that

$$\frac{\partial P^L}{\partial \phi^L} = \frac{S_0^L}{n S^L} \frac{\partial P^L}{\partial S_0^L} \quad (42)$$

where n is the porosity. But, in [6], it is shown that

$$\frac{\partial P^L}{\partial S_0^L} = \frac{\sigma^{LG}}{\sigma_0^{LG}} \frac{\partial \tilde{P}^L}{\partial S_0^L} \quad (43)$$

where $\tilde{P}^L = P^L(S^L)$ is the pressure corresponding to an equivalent saturation of zero-salt water [6], and is therefore

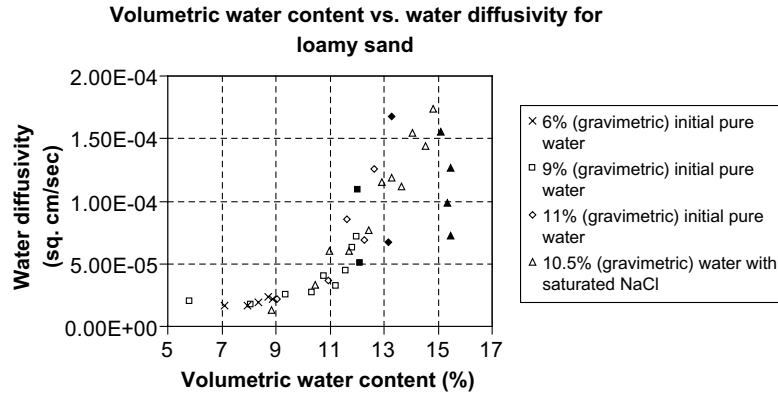


Fig. 2. Scotter’s raw data converted to volumetric *water* content. The solid symbols represent anomalies associated with initiation of the experiments (discussed in text). The gravimetric labels have been retained in the legend to facilitate comparison of the results with Scotter’s work.

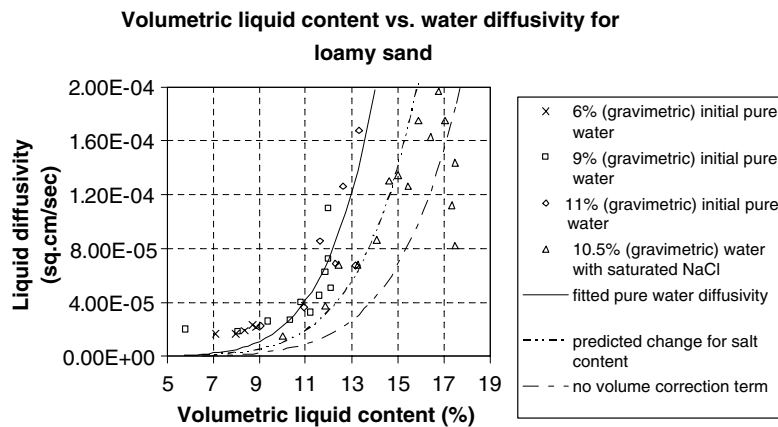


Fig. 3. The data from Fig. 2 plotted in terms of the volumetric *liquid* (i.e., not equivalent water volume, but true liquid volume) content vs. the *liquid* diffusivity. Also, the original water diffusivity curve and the computed shift of this curve (Eq. (47)) are shown. A shifted curve that only neglects the volume correction term in (47) is also shown.

given by the zero-salt saturation–pressure relationship. $\sigma^{LG}/\sigma_0^{LG}$ is the surface tension ratio for the liquid–gas interface, and it is not related to the entropy production; note that σ is the commonly accepted symbol for both entropy production and surface tension. Even though any saturation–pressure relationship may be used, the functional form given by Brooks and Corey [3] is used here

$$S_0^L = \left(\frac{P_{cr}^L}{P_0^L} \right)^\lambda \tag{44}$$

where P_{cr}^L and λ are fitting parameters and $\eta = \frac{2}{\lambda} + 3$ [3].

Notice that \tilde{P}^L is not the true pressure, and in order to convert it to the actual liquid pressure, it must be corrected for changes in surface tension. The functional form of \tilde{P}^L depends only on geometric constraints, and S^L is an implicit function of both water and salt contents. So, the differential may be rewritten as

$$\frac{\partial P^L}{\partial \phi^L} = \frac{1}{n} \frac{\sigma^{LG}}{\sigma_0^{LG}} \frac{\partial \tilde{P}^L}{\partial S^L} \tag{45}$$

Incorporating the above yields one form of the desired correction to the liquid diffusion coefficient:

$$D^L = D_0^L \left(\frac{\rho_0^L}{\rho^L} \right) \left(\frac{\mu_0^L}{\mu^L} \right) \left(\frac{\sigma^{LG}}{\sigma_0^{LG}} \right) \left(\frac{S^L}{S_0^L} \right)^\eta \left(\frac{\left(\frac{\partial \tilde{P}^L}{\partial S^L} \right)}{\left(\frac{\partial \tilde{P}_0^L}{\partial S_0^L} \right)} \right) \tag{46}$$

where the terms on the right hand side are the pure water diffusivity, a density correction, a viscosity correction, a surface tension correction, and the last two terms are volume corrections. Using the Brooks and Corey relation (44) to evaluate the derivative, the above simplifies to

$$D^L = D_0^L \left(\frac{\rho_0^L}{\rho^L} \right) \left(\frac{\mu_0^L}{\mu^L} \right) \left(\frac{\sigma^{LG}}{\sigma_0^{LG}} \right) \left(\frac{S^L}{S_0^L} \right)^{\frac{1}{\lambda} + 2} \tag{47}$$

This equation is the general correction to the diffusivity for saline fluids moving through variably saturated porous media assuming the soil is described well by the Brooks and Corey relations ((34) and (44)) and assuming there are no significant gravity driven flows. The D_0^L term is a function of the equivalent saturation of salt-free water, the other ratios may be calculated as functions of salt concentration, and the value of λ ensures that the hydraulic character of the soil is represented. The above method of

estimation may be accomplished for any functional relationships for hydraulic conductivity and pressure. The Brooks and Corey relationships were selected only for convenience and to allow a comparison with real data.

In order to compute the effects of salt on Scotter's diffusion coefficient data (Fig. 3), the above equation may be used. It is first necessary to estimate each of the four ratios and the exponent of the volumetric term. Estimated values for λ are obtained by fitting the Brooks and Corey saturation–pressure relation to only the pure water data of Scotter (Fig. 1). The volumetric correction can be estimated using the definition of saturation to obtain

$$\frac{S^L}{S_0^L} = \frac{V^L}{V_0^L} \quad (48)$$

The method of Heyrovská [11] provides functional forms for computation of the non-idealities associated with density, volume, and activity for non-dilute strength NaCl solutions; and therefore may be used to compute the volumetric term for any salt concentration. Diffusion data compiled by Scotter is only for pure water and a saturated salt solution. For this reason, it is only necessary to estimate the terms in Eq. (47) for saturated salt conditions. For any fixed salt concentration, each correction is fixed (i.e., a constant), so estimates may be taken from the literature. Here a volume correction term of 1.131 results (computed using the method of Heyrovská [11]). The experimental surface tension data of Belton [2] may be used to estimate the surface tension correction term as 1.15. Kestin et al. [14] provides a table of tabulated viscosities using correlations established from experimental data. Kestin et al. estimate an overall accuracy of within 0.5%. Using the tabulated values, the viscosity ratio is estimated as 0.5123. Using these parameters, and a density correction of 0.8326 (computed using the method of Heyrovská [11]) for the saturated salt solution, it is possible to compute the correction to the curve shown in Fig. 3.

5. Results and subsequent discussion of Buckingham–Darcy salt correction

The results are shown in Fig. 3 where the axes and data have been changed appropriately to reflect liquid content, rather than water content (i.e., since the salt changes the volume of the saline solution, the computed equivalent volume of zero-salt water is less than the volume computed when accounting for salt). Only the saturated salt solution data points shift on this new figure, because only the liquid corresponding to these data occupy more volume than the corresponding amount of pure water would. This is accomplished by multiplying both the x and the y coordinate of the high salt data by the volume correction. The fitted pure water curve in Fig. 3 is a fit of (37), and the “predicted change” curve is the fitted curve multiplied by the corrections (i.e., Eq. (47)). Also shown is a curve corrected for only viscosity, density, and surface tension. Since failure to also correct for surface tension only worsens the fit by

a factor of 1.15, the volume correction is necessary to obtain accurate results.

While the corrected curve substantially predicts the shift of the data, the fit is not perfect. Several factors may affect the data, and therefore the correlation between the data and the curve. These include hysteresis, chemical interaction of soil with the salt, the variability of the samples, and use of (34) with no experimental validation of the relation between λ and η .

Since Scotter conducted all experiments from a specific initial water content (i.e., a soil prepared at some uniform water content), it was necessary that as the soil drained, the soil moisture must move first from the initial state to the state described by the primary drainage curve (i.e., the distributed water must re-align and connect to form the flow-paths utilized to transmit water). The estimated soil water diffusivity for water contents very close to the initial water content consistently shows anomalous and noisy behavior, predicting values of diffusivity lower than would be expected by projecting the low water content data back to higher water contents. This hysteresis effect potentially explains the consistently noisy behavior and poor fit for the data at the start of many of the experiments (i.e., high-est water content observed for each experiment).

It is also noted that Scotter used a loamy sand for his experiments. It is likely that there is an appreciable fine fraction in this soil. This fine fraction, having higher surface areas with surface charges, may affect the flow of the liquid due to electrostatic interactions with the dissociated (or partially dissociated) salts. It is unclear from the theory developed here how significant an effect this may be, but it may be one reason for the larger scatter of the high-salt data and may partially explain any systematic discrepancies between predicted and observed values for the high salt strength experiment. Since systematic discrepancies appear to be more prevalent at higher liquid content, the assumption of negligible gravity driven flows also becomes suspect.

Scotter's experiments are all performed on different preparations of the same soil. For this reason, dry bulk densities ranged from 1.24 to 1.48 g/cm³, with no reported value for the soil sample used to generate the water release curve (Fig. 1). Unfortunately, the high density soils are the 6% initial content and the saturated salt solution experiments. Since the 6% experiment had no appreciable liquid water diffusion, it is impossible to see if the shift is more consistent based on bulk density.

As a result of the above observations, it is recommended that future experiments be conducted with a porous medium that is not likely to interact with the salt being studied. Multiple experiments performed on the same soil samples over a range of salt concentrations would permit further analysis of the theoretical results. Experimental validation of (34) is also important.

It might be argued that a single volumetric water content versus water diffusivity curve would also adequately describe the water content/diffusivity relationship for a saturated salt solution for this soil. Rather than incorporating any

corrections, one might be tempted to fit the data in Fig. 2 with a single curve representing all of the data. For sodium chloride in this soil, this appears to be a reasonable assumption as long as both the dependent and independent variables are related to equivalent pure water content (i.e., not true liquid saturation or liquid pressure). This is true because the product of the corrections for NaCl in this soil is ≈ 1 with the density and viscosity effects approximately balancing the volumetric and surface tension effects. This implies that the shift in Fig. 3 is directly to the right as water saturation is converted to liquid saturation. In this case, it is arguably preferable to neglect all of the corrections, rather than haphazardly incorporating a few, provided that the appropriate primary variables are retained. The shift in Fig. 3 resulting from accounting for changes in density, viscosity, and surface tension only, shows the hazard associated with arbitrarily correcting the curve (recall that the pure water measurements are not altered when moving from Figs. 2 to 3).

Liquid (i.e., water and a variable amount of salt) flow properties may be non-negligibly affected by the addition of a solute (Fig. 3). Since a first-principles derivation of a flow model for a saline solution would arise naturally by conserving momentum of the center of mass of a unit of liquid, it is necessary to formulate the problem in terms of liquid movement, and not movement of water in the liquid. For this reason, it is desirable that experimental parameters that are measured for pure water may be extended to the case where the water is not pure. This results in savings of time and effort that would otherwise be spent characterizing a particular porous media for the appropriate flow properties. The approach described above provides this method of correction, where the viscosity, surface tension, and saturation (volumetric) ratios are all functions of only the effect of the solute on the solution; and λ depends only on the soil texture.

Notice that unlike Hubbard’s [12] heuristic derivation, no assumption has been made about the density inside the gradient term for Darcy’s Law (Eq. (32)). This implies that in the case where there exist gradients in concentration and temperature, the local temperature and concentration affect the hydraulic conductivity and the density without losing the generality of the resulting flow law. The changes to flow resulting from these other gradients would be accounted for by the other terms in the general mass flux equation (i.e., (29)). Recall that principle C requires that the mass flux is an explicit function of the mechanical energy potential and an implicit function of all other intensive variables. This implies that (29) may be rewritten as

$$\begin{aligned} \tilde{q}^z = & \left(\frac{\delta \tilde{q}^z}{\delta(\nabla \psi^z)} \right)_{T^z, \mu^{\beta z}} \left(\nabla \psi^z + \left(\frac{\delta(\nabla \psi^z)}{\delta(\nabla T^z)} \right) \nabla T^z \right. \\ & \left. + \left(\frac{\delta(\nabla \psi^z)}{\delta(\nabla \mu^{\beta_1 z})} \right) \nabla \mu^{\beta_1 z} + \dots + \left(\frac{\delta(\nabla \psi^z)}{\delta(\nabla \mu^{\beta_N z})} \right) \nabla \mu^{\beta_N z} \right) \end{aligned} \quad (49)$$

Under the same simplifying conditions as above, the first coefficient again reduces to the hydraulic conductivity.

Examination of the remaining terms with coefficients shows that each term may be regarded as the portion of the net potential gradient resulting from a gradient in the corresponding intensive variable, or similarly, each partial derivative coefficient might be viewed as the *efficiency* with which the potential is converted into a pressure gradient. These efficiencies may now be estimated using equilibrium thermodynamic methods, for example, and these estimates may be used to show which terms are negligible by non-dimensionalizing the problem.

The notions of efficiencies are precisely what Low [16] and Letey et al. [15] observed, though Low’s derivation is restricted to infinitely dilute solutions and the work by Letey et al. is restricted to empirical measurement of coefficients. Care must be exercised when comparing results of papers using the term, osmotic pressure, because definitions may vary. This is evident in the case of Low and Letey et al. because Low has a one-to-one ratio between the usual pressure term and the osmotic pressure and Letey et al. describe the relation between the pressures by an osmotic efficiency that is significantly less than one.

As stated in the paragraph following Eq. (26), it is likely necessary to consider the summation of (26) over the phases. In this case, when the differentials in (29) are evaluated, it is for fixed gradients in all forces *in all phases*. This shows clearly that in the case where there are multiple fluid phases flowing, the “conductivity” of one phase will be a function of the gradient in the corresponding potential of the other phase. For the case of water and air (at low air velocities such as those that typically occur in soil) an assumption of weak mechanical coupling between the fluids is likely sufficient (which is essentially what was used above). But when considering two different viscous fluids (e.g., water and NAPL), process thermodynamics automatically ensures that “conductivity” is a function of the gradient in mechanical potential of the competing fluid.

6. General discussion of the process thermodynamics derivation

In (19), it was noted that the first three terms are written as intensive variables multiplied by the differentials of the *corresponding* localized extensive variables and the second set of three terms are the localized extensive variables multiplied by differentials of the *corresponding* intensive variables. Except for the unusual splitting of gravitational and kinetic terms, these six terms are related to the Gibbs and Gibbs–Duhem Relations as historically written (cf., [8]), though in most references the Relations are written only in terms of differentials. According to de Groot and Mazur [8], the specific energy equation is exactly the same as (16) (when written in the notation of this paper). The Gibb’s relation for a single phase is given as

$$du^z = P^z d\left(\frac{1}{\rho^z}\right) + T^z d\eta^z + \sum_{\beta} \mu^{\beta z} dX^{\beta z} \quad (50)$$

where u is the so-called specific internal energy, and the Gibbs–Duhem relation is given as

$$0 = \frac{1}{\rho^\alpha} dP^\alpha + \eta^\alpha dT^\alpha + \sum_{\beta} X^{\beta\alpha} d\mu^{\beta\alpha} \quad (51)$$

By definition, de Groot and Mazur state that the differential of the total specific energy is

$$de^\alpha = P^\alpha d\left(\frac{1}{\rho^\alpha}\right) + T^\alpha d\eta^\alpha + \sum_{\beta} \mu^{\beta\alpha} dX^{\beta\alpha} + d\left(\frac{1}{2} \vec{v}^\alpha \cdot \vec{v}^\alpha\right) + d(\vec{g} \cdot \vec{x}) \quad (52)$$

In effect, de Groot and Mazur, have said that (52) is the differential of (16), and this assumption is commonly used. But, no particular reason for the inclusion of the entire differential of the kinetic and gravitational terms with the Gibbs Relation is given, and consistent thermodynamic results may be derived by allowing other splits between localized extensive and intensive variables (a more complete discussion of this is contained in [5]). Ostensibly, the split represented by de Groot and Mazur was made to preserve the notion of internal energy as a separate energy form, whereas it is conceivable to believe that both kinetic and potential energies are also “internal” to a continuously deforming body. If one allows this alternate idea, then the specific kinetic energy and the position dotted with the potential field are allowable intensive variables associated with the mass-density. However, this results in an altogether different split of variables when deriving the continuous formulations of the Gibbs and Gibbs–Duhem Relations.

If it is assumed that the first three terms in (19) are associated with a more general Gibbs Relation, then the procedure that follows (19) is merely the application of the thermodynamic notion that the mechanical work, the chemical work, and the heat flow must be conserved. Further, if it is assumed that subtracting these conserved portions of the energy from the general energy equation is the proper method of deriving the Gibbs–Duhem relation, then this leaves (24) as the proper continuous form of the Gibbs–Duhem Relation for a given phase. In fact, considering a single-phase, homogeneous, system of fixed volume with no spatial gradients, and averaging (24) over the volume yields the expected equilibrium thermodynamic Gibbs–Duhem Relation being equal to the entropy production. For a reversible process, the entropy production is zero, and the usual form of the equilibrium Gibbs–Duhem Relation is recovered, so consistency with equilibrium thermodynamics is preserved.

As a second example, consider a multi-phase system with no mass exchange. Upon summation of (24) (analogously (25)) over all of the phases, and recognizing that $\hat{H}^{\alpha\gamma} = -\hat{H}^{\gamma\alpha}$ it may be shown that a sufficient condition for the right hand side of the equation to reduce to

$\sigma \equiv \sum_{\alpha} \sigma^\alpha$ is that the temperature of each phase is equivalent to the temperature of the other phases at each point (i.e., local thermal equilibrium). In this case, if the entropy production is non-zero, then this new “Gibbs–Duhem Relation” does not equal zero. This implies that for dissipative processes (or irreversible processes in general), there is *no Gibbs–Duhem Relation* in the general sense (i.e., that identically equals zero). Instead, there exists an equation that is consistent with use of an entropy inequality. An entropy inequality is usually derived by writing an energy equation and subtracting all reversible processes, leaving only irreversible processes, though it remains to prove that only irreversible processes remain.

Also of note, are the forms of the differential operators implied by the above derivation. In standard process thermodynamics (e.g., [8]) it is commonplace to consider only the differential of the variable of interest and not the derivative. While this does not affect the temporal derivatives, the spatial differential operators are different between the “Gibbs” and “Gibbs–Duhem” Relations above. The “Gibbs” Relation has the divergence of the *net* flux, and the “Gibbs–Duhem” Relation has terms that are the *net* flux dotted with the gradient of the force (almost the material derivative except the velocity is the net velocity of the localized extensive variable and not the phase velocity). In this way, the total derivative (i.e., spatial and temporal) for the “Gibbs” Relation attempts to conserve the localized extensive variable, and the total derivative for the “Gibbs–Duhem” Relation is a pseudo-material derivative. These differential operators are the natural choices for the case where conservative energy fluxes need to be removed from the general energy formulation given by (18), leaving only energy dissipations. Because the differential operators are different, attempts to formulate general relationships in terms of differentials for continuously deforming systems (e.g., [9,10]) may result in confusion during application of the resulting theory.

The last item worth discussing is the *implicit* use of Gibbs–Duhem Relations of the same form as (51). This is most commonly accomplished by using some form of Eq. (52). Notice that if (52) is assumed to be correct, (51) follows immediately from (16). This occurs more commonly than not throughout the relevant literature. The question of why mathematical inconsistencies are not noted during these potential misapplications of the Gibbs–Duhem Relation is of interest. To understand this, recall that the endpoint of most rigorous process thermodynamic derivations is the entropy inequality. At this point, a leap is then made wherein the Onsager Reciprocal Relations are invoked, resulting in creation of coefficients that require empirical determination (as shown in the derivation above), and a subsequent departure from use of the energy equations for any further calculations. So, the equation with the error in it has been discarded. In order to resolve the issues above, it will be necessary either to solve the equations above explicitly for simplified conditions or to mathematically develop the Onsager Relations from

physical principles that allows a priori estimation of the terms.

7. Conclusions

General thermodynamic relations were motivated and derived using intuitive physical principles. The resulting equations differ from historical formulations of Gibbs and Gibbs–Duhem Relations for continuous systems, but the standard equilibrium relations are recovered under the appropriate simplifying assumptions. This implies that the new system of equations is consistent with well-established theory. The new relations were subsequently used to understand the functional dependence of the hydraulic conductivity coefficient of the Buckingham–Darcy Law, and this dependence was used to correct the law for high ionic salt strength of the liquid phase. The theoretical relation showed good agreement with the data.

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