

# Modified Darcy's Law, Fick's Law, and Terzaghi's Effective Stress Principle for Swelling Clay Soils

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## Abstract

Governing equations often used in soil mechanics and hydrology include the classical Darcy's law, Terzaghi's effective stress principle, and the classical Fick's first law. It is known that the classical forms of these relations apply only to non-swelling, granular materials. In this paper we summarize recent generalizations of these results for swelling porous media obtained using hybrid mixture theory by the authors. Hybrid mixture theory (HMT) is a methodical procedure for obtaining macroscopic constitutive restrictions which are thermodynamically admissible by exploiting the entropy inequality in the spirit of Coleman and Noll for spatially averaged properties. HMT applied to the modeling of swelling clay particles, viewed as clusters of adsorbed water and clay minerals, produces additional terms necessary to account for the physico-chemical forces between the adsorbed water and clay minerals, or more generally, for swelling colloids. New directions for modeling consolidation of swelling clays are proposed based on our view of clay particles as a two phase system

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## 1 Introduction

Because swelling colloids are so pervasive, the modeling of swelling soils affects all disciplines dealing with naturally occurring soil, as well as the design of structures containing swelling colloids as a component. In particular, smectite affects the transport of nutrients and contaminants, the design of clay barriers used to line commercial land fills and low-level radioactive depository sites, and the design (and failure) of foundations for buildings, bridges, highways, and runways. As such, it is imperative that any mathematical model used to determine the flow through, or deformation of, clay contain the appropriate constitutive relations to account for the swelling nature of most of these systems. Here we concentrate on three relations commonly used to predict the behavior of processes for soils: Darcy's law which governs the rate of flow through soil; Terzaghi's effective stress principle which dictates the load distribution between the liquid and solid phases; and Fick's law which governs diffusion of contaminants through soil.

The classical forms of these equations apply to a fluid flowing at low velocity through a non-swelling granular medium. They do not take into account the physico-chemical forces present in swelling colloids, or in particular, clay particles. Swelling clay particles consist of clusters of platelets and adsorbed water which swell under imbibition and shrink under desiccation. The large specific surface areas of the 2:1 layer silicate platelets magnify the effects of the physico-chemical forces present causing the macroscopic behavior of clays to differ significantly from granular media. There are at least three components of physico-chemical forces: Van der Waals attraction, electrostatic (or osmotic) repulsion, and surface hydration. By "surface hydration" we mean the short range bonding forces between the mineral surfaces and the water (Israelachvili [1]). These forces perturb the water in close proximity to the clay platelets (vicinal or adsorbed water), so that it behaves differently from its bulk-phase counterpart (water free of adsorptive forces) (Low [2, 3, 4], Grim [5]). Experiments by Low [6, 7] indicate that the macroscopic effects of these interactions are due primarily to hydration forces, and it is these forces which we account for when modifying the aforementioned classical results. A more detailed discussion on the influence of hydration forces on swelling clays can be found in the works of Low and co-workers [6, 7], Derjaguin and co-workers [8, 9, 10] and Israelachvili and co-workers [1, 11, 12].

Darcy type laws were initially used to describe the flow of a single-phase

fluid through a porous medium. First derived experimentally in 1856 [13] for negligible body forces it states that the flux is proportional to the pressure gradient, i.e.

$$\varepsilon_l \mathbf{v}_l = -\mathbf{K} \nabla p, \quad (1)$$

where  $\mathbf{v}$  is the average fluid velocity,  $\mathbf{K}$  is the conductivity of the porous material,  $\varepsilon_l$  is the volume fraction of the fluid, and  $p$  is the pressure in the fluid. In this simple form, Darcy's law applies to a fluid flowing at low velocity through a non-swelling granular medium. If there are strong interactions between the fluid phase and solid, such as occurs in montmorillonite clays, the above form of Darcy's law no longer applies [14, 15, 16]. This form of Darcy's law has been heuristically extended for more complicated systems, such as multi-phase flow and swelling media, by postulating the dependence of  $\mathbf{K}$  on additional variables, such as the porosity and the saturation. Clearly it would be advantageous to systematically derive a more general form of the above equation which would apply to swelling soils.

Since the introduction of the concept of an effective stress by Terzaghi [17], this quantity has been widely used to describe the failure of soils. The effective stress ( $\mathbf{t}_s^e$ ) is defined as the difference between the total applied stress ( $\mathbf{t}$ ) and the bulk water pressure ( $p$ ), i.e.

$$\mathbf{t} = p\mathbf{I} + \mathbf{t}_s^e. \quad (2)$$

Intuitively, the effective stress is viewed as the stress in the solid matrix when no fluid is present. They primarily control the deformation of coarse-grained soils with a connected skeleton such as sands, silts, and low and medium plastic clays such as kaolinite or illite. On the other hand, relation (2) is not a realistic model for swelling clays, especially active plastic clays such as bentonite and montmorillonite. The reason is that the classical effective stress principle assumes the load is supported only by the effective stress and the pore pressure. Consequently, the existence of physico-chemical forces within and between the clay particles are excluded.

Researchers have heuristically modified Terzaghi's effective stress principle to account for physico-chemical forces, and as a result different mechanistic pictures of the various stresses have been derived [18], [19], [20], [21]. A detailed discussion on the different variants of (2) can be found in [22],[23],[24]. In these approaches physico-chemical forces are heuristically incorporated in

Terzaghi's principle via terms representing net repulsive ( $R\mathbf{I}$ ) and net attractive ( $A\mathbf{I}$ ) forces between particles. This stress is commonly denoted by  $(R - A)\mathbf{I}$  (see [18],[20]), and results in the following modified Terzaghi stress principle:

$$\mathbf{t} = -p\mathbf{I} + \mathbf{t}_s^e + (R - A)\mathbf{I}. \quad (3)$$

Except for the authors work the authors know of no rational basis for these modified Terzaghi stresses.

Fick's first law is used to describe the diffusive nature of a constituent (e.g. nutrient or contaminant) in single-phase flow [25]. In its simplest form, it states that the diffusive velocity,  $\mathbf{u}_l^j$ , defined to be the velocity of the  $j$ th constituent relative to the mass averaged bulk phase velocity, is proportional to the gradient of the concentration of that constituent, i.e.

$$\mathbf{u}_l^j = D^j \nabla C^j, \quad (4)$$

where  $D^j$  is the diffusion coefficient. Several researchers have attempted to provide a rational basis for a more general form of Fick's law. For example in [26, 27] the following generalized form of Fick's law was derived:

$$R_\alpha^j \mathbf{u}_\alpha^j = \nabla \widetilde{\mu}_\alpha^j \quad j = 1, \dots, N - 1 \quad (5)$$

where  $R_\alpha^j$  is a coefficient which arises from a linearization procedure and  $\widetilde{\mu}_\alpha^j$  is the chemical potential of the  $j^{\text{th}}$  component relative to the  $N^{\text{th}}$ . This is in contrast to the more general form of Fick's law, which according to classical irreversible thermodynamics, states that flow is driven by an absolute chemical potential gradient (i.e.  $\nabla \mu_\alpha^j$ ) [28]. Note that equation (5) states that flow is driven by a chemical potential gradient *relative* to the  $N^{\text{th}}$  component, implying that the diffusive velocity is a function of how the constituents are labeled. The thermodynamical definition of the chemical potential is crucial in understanding the driving forces for diffusive flow. In this paper we discuss the thermodynamic definition of a "macroscale" chemical potential whose gradient is the driving force for diffusive flow and which has many of the properties of the classical chemical potential, such as the equality of chemical potentials of a single constituent in two phases, i.e.  $\mu_s^j = \mu_l^j$ , where  $s$  and  $l$  denote the solid and liquid phases respectively.

The derivations of the generalized forms of (1), (2) and (4) which govern flow, deformation, and diffusion in swelling porous media can be accomplished within the framework of the hybrid mixture theory, HMT, which is a slight modification of the classical mixture theory of Bowen [29]. Developed in [30, 31, 32], it involves averaging the field equations (e.g. conservation of mass, momentum balance, energy balance) and obtaining constitutive restrictions subject to the second law of thermodynamics. Among the first applications of this theory was the derivation of the governing equations for a nonswelling, single constituent flow in granular media [32] such as Darcy's law. HMT has since been extended to incorporate interfacial effects [33, 27] and multi-constituent effects [26, 27], as well as to multi-phase flow [34, 35, 36] where a multi-phase Darcy-type law as well as a near equilibrium capillary relation were derived.

The purpose of this paper is to present the generalized forms of (1), (2) and (4) for swelling media derived by applying HMT and then to show how these results can be used to construct a new system of governing equations capable of capturing the swelling of the particles. Further we show how the model leads to new directions in the modeling of consolidation of active clays.

In the next section we discuss the macroscopic view of clay particles and review the underlying assumptions of hybrid mixture theory which pertain to the results presented herein. Next we examine a modified Terzaghi's stress principle and show how it affects consolidation. In the subsequent section, we briefly mention the effects swelling has on Darcy's law. Following this we discuss the implications of the macroscale chemical potential and its effects on Fick's law. We then discuss the viscoelastic nature of the system and conclude with a brief summary.

## 2 Assumptions Involved in HMT

Here we review some of the underlying assumptions needed to obtain later results. In so doing it is necessary to distinguish between two types of governing equations, namely, field and constitutive. Field equations include conservation of mass, momentum balance, energy balance, and entropy balance (also known as the entropy inequality). These equations hold for all materials without any modifications. On the other hand, constitutive relations depend upon the material and involve coefficients which must be measured experimentally. Some examples include Hooke's law for an elastic solid and

Newton's law for a viscous fluid. In continuum mechanics, in which intermolecular forces are not explicitly accounted for, the determination of the exact constitutive relations is not always possible. However, restrictions on the *form* of the constitutive relations can be obtained by exploiting the entropy inequality [37]. This has been done for a single phase continuum for over 25 years [38].

Originally, the continuum approach was extended to multi-phase media by Bowen, who employed a mixture theoretic approach [39, 40]. In his approach, the field equations for each phase are postulated in such a way as to account for interactions with other phases. In this manner, the scale of observation is such that the two phases are viewed as overlaying continua so that at each point thermodynamic properties such as density, energy, and momentum are defined spatially everywhere. This scale of observation is denoted the *macroscale*.

Hybrid mixture theory is a slight modification of mixture theory, in that the macroscale field equations are obtained formally by spatially averaging the microscale field equations [30, 41]. The macroscale variables are defined to be as consistent as possible with their microscale counterparts, so that an analogue of classical Gibbsian thermodynamics can be developed. Furthermore, averaging gives explicit expressions for the exchange terms of mixture theory in terms of the microscale thermodynamic properties and the geometry of the medium. Interfacial effects can be explicitly accounted for by spatially averaging interfacial balance laws [33]. It is assumed there is a single averaging volume for each field variable which is invariant in space and time. Such a volume is called a Representative Elementary Volume (REV). It must be much larger than the smaller scale, and it must be at such a size so that making the volume slightly larger or smaller yields the same value for the averaged thermodynamic property [42]. Certainly if the medium is too heterogeneous (i.e. has continuous evolving hierarchy [43]) such an REV does not exist. A medium which is homogeneous on the scale of observation possesses an REV.

Just as in classical mixture theory, constitutive restrictions are obtained by exploiting the entropy inequality in the spirit of Coleman and Noll [37, 38]. This guarantees that the second law of thermodynamics is not violated. In order to exploit the entropy inequality, it is necessary to identify the measurable variables which define the medium. These variables are denoted as independent constitutive variables. For an elastic solid phase the independent constitutive variables might include the strain, the temperature, and

the gradient of the temperature. By including the strain, the exploitation of the entropy inequality yields Hooke's law [38]. By including temperature and its gradient, Fourier's law of heat conduction can be derived [38]. For a viscous fluid, the rate of deformation tensor is included in the list of constitutive independent variables. Exploiting the entropy inequality yields a constitutive relation for the stress tensor, which when substituted back into the momentum balance yields the Navier-Stokes equation [38]. It should be noted that in deriving these constitutive restrictions the list of constitutive independent variables is critical. And in fact, it is this list of variables which *defines* the material.

In recent articles [44, 45, 46, 47, 48, 49] the authors have proposed a set of constitutive independent variables which yields a description of swelling porous media. The validity of the set of constitutive independent variables is borne out through experiments and the recovery of classical results. Although several experiments have been performed which partially validate this theory (mentioned further in the paper), there are many more experiments needed.

Consider the clay particles as a mixture of two phases (the solid clay platelets and liquid adsorbed water) viewed as coexisting continua, which undergo independent motions  $\mathbf{x} = \mathbf{x}_\alpha(\mathbf{X}_\alpha, t)$ ,  $\alpha = l, s$  with respect to each reference configuration (here  $\mathbf{x}$  denotes the spatial position of the particle of the  $\alpha$ -phase at time  $t$  with respect to a reference position  $\mathbf{X}_\alpha$ ). Let the subscript  $\alpha = l, s$  denote the adsorbed liquid and solid phase respectively and consider that each phase  $\alpha = l, s$  may contain  $N$  miscible components which may transfer between phases (e.g., adsorption/desorption). Assuming the macroscopic medium is non-heat conducting, the macroscopic fluid is non-viscous, and interfacial effects are negligible, the behavior of the system is dictated by the following macroscopic constitutive independent variables [50]:

$$\begin{aligned} & T, \mathbf{v}_{l,s}, \\ & \rho_l, \nabla \rho_l, \mathbf{d}_l, C_l^j, \nabla C_l^j, \mathbf{u}_l^j, \\ & \rho_s, \nabla \rho_s, \mathbf{E}_s, \nabla \mathbf{E}_s, C_s^j, \nabla C_s^j, \mathbf{u}_s^j \quad j = 1, \dots, N-1. \end{aligned} \quad (6)$$

The variables in the first row include temperature,  $T$ , assumed to be equal for the liquid and solid phase at any given point in space, and the velocity of the liquid phase relative to the solid phase,  $\mathbf{v}_{l,s}$ .

The second row of variables include the mass density of the liquid phase,  $\rho_l$ , the rate of deformation tensor for the liquid phase,  $\mathbf{d}_l \equiv \frac{1}{2}(\nabla \mathbf{v}_l + (\nabla \mathbf{v}_l)^T$ ,

the mass concentrations,  $C_l^j$ , and the diffusive velocities,  $\mathbf{u}_l^j \equiv \mathbf{v}_l^j - \mathbf{v}_l$ . In the limiting case in which the thermodynamic properties of the liquid phase are not affected by the presence of the solid phase (e.g. sandstone), the liquid is usually considered Newtonian. Hence the inclusion of the mass density and the rate of deformation tensor which are classically listed as constitutive independent variables for a Newtonian fluid [38]. To account for contaminant transport it is necessary to incorporate the concentrations and the diffusive velocities, which eventually allow us to derive a generalized Fick's law.

The third row of variables in (6) describe the solid phase. These include the mass density of the solid phase,  $\rho_s$ , the mass concentration of the constituents of the solid phase,  $C_s^j$ , the diffusive velocity of the solid phase  $\mathbf{u}_s^j$ , and the macroscale solid phase strain tensor,  $\mathbf{E}_s$ . This latter quantity is given as

$$\mathbf{E}_s = \frac{1}{2}(\mathbf{C}_s - \mathbf{I}) \quad (7)$$

where  $\mathbf{C}_s = \mathbf{F}_s^T \mathbf{F}_s$  with  $\mathbf{F}_s = \text{grad } \mathbf{x}_s$  denoting the deformation gradient of the solid phase (with grad denoting the differentiation with respect to a material particle on the averaged scale). For the case in which the solid is connected (e.g. sandstone), the solid is usually considered elastic, and hence the necessity of including the macroscale solid phase strain tensor. However colloids are not connected, and although the macroscale solid phase strain tensor incorporates the microscopic strain of the solid phase, it is more often dominated by the relative displacement of the colloids. Hence, for the case of clay soils, the macroscale strain tensor carries the geometric information about the relative placement of the clay minerals.

Besides listing the variables which are assumed to define the material at the macroscale, it is necessary to list the subset of variables given in (6) of which the Helmholtz free energies,  $A_s$  and  $A_l$ , depend. For instance, it is well known that the energies do not depend on time rate of change, and therefore variables such as  $\mathbf{v}_{l,s}$  and  $\mathbf{u}_\alpha^j$  are excluded from this subset. Incorporating only the dominating terms, since including all constitutive independent variables listed in (6) leads to unnecessary complications, the dependence of the energies are [50]

$$A_l = A_l(T, \rho_l, \mathbf{E}_s, C_l^j) \quad (8)$$

$$A_s = A_s(T, \rho_s, \mathbf{E}_s, C_s^j). \quad (9)$$

In the above, the adsorbed water is distinguished from the bulk phase counterpart by postulating the dependence of the free energy of the fluid,  $A_l$ , on



the proximity of the solid, i.e. the dependence of  $A_l$  on  $\mathbf{E}_s$ . If the thermodynamic properties of the liquid phase are not affected by the presence of the solid phase (e.g. sandstone), the liquid is considered a bulk fluid. As a special case of (8), for which the deviatoric part of the strain tensor has negligible effect on the liquid phase, we may replace  $\mathbf{E}_s$  with the volume fraction of the liquid phase  $\varepsilon_l$ . This can be accomplished formally by using the mass balance of the solid phase to eliminate  $\mathbf{E}_s$  in favor of  $\varepsilon_l$  when the loss of mass of the solid phase to the liquid phase is negligible [30, 49]. The use of the volume fraction as a constitutive independent variable for the free energy of the fluid phase has been partially experimentally justified by Low [3, 4, 2] who has shown that the thermodynamic properties of the adsorbed water in montmorillonite clays are strongly dependent on the separation of the clay platelets. In these experiments, the clay minerals are separated by a distance equivalent to 10 to 30 layers of water where the adsorbed fluid can withstand the normal hydrostatic swelling pressure, but not shear stress. If one wants to consider a dryer system, say on the order of one to ten layers of water (2.5 to 25Å), then the vicinal fluid is even more anomalous and its behavior may depend on the alignment of the clay platelets (see e.g. [51]). In this case the vicinal water is more structured and can actually support a shearing force. In this range of low moisture content it is then appropriate to replace the volume fraction by the solid phase strain tensor [50, 49]. The inclusion of the deviatoric part of  $\mathbf{E}_s$  extends the validity of the theory to  $h < 25\text{Å}$ .

At this point we have discussed the primary assumptions necessary to derive the results presented in the following sections. These include the existence of an REV and the postulation of constitutive independent variables. Other assumptions which are discussed in more detail in [50] include the postulation that each phase represents a simple thermomechanical process [38], i.e. we have not extended the assumptions regarding entropy flux and entropy sources to account for systems far from equilibrium [52]. In addition, we have assumed the material time derivative of the volume fraction,  $\dot{\varepsilon}_l$ , is a constitutive variable in order to close the system [53, 48]. As in all upscaling approaches, there exists an additional variable, the volume fraction in this case, for which there is no additional equation. The appearance of the additional variable is a consequence of losing information about the microscopic geometry (for a detailed discussion see [53]). Another popular means of closing the system is to postulate the existence of a balance law for which the volume fraction must satisfy, see e.g. [54, 55]. Our choice of closure is crucial

in our formulation since this yields a material with viscoelastic behavior.

The Coleman and Noll method [37] is used to exploit the restrictions placed by the entropy inequality on the constitutive theory. Three sets of results can be obtained: results which hold far from equilibrium (non-equilibrium results), results which hold only at equilibrium, and results which hold near equilibrium. The first two sets of results are standard [38], but we should comment briefly about how we obtained the near-equilibrium results, which include Darcy's and Fick's laws.

Equilibrium is defined to be the state when the constitutive independent variables  $\mathbf{v}_{l,s}$ ,  $\mathbf{d}_l$ ,  $\mathbf{u}_\alpha^l$  are all zero. It is also assumed that the dependent variable,  $D_s \varepsilon_l / Dt$ , is zero at equilibrium. Then the near-equilibrium results are obtained by linearizing about the above variables so as to obtain a positive quadratic form in the entropy inequality. So for example, if  $z$  is one of the above mentioned variables which vanishes at equilibrium, and  $f$  is the coefficient of  $z$  within the entropy inequality, the linearization gives  $f_{neq} \approx f_{eq} + Cz$  where subscripts neq and eq denote the near-equilibrium and equilibrium quantities, respectively. The constant  $C$  is the linearization quantity, and it may be a function of all variables which are not zero at equilibrium, i.e.  $\varepsilon_l$ ,  $T$ ,  $\rho_l$ ,  $C_l^j$ ,  $\rho_s$ ,  $C_s^j$  as well as (in a higher order theory)  $\nabla \varepsilon_l$ ,  $\nabla \rho_l$ ,  $\nabla C_l^j$ ,  $\nabla \rho_s$ ,  $\nabla C_s^j$ .

Because this approach is methodical, everything which follows is a consequence of these assumptions and no heuristic or empirical arguments are needed. We will not present the details of the derivations - the essence can be found in Eringen [38] for a single phase medium, and in Bowen [29] for a multi-phase medium. Extensions to swelling porous media have been discussed in [27, 48, 46].

The results obtained by exploiting the entropy inequality using the Coleman and Noll method are presented in the following sections. It should be noted that we have made no distinction between inter-particle forces and intra-particle forces. By a particle we mean a cluster of clay minerals tightly bound together by absorbed water. In this approach, the modeling of clay particles with bulk phase water (i.e. water unaffected by the solid phase) or gas requires an additional upscaling, so that at this larger scale one cannot distinguish between the clay particles and the bulk phase fluid (see Figure 1). This upscaling has been performed using homogenization [48, 49] and by implementing hybrid mixture theory [50, 44, 45]. The results presented in this paper are related to the upscaling from microscale to the mesoscale depicted in Figure 1 and assumes that the clay particles contain only one liquid phase,

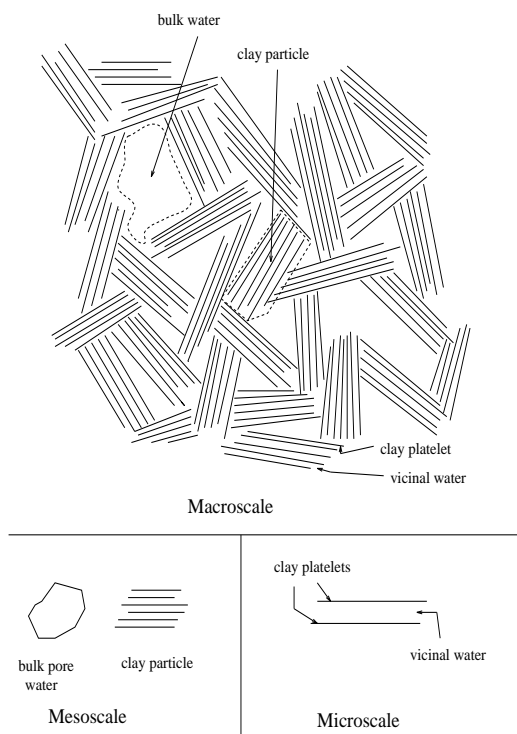


Figure 1: Three-Scale Model for Clay

the adsorbed water. This is done so as to illustrate the simplest extension of the three classical expressions. The results presented in [48, 49, 50, 44, 45] would require much more extensive preliminaries, and the conclusions are much more complex. We feel that the results presented herein give a more intuitive introduction into the research which has been done in this area.

### 3 Modified Terzaghi's Effective Stress Principle

By postulating the more general constitutive dependence of the free energies, (8), (9), and using the Coleman and Noll method of exploiting the entropy inequality [37], the authors [50, 45, 49] obtained a new stress principle for swelling clay soils. In terms of the averaged stress tensor,  $\mathbf{t}_\alpha$ , and thermodynamic pressures of the  $\alpha$ -phase,  $p_\alpha$ , the results for the case of a single

component per phase, are given by

$$\varepsilon_l \mathbf{t}_l = -\varepsilon_l p_l \mathbf{I} - \rho_l \boldsymbol{\mu} : \mathbf{d}_l \quad (10)$$

$$\varepsilon_s \mathbf{t}_s = -\varepsilon_s p_s \mathbf{I} + \mathbf{t}_s^e + \mathbf{t}_s^l, \quad (11)$$

where  $\boldsymbol{\nu}$  is a material coefficient, and the tensors  $\mathbf{t}_s^e$  and  $\mathbf{t}_s^l$  are defined by

$$\mathbf{t}_s^e = \rho_s \varepsilon_s \mathbf{F}_s \frac{\partial A_s}{\partial \mathbf{E}_s} \mathbf{F}_s^T, \quad \mathbf{t}_s^l = \rho_l \varepsilon_l \mathbf{F}_s \frac{\partial A_l}{\partial \mathbf{E}_s} \mathbf{F}_s^T. \quad (12)$$

Equation (10) holds near equilibrium whereas equation (11) is a general nonequilibrium result. To exploit the physical significance of the above result let us introduce the total particle stress tensor  $\mathbf{t}$  and the particle thermodynamic pressure  $p$  as

$$\mathbf{t} = \varepsilon_s \mathbf{t}_s + \varepsilon_l \mathbf{t}_l, \quad p = \varepsilon_l p_l + \varepsilon_s p_s. \quad (13)$$

By adding (10) and (11), where the viscous component of  $\mathbf{t}_l$  has been neglected, and using (13) we obtain

$$\mathbf{t} + p \mathbf{I} = \mathbf{t}_s^e + \mathbf{t}_s^l. \quad (14)$$

The above result gives important insight into the stress in swelling particles. To elucidate this consider a fixed solid strain  $\mathbf{E}_s$  and define the bulk phase  $B$  to be fluid unaffected by the solid phase (e.g. non-swelling granular media). By definition, the free energy of a bulk fluid  $A_B$  does not change with the proximity of the solid and therefore is independent of  $\mathbf{E}_s$ . Therefore  $\mathbf{t}_s^l$  is zero and because  $\mathbf{t}_s^e$  only depends on the fixed solid strain  $\mathbf{E}_s$ , equation (14) reduces to

$$\mathbf{t}_B + p_B \mathbf{I} = \mathbf{t}_s^e \quad (15)$$

where now the subscript  $B$  is used to denote the corresponding property for a non-swelling granular medium. Equation (15) has been derived by Hassanizadeh and Gray [32] within the context of hybrid mixture theory for non-swelling granular media. In classical soil mechanics the above result resembles in form Terzaghi's effective stress principle at the mesoscale for non-swelling media with  $p_B$  and  $\mathbf{t}_s^e$  normally referred to as the pore pressure (or bulk phase pressure) and the effective stress tensor, respectively. The effective stress tensor  $\mathbf{t}_s^e$  measures stresses induced by mineral to mineral contact and primarily controls the deformation of non-swelling systems such as sands, silts, and low and medium plastic clays such as kaolinite or illite.

The modified effective stress principle (14) for swelling media has the additional term,  $\mathbf{t}_s^l$ , which is the stress in the fluid phase due to the strain of the macroscale solid matrix. It is this term which accounts for the effects of the solid-fluid interaction. Recall that the thermodynamic definition of the effective stress tensor involves  $\partial A_s / \partial \mathbf{E}_s$ , whereas the hydration stress tensor involves  $\partial A_l / \partial \mathbf{E}_s$ . For a soil in which the solid phase is connected and for which there is no interaction between the solid and liquid phases,  $\mathbf{t}_s^l$  is zero. On the other hand, for a clay soil in which the solid minerals are highly ordered so that there is no solid-solid contact,  $\mathbf{t}_s^e$  is negligible, which means that straining the solid matrix does not change the energy of the solid  $A_s$ . In reality, the clay is not well ordered. The resulting stresses due to the entanglement present are manifested in the effective stress tensor,  $\mathbf{t}_s^e$ . When surface hydration is the dominant component of physico-chemical forces,  $\mathbf{t}_s^l$  may be identified with the  $R - A$  component in equation (3). Whence we denote  $\mathbf{t}_s^l$  the *hydration stress tensor*, as in Murad and Cushman [49].

A simplified scalar concept of hydration stresses can be obtained by considering a moderate moisture content greater than that occupied by 10 fluid monolayers. In this range the adsorbed water can not withstand shear at equilibrium and therefore a well ordered particle composed of parallel platelets can only compress or expand. The assumption of moderate moisture content can be easily imposed by postulating that  $A_l$  does not depend on the deviatoric part of the solid strain  $\mathbf{E}_s$ , but instead depends upon the volumetric strain, or the volume fraction  $\varepsilon_l$  (see Achanta et al. [27] or Murad et al. [48]). Thus, using  $A_l = A_l(\varepsilon_l)$  in definition (12) yields (see [49])

$$\mathbf{t}_s^l = \rho \varepsilon_l \varepsilon_s \frac{\partial A_l}{\partial \varepsilon_l} \mathbf{I}.$$

This shows that in the range of moderate moisture contents  $\mathbf{t}_s^l$  reduces to a multiple of the identity.

The authors believe that one major contribution of the HMT approach for modeling active clays is the treatment of particles as a two-phase system i.e. a clay platelets and adsorbed water system. This is in direct contrast with the phenomenological approaches of e.g. Sridharan and Rao [18] or Lambe [20] who have treated particles as a single solid phase and who have heuristically incorporated the effect of the net repulsive ( $R\mathbf{I}$ ) and attractive ( $A\mathbf{I}$ ) forces between particles. Constitutive equations for the clay platelets and adsorbed water allow us to capture the swelling of particles and secondary adsorbed-

bulk water flow (see Section 6). The approach presented herein is also more rational than the earlier theories of Ma and Huackel [56] and Hueckel [23] where the adsorbed water is treated as “immobile” water and considered to be part of the solid phase. Furthermore Lambe [20] assumed that only one stress exists in the platelet-adsorbed water particles, defined as the difference between the total macroscopic stress and bulk phase pressure. Consequently Lambe has neglected particle swelling due to the adsorbed water flow and overlooked the existence of an interfacial pressure between the solid and fluid phases.

## 4 Darcy’s Law for the Adsorbed Water

We summarize an extension of Darcy’s law which applies to swelling soils. In the current formulation, Darcy’s law is derived by linearizing about  $\mathbf{v}_{l,s}$ . The details of the derivation are given in [27, 50], and for moderate moisture contents the form of Darcy’s law for a single constituent fluid flowing through a swelling colloid is given by [27]:

$$\varepsilon_l \mathbf{v}_{l,s} = -\mathbf{K}(\varepsilon_l) \left( \nabla p_l + \rho_l \frac{\partial A_l}{\partial \varepsilon_l} \nabla \varepsilon_l \right) \quad (16)$$

where gravity has been neglected and the conductivity,  $\mathbf{K}$ , is a second-order positive definite tensor which arises from the linearization process. The first term on the right hand side of (16) leads to the traditional Darcy’s law. The remaining term implies that vicinal fluid flows from regions of high volume fraction to regions of low volume fraction. Note that if the pressure gradient is counter-balanced by a gradient in the volume fraction, it is possible to have no flow even with a net pressure difference across the soil. The coefficient of  $\nabla \varepsilon_l$  can be a function of any of the variables listed as constitutive independent variables for  $A_l$  (see (8)) and must be determined experimentally. In [mucu2] this coefficient has been identified with a hydration pressure and its relation to Low’s experimentally observed swelling pressure [4, 7] at equilibrium was also derived.

Non-linear effects can also be derived within the HMT formulation. The Brinkman law [57] can be recovered by not neglecting the viscous term of the stress tensor for the fluid phase, (10), [45, 50], just as it has been done for mixture theory (see, e.g. Vardoulakis and Aifantis, [55]). The Forchheimer correction term can also be derived, although the analysis is slightly more complicated. For a single phase flow see [58], and for two-phase flow see [59].

## 5 Fick's First Law

Fick's classical first law states that the diffusive velocity in the liquid phase of the  $j^{\text{th}}$  species,  $\mathbf{u}_l^j$ , is proportional to the gradient of the mass concentration,  $C_l^j$ . Here we are interested in a more general form of Fick's first law, which states that the diffusive velocity is proportional to the gradient in the chemical potential. If gravity is considered as an external source, then this is expressed as

$$R_\alpha^j \mathbf{u}_\alpha^j = -\rho_\alpha C_\alpha^j \nabla \mu_\alpha^j + \rho_\alpha C_\alpha^j \mathbf{g} \quad \alpha = l, s \quad j = 1, \dots, N \quad (17)$$

where  $R_\alpha^j$  is the constant of proportionality,  $N$  is the number of constituents, and  $C_\alpha^j$  is the mass concentration of constituent  $j$  in phase  $\alpha$  subject to  $\sum_{j=1}^N C_\alpha^j = 1$ . Note that some authors incorporate the gravitational head into the definition of the chemical potential, in which case it is termed the *gravi-chemical* potential.

For a liquid system which is composed of  $M_j$  molecules of the  $j$ th constituent, the chemical potential is defined to be

$$\mu_l^j = \frac{\partial U}{\partial M_j}, \quad (18)$$

where  $U$  is the total energy of the system. Thus the chemical potential represents the change in the energy of the system due to the change in the number of constituent  $j$  molecules holding everything else fixed. In addition, the classical Gibbsian chemical potential has the property that it is constant for a single constituent coexisting in two phases at equilibrium, i.e.  $\mu_l^j = \mu_s^j$ . These are the properties which are used to define the thermodynamical definition of a macroscale chemical potential in a swelling porous medium. This was first accomplished for a nonswelling porous medium in [46], and in [47] these definitions were extended to swelling porous media and some consequences are analyzed for some simple systems. In this section we review some of these results.

In mixture theory it is difficult to define a chemical potential as in (18) because the number of molecules is not a constitutive independent variable. The difficulty in arriving at an appropriate definition of the chemical potential inherently arises due to the fact that the system under consideration is open, making it impractical to consider the number of molecules as one of the constitutive independent variables. Instead, the mass concentrations are

the relevant variables, and since the mass concentrations are inter-dependent ( $\sum_{j=1}^N C_\alpha^j = 1$ ), there is some latitude as to the exact definition of the chemical potential. The definition for the macroscale chemical potential which is completely analogous to the classical Gibbsian chemical potential is for swelling systems

$$\mu_l^j \mathbf{I} \equiv A_l^j \mathbf{I} - \frac{1}{\rho_l C_l^j} \mathbf{t}_l^j, \quad (19)$$

$$\mu_s^j \mathbf{I} \equiv A_s^j \mathbf{I} - \frac{1}{\rho_s C_s^j} \mathbf{t}_s^j + \frac{1}{\rho_s} \mathbf{t}_s^e + \frac{\varepsilon_l}{\varepsilon_s \rho_s} \mathbf{t}_s^l, \quad (20)$$

where  $\varepsilon_s$  is the volume fraction of the solid phase,  $\mathbf{t}_\alpha^j$  are the partial stress tensors for the liquid ( $\alpha = l$ ) and solid ( $\alpha = s$ ) phases,  $\mathbf{t}_s^e$  is the effective stress tensor for the solid phase, and  $\mathbf{t}_s^l$  is the hydration stress tensor. The partial stress tensors are related to the overall bulk phase stress tensor for phase  $\alpha$  by  $\mathbf{t}_\alpha = \sum_{j=1}^N (\mathbf{t}_\alpha^j - \rho_\alpha C_\alpha^j \mathbf{u}_\alpha^j \mathbf{u}_\alpha^j)$ . For a perfect (non-viscous) fluid,  $\mathbf{t}_l = -p_l \mathbf{I}$  where  $p$  is the pressure. The physical interpretation of the effective and hydration stress tensors were discussed in a previous section. In [46] it is shown that the chemical potentials, as defined here, are indeed scalar quantities.

With these definitions it can be shown [46] that the following relations are satisfied:

$$R_\alpha^j \mathbf{u}_\alpha^j = -\varepsilon_\alpha \rho_\alpha C_\alpha^j (\nabla \mu_\alpha^j - \mathbf{g}) \quad \alpha = l, s, \quad (21)$$

$$\sum_{j=1}^N C_\alpha^j \mu_\alpha^j = A_\alpha + \frac{1}{\rho_\alpha} p_\alpha \quad \alpha = l, s, \quad (22)$$

$$\mu_l^j = \mu_s^j. \quad (23)$$

Equation (21) is the near-equilibrium expression for the diffusive velocity (Fick's first law). Equation (22) states that, just as in the classical Gibbsian chemical potential, the weighted sum over all chemical potentials yields the Gibbs free energy; and equation (23) is an equilibrium expression which states that at equilibrium, the chemical potentials of the same constituent in two phases are identical. Thus we have an exact analogy with classical thermodynamics.

What makes the definitions so intriguing is that we have incorporated the effective and hydration stress tensors in the definition of the solid phase chemical potential. Other authors have defined the macroscale chemical potential without these quantities [27, 26, 29], and in those theories the resulting



chemical potential is no longer a scalar, and equations (21) - (23) must be modified accordingly. Essentially we can draw a parallel with the classical chemical potential and gravi-chemical potential. The gravi-chemical potential incorporates the gravitational head into the definition of the chemical potential so that the gravitational force is viewed as internal to the system. In an analogous manner, the solid phase macroscale chemical potential as defined in (20) views the effective and hydration stress tensors as part of the system.

Whether one views the two stresses as internal or external to the system, it is important to note the consequences. In particular, a stressed solid matrix (either a stressed effective or hydration stress tensor) affects the equilibrium balance of the distribution of the constituent between the solid and liquid phase (23), as well as the diffusive flow of a constituent within the solid matrix (21). Thus, compressing a clay soil in such a manner as to change the volume fraction,  $\varepsilon_l$ , certainly affects the adsorption of the constituents on the solid phase.

## 6 Viscoelasticity and Relaxation

By invoking the closure issue discussed in Boure [53], an additional near-equilibrium result is obtained by linearizing the entropy inequality about  $D_s \varepsilon_l / Dt$ . The following result is obtained (see [49])

$$p_l - p_s = \mu_* \frac{D_s \varepsilon_l}{Dt}. \quad (24)$$

Equation (24) tells us that near equilibrium, the thermodynamic pressure of the adsorbed fluid and solid phases are not necessarily equal. Thus, the commonly assumed equality between  $p_l$  and  $p_s$  for granular non-swelling media (see [??]) may not necessarily hold, especially for swelling systems.

The magnitude of the coefficient  $\mu_*$  is not known, and most likely it varies depending on the composition and the interaction of the vicinal fluid and solid minerals. This coefficient may be thought of as a relaxation factor which among other effects, accounts for the re-ordering of the adsorbed water, i.e. the redistribution of the fluid molecules over the interlamellar spaces as they are disturbed from the equilibrium state. Flow towards equilibrium is characterized by its specific time relaxation which depends on the size of the pores. For bulk fluids in macropores the relaxation time is usually much

smaller than the macroscopic flow time. It then follows that for a granular medium,  $\mu_* \approx 0$ , since there is very little ordering of the bulk liquid phase. On the other hand, the combination of physico-chemical forces and narrow pores increases the magnitude of the relaxation time of the vicinal fluid.

Some information about the magnitude of  $\mu_*$  can be obtained by comparing this term with what is being used in other fields. For example, in polymer literature, this term has been empirically derived and used in describing diffusion [60, 61]. Likewise, some information can be obtained by identifying this term with the non-equilibrium part of the swelling pressure (or averaged viscous disjoining pressure) in the sense of [62, 63]. In [62, 63] it has been advocated that the microscopic counterpart of the viscous disjoining pressure accounts for the excess of the thin film viscosity relative to the bulk phase. Thus, one can extend this argument to the mesoscale and possibly identify the coefficient  $\mu_*$  with the difference between the averaged mesoscopic volumetric viscosity of the adsorbed and bulk water. This averaged excess in viscosity, has been measured by Low [2].

By substituting (24) in (11) we obtain

$$\mathbf{t}_s = -p_l \mathbf{I} + \frac{1}{\varepsilon_s} \left( \mathbf{t}_s^e + \mathbf{t}_s^l + \mu_* \frac{D_s \varepsilon_l}{Dt} \right) \quad (25)$$

illustrating how the viscoelastic nature of the soil enters into the governing system of equations. This viscoelastic nature is a remarkable result because it was initially assumed that the soil was composed only of a viscous fluid and an elastic solid.

Neglecting the flow of adsorbed water and heuristically adding physico-chemical forces through an  $R - A$  component leads to a simplified system of PDE's which does not capture particular features of smectic clays. For example, Sridharan and Rao [64] have suggested that secondary compression is related to the delayed deformation of the clay particle after the bulk water has been drained from the larger pores in the primary structure (see also Hueckel [23]). The secondary deformation appears somewhat related to the delayed drainage of the adsorbed water relative to the bulk phase flow. Since the adsorbed water is strongly attracted to the clay surfaces, it is more difficult to drain than the bulk water. In addition, the interaction between the adsorbed water and clay surfaces produces an excess in the viscosity of the vicinal fluid relative to the viscosity of the bulk water and is manifest in a viscous stress relaxation (Zeevaart [65]). The delayed particle deformation due to the adsorbed water flow has also been discussed by Barbour and

Fredlung [66] in the context of “osmotically induced consolidation” resulting from osmotic concentration gradients.

## 7 Conclusions

In this paper we have discussed some modifications needed for Darcy’s law, Terzaghi’s effective stress principle, and Fick’s first law in order to apply these relations to a swelling soil. These relations can be derived in a methodical fashion with a minimum of assumptions. The most critical step in the analysis is to provide the list of constitutive independent variables for the solid and liquid phases. In particular, it has been shown that postulating the dependence of  $A_l$  on  $\mathbf{E}_s$  and including  $\nabla \mathbf{E}_s$  in the set of constitutive independent variables play a critical role for swelling colloids.

To modify Darcy’s law an interaction potential is needed to show the vicinal fluid flows from regions of high volume fraction to low volume fraction. It is not enough to simply modify the permeability coefficient and presume that it is a function of the volume fraction.

Terzaghi’s effective stress principle is modified by incorporating the hydration stress tensor. Thus the macroscale solid phase load at equilibrium is distributed between the liquid phase pressure, the effective stress tensor, and the hydration stress tensor. At low moisture content the hydration stress tensor allows the vicinal fluid to support shear. At higher moisture content, where the thermodynamic properties of the liquid phase are still affected by the presence of the solid phase, the vicinal fluid does not support any shearing force at equilibrium, but still supports some of the load due to the bonding between the vicinal fluid and clay minerals. In a medium with a disconnected solid phase, such as clay, the effective stress tensor represents the entanglement of the clay minerals. In addition, a term involving the time rate of change of the volume fraction indicates that the overall balance is different at equilibrium and near-equilibrium. The magnitude of this term is as yet, unknown, but a similar empirical term has been in use by scientists studying swelling polymers.

The chemical potential can be defined in such a way as to recover the familiar form of the generalized Fick’s first law, i.e. the diffusive velocity is proportional to the gradient of the chemical potential. It is pointed out that a stressed solid matrix (in either a swelling or non-swelling media) affects the adsorption of contaminants onto the solid phase, as well as the diffusion of

the contaminants within the solid phase matrix.

The main point the authors wish to make is that equations (13), (14), (16), and (24) coupled with the mass and momentum balance equations yield a transient system of equations governing the time evolution of particles swelling due to the adsorbed water flow. This allows for a more accurate description of the clay particles compared to the models that treat the particles as a single solid phase. The elasticity models based on Biot [67], or the Cam-Clay plasticity models of Roscoe and Burlan [68] or the Physico-Chemical approach of Sridharan and Rao [64] all treat particles as a single solid phase and assume that particles reach equilibrium instantaneously as they are disturbed by the bulk fluid. In particular, it has been shown that Biot's model of consolidation can be derived by upscaling the coupled equations based on linear elasticity equations for the particles and the Stokesian bulk water flow (see e.g. Auriault [69]). The resulting Biot system of equations are elliptic, implying the time scale associated with the transient effects within the particles is simply neglected. The authors believe it makes no sense to try and heuristically extend Biot's consolidation model, for example, without critically examining the assumptions used to develop such a model. In this paper we have made an attempt to re-examine the assumptions used to develop a continuous model for clay, and to arrive at constitutive restrictions which accounts for the swelling of clay particles.

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