A THEORETICAL FRAMEWORK FOR MODELING THE CHEMO-MECHANICAL BEHAVIOR OF POROUS MEDIA WITH MULTIPHASES AND MULTISPECIES

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Summary A chemo-mechanical theory of porous media with multiphase and multispecies is developed based on the Hybrid Theory of Mixtures. It is shown that the coupled processes in porous media such as skeletal deformation, fluid flow, heat conduction, material diffusion, chemical reaction, phase transition, pressure solution, and so on, can be consistently described within this unique theoretical framework. Central to the theory is a general expression for the electrochemical potential of species, based on which the colligative properties of porous media are discussed, including osmotic pressure, Donnan effect, Gibbs-Thomas effect, supercooling and superheating. In particular, the components of pore fluid pressure are identified and formulated, and the concept of effective stress is clarified. It is found that whenever electro-chemical effect comes into play, the total pore pressure cannot be directly measured *via* a traditional transducer. The impact of this result is far-reaching, since the concept of effective stresses is generally adopted in theoretically modeling and numerically simulating the coupled processes in porous media.

INTRODUCTION

The chemo-mechanical behaviour of porous media with multiphases and multispecies is of great interest in many diverse fields of science and engineering. Traditionally, the coupling of multi-physical processes in porous media such as deformation, damage, seepage, diffusion and heat conduction, have been extensively investigated, and the poromechanic theory that can be used to describe these coupled processes has been very well developed. Thus far, however, little effort has been devoted to modelling the electro-chemical effects in porous media. It has been recognized that many unresolved scientific and engineering issues are tightly related to these effects. In this paper, we shall develop a theoretical framework that can be used to effectively describe the chemo-mechanical behaviour of porous media with multiphase and multispecies based on the Hybrid Theory of Mixtures (HTM).

THEORETICAL FRAMEWORK

Our theoretical derivation parallels to the approach followed by Bennethum & Cushman (1996I). Unlike the latter, however, we introduce a relationship between the Helmholtz free energies of a phase and its species, in which a kinetic contribution due to the diffusion of species is added. Such a treatment leads to a theory in which porous media are explicitly viewed as highly reactive ones in the sense of Bataille and Kestin (1977), i.e., the linear momentum balance equation can be formulated only for a phase, but not for single species. Such a theory is more numerically tractable and meaningful from an engineering standpoint.

Balance equations and the second law of thermodynamics

A whole set of balance equations and the expression of the second law of thermodynamics were originally developed by Hassanizadeh and Gray (1979I, II) for multiphasic porous media, and generalized by Bennethum & Cushman (1996II) to multispecies porous media, based on the averaging procedure. One of the salient features of these balance equations is that all the exchange rates of mass, momentum, energy and entropy between various phases are explicitly defined. It is remarkable that clearly defining these exchange terms is crucial in modelling a highly reactive multiphasic material.

Constitutive assumptions

Given all the balanced equations, constitutive equations have to be developed so that a closure description of porous media can be achieved. This can be done by specifying the functional dependence of Helmholtz free energy functions for all the phases. To this end, the principle of phase separation principle is adopted. Explicitly, for α phase, we assume that $A^\alpha = A^\alpha(T, \rho^\alpha, C^{\alpha_i}, n^\alpha)$, where A is the free energy density function, i = 1, 2, …, Z-1 (Z is the total number of the species in the phase), T the temperature [K], n^α and ρ^α are the volume fraction and mass density of the phase (resp.), and C^{α_i} is the concentration of Species i in α phase. For the solid matrix, A^s also depends on its strain **E**. The free energy function as defined above implicitly assumes an elastic solid matrix. The irreversible response of the material can be addressed by introducing related internal state variables into the free energy functions (e.g., Wei & Dewoolkar, 2006), without adversely influencing the conclusions deduced in the following.

Thermodynamic constraints

Enforcement of the second law of thermodynamics yields equations of state, which enunciate the functional dependences of pressure, stress tensor and entropy of a phase on its respective independent state variables, and a residual dissipation inequality, accounting for the energy dissipation due to seepage, diffusion, chemical reaction, heat conduction, phase

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transition, and other dissipative processes. With the residual dissipation inequality, two cases are of interest and helpful, namely, the state at equilibrium and the state near equilibrium, at which we can deduce (resp.) the conditions for porous medium at mechanical, thermal and chemical equilibrium and the constitutive equations for the forces driving the dissipation processes mentioned above. It is remarkable that in our approach, thermodynamics imposes no constraints on the linear momentum exchange rates between species. That is to say, we can only develop the linear momentum balance equations for phases, but not for single species.

CONSTITUTIVE EQUATIONS FOR DISSIPATIVE FORCES

Assuming that the porous media slightly deviates from equilibrium, with the results deduced from the constraints of thermodynamics, we develop the constitutive equations for the dissipative forces driving fluid transport, diffusion, chemical reaction, heat conduction, phase transition, pressure solution, and other processes. Interestingly, we show that the driving forces for dissipative processes are all related to the electro-chemical potential of fluid species, given by

$$\mu^{f_k}(T,p^f,C^{f_i},n^f)=\mu_{\oplus}^{f_k}(T,p^f)+\frac{RT}{\mathrm{M}_k}\ln\left(\frac{\Theta_f C^{f_k}}{\mathrm{M}_k}\right)+\frac{\overline{\upsilon}^{f_k}p_c^f}{\mathrm{M}_k}+\frac{F\xi^f v_k}{\mathrm{M}_k}+\mu_{IntM}^{f_k} \qquad (1)$$

where $\mu_{\oplus}^{f_k}$ is the standard chemical potential, p^f the fluid pressure, M_k the molar weight, R the gas constant, F the Faraday's constant, $\overline{\upsilon}^{f_k}$ the molar volume, p_c^f the apparent capillary pressure depending on n^f, $\mu_{IntM}^{f_k}$ the contribution due to the surface adsorptive force that depends largely on T and adsorbed water content, v_k the ionic valence, and Θ_f the total number of moles in a unit mass of fluid. Noticeably, μ^{f_k} includes the contributions due to capillary effect and surface adsorption. In addition, we show that the film flow in the porous media with low saturation is driven by the gradient of $\mu_{IntM}^{f_k}$, which is consistent with the recent finding from the field of surface physics (Dash et al., 2006).

BEHAVIOR OF POROUS MEDIA AT EQUILIBRIUM

At equilibrium, the chemical potential of any species must be spatially uniform and remain the same across different phases. Enforcing this condition yields rich colligative behaviour of porous media, such as osmotic pressure, Donnan effect, Gibbs-Thomas effect, supercooling and superheating. We obtain the expressions for osmotic pressure, Donnan osmotic pressure, Kevin's law and Clapeyron's equation, which are all consistent with those results derived from the classical Gibbsian thermodynamics. However, the new theory explicitly takes into account the effect of surface absorptive forces. It is noted that failure to consider these forces may yield inconsistency (Nitao and Bear, 1996).

As an example of application, consider the measurement of pore water pressure. We show that pore water pressure p^f is not the same as the measurement of the transducer (denoted as p_0^f), and $p^f = p_0^f + \Pi$, where Π is the generalized osmotic pressure given by

$$\Pi=-\frac{RT}{\overline{\upsilon}^{f_w}}\ln\left(\frac{\Theta_f C^{f_w}}{\Theta_{f0}C_0^{f_w}}\right)-p_c^f-\rho^{f_w}\mu_{\mathrm{intM}}^{f_w} \qquad (2)$$

Clearly, the discrepancy stems from Donnan effect, capillary effect and surface adsorptive force. This observation is important, since the concept of effective stress (total stress minus pore pressure) is generally adopted in modelling the mechanical behaviour of porous media. Figure 1 depicts the variation of Π with the concentration of pore water for different concentrations of fixed charges in a fully saturated soil. It can be seen that if the concentration of pore solution is altered, Π could change significantly, i.e. large difference would be expected between the true pore pressure and the measurement.

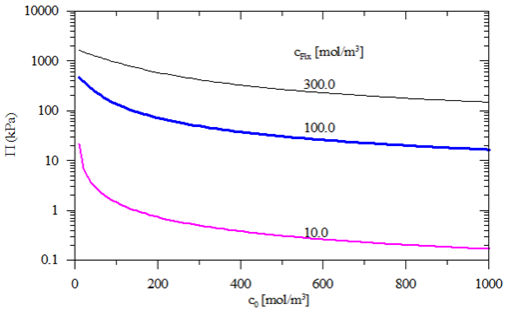

Figure 1 Donnan osmotic pressure in a fully saturated charged soil

CONCLUSIONS

A theoretical framework is developed for modelling the chemo-mechanical behavior of porous media with multiphase and multispecies. The new theory consistently describes various coupled processes in porous media, *via* the concept of electro-chemical potential. An explicit expression of electro-chemical potential is derived and the colligative properties of porous media are discussed, shedding new insights into modelling the behaviour of porous media.

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