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COMMENT ON "MULTICOMPONENT, MULTIPHASE THERMOMECHANICS WITH INTERFACES" BY S. ACHANTA, J. H. CUSHMAN AND M. R. OKOS, *Int. J. Engng Sci.* 32, 1717–1738 (1994)

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INTRODUCTION

The authors are pleased that Achanta *et al.* [1] have found the multiphase derivations of Hassanizadeh and Gray [2–5], Hassanizadeh [6], and Gray and Hassanizadeh [7–9] to be of apparent value in their work, even to the extent of building on our notation. The work that we have done provides a systematic averaging procedure for phase and interface balance equations written at the microscale. Once the average equations are obtained, the Coleman and Noll method may be applied to exploit the entropy inequality and obtain macroscale constitutive relations. We have applied this formalism to obtain equations for a single pure fluid phase in a porous medium, for a multicomponent fluid in a porous medium, and for two immiscible fluid phases in a porous medium along with the associated interfaces. The work of Achanta *et al.* [1] extends our work by including species transport in the formulation. We admire the diligence of Achanta *et al.* in completing this derivation as it is very tedious and laborious. We also note that our own efforts in this area have spanned more than 15 years. Over that span, we have come to a better understanding of the ways in which the equations provide guidance in developing constitutive theory. With this understanding and in light of some misconceptions in Achanta *et al.* [1] comes an awareness of the need to sharpen the statement of assumptions in our own work as well as to correct the misconceptions. We attempt to do that here in hopes that the strengths of our formalism will be better understood.

COMMENTS

In their Introduction, Achanta *et al.* [1] make the statement in regard to our papers, "These works are applicable to granular porous media in which the different phases do not interact." In fact, this assessment is inaccurate. When developing basic equations that describe a system, two sets or levels of equations must be employed. The first set is conservation laws, fundamental principles that describe conservation of mass, momentum, and energy. The second level of expressions is constitutive forms, approximations designed for specific systems that attempt to relate functions accounting for certain phenomena to some of the independent variables of the system. In all our works, the conservation laws are valid for multiphase systems in which various phases may exchange mass, momentum, energy, and entropy. No restrictions are imposed that limit these equations to granular media. In considering a three-phase system with interphases, interactions are allowed not only between phases and interfaces but also among the interfaces through a common line. In the development of constitutive relations for these conservation laws, momentum, energy, and entropy interactions have invariably been taken into account. Our results are not limited to granular media or unsaturated systems by any means. In fact, equation (127) of Achanta *et al.* [1], which is one of their central results, is basically identical to equation (25) of Gray and Hassanizadeh [9] for single component phases. The claim by Achanta *et al.* [1] that our development neglects interaction among the phases is therefore puzzling and needs correction.

Later in their manuscript, in the paragraph following equation (95), Achanta *et al.* [1] state, "Earlier theories do not adequately account for the liquid–solid interfacial interactions at the macroscale." As justification for this statement, they point to Gray and Hassanizadeh [9] and claim that in that reference ε^l, the volume fraction of the liquid phase, is discarded and replaced with the situation, s. The statement is not accurate. In our work, the volume fraction is not discarded but replaced by porosity, ε, and saturation where $\varepsilon^l = s\varepsilon$. This substitution in no way restricts liquid–solid interactions at the macroscale but leads to constitutive equations that are as general as the set obtained in Achanta *et al.* [1].

There is another very important misunderstanding of our papers in Achanta *et al.* [1]. They state that in our cited papers, there is "a rule that says the macroscale chemical potentials of two phases at equilibrium must be equal." This interpretation of our results is not right, and no such *a priori* requirement needs to be imposed in the development of conservation laws or constitutive equations. We believe that as we have studied more complex systems, we have gained additional insight into the correct definition of equilibrium states such that by properly defining such states the misunderstanding concerning equality of chemical potentials can be eliminated. At equilibrium for a multiphase system including interfaces and contact lines, the rates of mass exchange between phases and interfaces and between interfaces and contact curves must all be zero. Mathematically, these equilibrium conditions on mass transfer may be stated as:

For single component phases

- mass transfer between α-phase and $\alpha\beta$-interface is zero;

$$\hat{e}^{\alpha}_{\alpha\beta} = 0 \tag{1a}$$

- mass transfer between $\alpha\beta$-interface and $\alpha\beta\gamma$-contact line is zero; and

$$\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} = 0 \tag{1b}$$

For multi-component phases

- mass transfer of jth component between α-phase and $\alpha\beta$-interface is zero;

$$\hat{e}^{\alpha_i}_{\alpha\beta} = 0 \tag{1c}$$

- mass transfer of jth component between $\alpha\beta$-interface and $\alpha\beta\gamma$-contact line is zero;

$$\hat{e}^{\alpha\beta_i}_{\alpha\beta\gamma} = 0. \tag{1d}$$

Achanta *et al.* [1] have also adopted these conditions of equilibrium. The consequence of these requirements, when considered in conjunction with the entropy inequality, is that the Gibbs free energies of the corresponding phases, or the chemical potentials of the corresponding components, will have to be equal at equilibrium. These equilibrium equalities of free energies of mass-exchanging phases is a derived result and not an *a priori* condition. It must be emphasized that whenever two phases do not exchange mass, such that a chemical constituent is present in one phase but not an adjacent one, the corresponding mass exchange rate terms are zero even when the total system is not at equilibrium. In that case, the corresponding differences between free energy or chemical potential functions actually do not appear in the entropy inequality since they multiply zeros. Therefore, no information will be obtained regarding the relative values of the chemical potentials or free energies of constituents in adjacent phases at equilibrium. For example, in a porous medium saturated with a single-constituent fluid phase where the fluid and the solid do not react, the free energy of the fluid phase at equilibrium will be determined by its temperature and pressure, and that of the solid will be determined by its temperature and state of strain; they will be independent of each other. However, if the single-constituent fluid and the solid do exchange mass across a massless interface (considered to be massless for convenience), a relation of equality must exist between the Gibbs free energies of the phases at equilibrium. However, the restriction that the fluid is a single constituent would imply that the system being considered is, for example, an ice and water system where the transfer between phases would not affect the chemical make-up of the fluid. In this instance, the term related to the mass exchange between the water phase, w, and solid or ice phase, s, in the residual entropy inequality will read:

$$-(G^{w} - G^{s})\hat{e}^{w}_{ws} \geq 0. \qquad (2)$$

With equilibrium defined as in equation (1a), the Gibbs free energies G^{w} and G^{s} must be equal at equilibrium. If one were to consider a three-phase system consisting of water, steam, and a solid phase corresponding results are also obtained. If the solid phase is ice, the entropy inequality will indicate that the Gibbs free energies of all phases will be equal at an equilibrium state where all three phases are present. If, on the other hand, the solid phase is a sand that does not exchange water with the fluid phases, the free energy of water and steam will be found to be equal at equilibrium; but the free energy of the sand will be independent of their values since mass exchange terms involving the solid phase will be zero at all conditions.

Similar results will be obtained for the mass exchange of constituents between phases of a multi-component, multiphase system. If a chemical constituent may be exchanged between two different phases, then at equilibrium, because of requirement (1c), the chemical potentials for this constituent in each of the phases can be shown to be equal.

The approach outlined above has been adopted in our recent work, such as Hassanizadeh and Gray [5] and Gray and Hassanizadeh [8]. In their own development, Achanta *et al.* [1] proposed an axiom they call Equipresence of Constituents. This axiom requires that in development of a constitutive theory for multiphase mixtures, each phase and each interface must contain the same list of constituents. This axiom is unnecessary and requires one to start with a condition that may be different from reality and consequently may lead to unrealistic results. For example, the equalities (122) in Achanta *et al.* [1] do not all hold for species that are not present in some phases and/or interfaces. The chemical potentials of such species will be independent of each other. Besides being aphysical, the proposed axiom is extraneous.

CONCLUSION

We are pleased that the framework of our efforts has been adopted by Achanta *et al.* [1] virtually without alteration. They have done an admirable job in managing the large number of equations that arise in derivations involving multiphase, multicomponent systems. The resulting constitutive equations they obtain seem to be correct. They have successfully derived appropriate relations for multicomponent systems and for a colloidal system. We are pleased that they have found our work to be a useful basis for their study of multiphase multicomponent systems and are also encouraged by the results they have obtained.

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