CLARIFYING MIXTURE THEORY AND THE MACROSCALE CHEMICAL POTENTIAL FOR POROUS MEDIA

LYNN SCHREYER BENNETHUM and JOHN H. CUSHMAN [†]

Center for Applied Mathematics, Purdue University, West Lafayette, IN 47907-1395, U.S.A.

MÁRCIO A. MURAD [‡]

Laboratório Nacional de Computação Científica, LNCC/CNPq, Rua Lauro Muller 455, 22290 Rio de Janeiro, Brazil

Abstract—Hybrid mixture theory (HMT) consists of classical mixture theory applied to a multiphase system with volume averaged field equations. HMT is applicable to a multiphase mixture in which the characteristic length of each phase is 'small' relative to the extent of the mixture. A porous body is the canonical model of a system to which HMT is applicable. When a phase contains N constituents, the linearized fluxes derived through HMT are historically expressed relative to the Nth constituent, e.g. Fick's law for the jth species is expressed in terms of a gradient of the jth chemical potential relative to the Nth. This is in contrast to classical Gibbsian thermodynamics, which gives rise to results of similar form, but with absolute (non-relative) driving forces. Here we modify HMT to construct results which are completely analogous to Gibbsian thermodynamics. This is accomplished by modifying the way the entropy inequality is exploited and by re-examining the definition of the averaged chemical potential of a constituent and the averaged Gibbs energy of a phase. Particular emphasis is placed on the relations between the scalar chemical potential of Gibbs and the tensorial chemical potential of Bowen. Previous HMT results gave rise to an averaged chemical potential that may experience a jump between the solid and fluid phases at equilibrium; a result in clear contrast to Gibbsian theories. This discontinuity in the potential is due to an 'effective' external field (e.g. the effective stress induced by a load in the solid phase). A notable consequence of the approach proposed herein is a HMT chemical potential in complete analogy with the Gibbsian chemical potential. Copyright ©1996 Elsevier Science Ltd

1. INTRODUCTION

In classical mixture theory a single phase medium composed of N constituents is viewed as N overlaying continua. Bowen [1–3] extended this idea to model a porous medium so that at the macroscale a two-phase medium is viewed as two overlaying continua. In his work, macroscale forms of the field equations (conservation of mass, momentum balance, and conservation of energy), which incorporate exchange terms between the overlaying continua, are postulated. Hassanizadeh and Gray [4–6] showed that if the microscale field equations are averaged then the terms in Bowen's macroscale field equations can be identified precisely with microscale counterparts. The combination of averaging and mixture theory is referred to as *hybrid mixture theory* (HMT). In both of these formulations, the constitutive restrictions are determined at the macroscale by exploiting the entropy inequality using the Coleman–Noll method [7].

Despite the growing use of HMT, we believe that the conventional treatment of obtaining constitutive restrictions which hold near equilibrium are not as concise as they could be. In particular, we are interested in deriving results about the chemical potential which are analogous to classical results. The classical Gibbsian chemical potential, μ_j, which is defined to be the derivative of the extensive Helmholtz energy with respect to the number of molecules of constituent j [8], has the following characteristics: (1) it is a scalar and measures the energy required to insert a particle into the system (see e.g. [9]); (2) its gradient is the driving force for diffusive flow (Fick's law) [8,10]; and (3) it is constant for a single constituent coexisting in two phases at equilibrium, i.e. for the solid, s,

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† Author to whom correspondence should be directed.
‡ Current address: Center for Applied Mathematics, Purdue University, West Lafayette, IN 47907-1395, U.S.A.