



Macroscale Thermodynamics and the Chemical Potential for Swelling Porous Media

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Abstract. The thermodynamical relations for a two-phase, N -constituent, swelling porous medium are derived using a hybridization of averaging and the mixture-theoretic approach of Bowen. Examples of such media include 2-1 lattice clays and lyophilic polymers. A novel, scalar definition for the macroscale chemical potential for porous media is introduced, and it is shown how the properties of this chemical potential can be derived by slightly expanding the usual Coleman and Noll approach for exploiting the entropy inequality to obtain near-equilibrium results. The relationship between this novel scalar chemical potential and the tensorial chemical potential of Bowen is discussed. The tensorial chemical potential may be discontinuous between the solid and fluid phases at equilibrium; a result in clear contrast to Gibbsian theories. It is shown that the macroscopic scalar chemical potential is completely analogous with the Gibbsian chemical potential. The relation between the two potentials is illustrated in three examples.

Key words: macroscale, chemical potential, mixture theory, porous media, swelling porous media.

Nomenclature

In general, a subscript Greek letter indicates a macroscale quantity from that phase. Superscript minuscules indicate the constituent, so that, e.g., \mathbf{v}_α^j is the macroscopic velocity of constituent j in the α -phase. A caret over the symbol, $\hat{}$, is used to emphasize that the quantity represents a transfer from either another phase or from other constituents.

A_α^j	Helmholtz free energy density of j th constituent in α -phase $A_\alpha^j = E_\alpha^j - T\eta_\alpha^j$.
b_α^j	external entropy source for j th constituent in α -phase.
C_α^j	mass concentration.
\mathbf{d}_α^j	symmetric part of $\nabla \mathbf{v}_\alpha^j$.
\hat{e}_α^j	rate of mass exchange from other phase to α -phase of j th constituent.
E_α^j	energy density.
\mathbf{E}_s	macroscale strain tensor of solid phase.
\hat{E}_α^j	energy gained by constituent j in phase α due to non-chemical, non-mechanical interactions with other constituents within phase α .
\mathbf{F}_s	deformation gradient, $\text{grad}x_s$, of the solid phase.