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Non-equilibrium thermodynamics for fully coupled thermal hydraulic mechanical chemical processes

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ABSTRACT

In this paper, a pioneering approach of reactive transport in porous media is introduced, which model thermal–hydraulic–mechanical–chemical processes. The novelties of this approach are: (i) non-equilibrium thermodynamics which is used as a unifying framework relating generalized fluxes to forces and (ii) fully coupled integration of the multi-physics processes, introduced within the framework of large transformations including logarithmic finite strain and co-rotational rates. This formulation opens the horizons for complex simulations which were difficult to conduct previously because of the lacking bridges between non-linear computational mechanics and reactive transport processes. As an illustration of the model, a sample of simple geometry is subjected to a non-linear deformation beyond the reversible regime. This perturbation from equilibrium produces a permanent deformation, an overpressure and a temperature change. The subsequent thermodynamic conditions trigger chemical reactions among the aqueous species which are not necessarily in equilibrium with their environment. The deformation also induces a change of porosity which affects the permeability as well as the pore pressure distribution.

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1. Introduction

Coupling of thermal–hydraulic–mechanical–chemical (THMC) processes in porous media is gaining momentum and attracting a considerable research interest. Several modern activities such as ore bodies' targeting, engineered geothermal systems (EGS), carbon dioxide capture and storage (CCS), unconventional oil and gas exploration, and radioactive waste management are direct applications of this research field. As these activities are vital for future economical development, advanced understanding of coupled multi-physics is becoming crucial. Yet, most of the existing THMC formulations that are now available are limited to equilibrium thermodynamics and/or to particular processes. Forcing equilibrium or time-independency simplifies multi-physics problems tremendously as the kinetic aspects are ignored and the fluxes become the only driving variables. In such context, minimizing stored energies and maximizing entropies dictate the evolutions of mixtures in poromaterials. Such approaches are attractive when dealing with steady state phenomena or infinite time processes. In practice, they fail in predicting real scenarios where the different processes have finite time and length scales (Regenauer-Lieb et al., 2010a,b).

In spite of the striking impact of THMC, the existing numerical tools allow only for decoupled or partially coupled solution methods for multi-physics problems. Several programs and committees such as the International Partnership for Geothermal Technology (IPGT), the Centre for Nuclear Waste Regulatory Analyses (CNWRA), the Predictive Mineral

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Discovery Cooperative Research Centre (pmd∗CRC) documented the necessity of introducing advanced THMC tools for future simulation (Ketilsson et al., 2011; Manepally et al., 2011; Sheldon, 2009). This urged researchers to come up with various combinations to address THMC coupling problems. Taron et al. (2009) proposed a combination where the thermal, hydraulic, and chemical (THC) processes are integrated by TOUGHREACT while the mechanical framework is solved using FLAC^{3D}. More recently, Poulet et al. (2011) proposed a similar combination where the THC processes are included in escriptRT and the rest is integrated using ABAQUS. Apart from the difficulties that each numerical tool has in addressing the basic physics of conservation of mass and energy, such combinations are limited to sequential integration and ignore key feedbacks which can be crucial for proper modeling of geological structures as shown by Regenauer-Lieb et al. (2006, 2008). In addition, the existing combinations of tools mostly rely on equilibrium thermodynamic and have to communicate with other numerical ramifications to minimize Gibbs free energy. This paper introduces a pioneering stand-alone framework which includes frame indifferent large transformations (Karrech et al., 2011a), coherent extension of the reciprocity effects (Onsager, 1931; de Groot and Mazur, 1984) to the context of poromechanics (Coussy, (2004, 2010)), and a scope broadening of the full THM coupling (Karrech et al., (2012)) to include additional feedbacks related to chemical reactive transport.

This paper is organized as follows: the first part addresses the principles of exchange of mass, energy, entropy and momenta between the different media. These principles result in the equations of continuity, conservation of energy, and motion as well as the Clausius–Duhem inequality in the context of THMC coupling. Based on the Clausius–Duhem inequality, different processes are identified which contribute to the creation of entropy within porous media. The second part uses the theories of convex analysis and subdifferential calculus (Moreau, 1966–1967; Rockafellar, 1970) as well as the principle of maximum dissipation (Ziegler, (1977); Martyushev and Seleznev, (2006)), to describe the relationships between dissipative thermodynamic forces and fluxes. Applying Schwartz' theorem to these flow rules delivers symmetric relationships which extend Onsager's (1931) reciprocity principle. At this level the reciprocity of chemical processes is extended to the more general case of thermal–hydraulic–chemical processes. As the dissipation function does not obey to the conditions of regularity of Schwartz' theorem, the flow rules for inelastic deformation are obtained uniquely using subdifferentials and Legendre–Fenchel transforms. Alternative approaches which consist in postulating a regular dissipation function could be examined as well (Karrech et al., 2011a; Regenauer-Lieb et al., 2010a). The third part of this paper summarizes the mathematical problem of multi-physics processes within the principles of non-equilibrium thermodynamics. At this level, the analysis shows, for instance, that the classical Dufour and Soret effects can be seen as particular cases of the current formulation. In the last part, a simple application study is used to illustrate the results of the formulation and examine some of its capabilities.

2. Energy, matter and entropy balance

2.1. Conservation of mass

Consider a system of $n+1$ species (crystals, water, and aqueous species) among which r reactions are possible. The assemblage of crystals forms a solid matrix while the union of the matrix, the pores and the interfaces of the different substances form the skeleton. The whole system as well as the fluid mixture (solvent and aqueous species) is treated as a continuum. For each species k, the rate of mass change can be expressed as follows:

$$\int_{\Omega}\left\{\frac{\partial \rho_k}{\partial t}+\boldsymbol{v}_k \cdot \nabla \rho_k+\rho_k \nabla \cdot \boldsymbol{v}_k\right\}d\Omega=\sum_{j=1}^{r}\int_{\Omega}\overset{\circ}{m}_{\to k@j}\,d\Omega \tag{1}$$

where ρ_k (kg m^{-3}) is the mass concentration (mass per total volume), $\boldsymbol{v}_k$ (m s^{-1}) is the velocity, and $\overset{\circ}{m}_{\to k@j}$ (kg m^{-3} s^{-1}) is the production rate of the species k through the jth reaction. The first term on the left hand side accounts for the variation of mass concentration as if the material volume was fixed, the second reflects the deformation, and the third represents the flux through the surface of the material volume. If no production of substances takes place, the accumulation of these three terms should be zero. Eq. (1) can be written in a local form as follows:

$$\frac{\partial \rho_k}{\partial t}+\nabla \cdot (\rho_k \boldsymbol{v}_k)=\overset{\circ}{m}_{\to k}=\sum_{j=1}^{r}\overset{\circ}{m}_{\to k@j}\quad \forall k=1..n \tag{2}$$

The right hand side term is the rate of production of k from the different reactions within the material volume. Note that the production rate of k by the reaction j is expressed as $\overset{\circ}{m}_{\to k@j}=\mathcal{M}_k v_{kj}\overset{\circ}{\xi}_j$, where $\mathcal{M}_k$ (kg mol^{-1}) is the molar mass of k, v_{kj} is the stoichiometric coefficient with which k appears in the reaction j, and $\overset{\circ}{\xi}_j$ (mol s^{-1}m^{-3}) is the rate of the reaction j. The conservation of mass in chemical reactions states that

$$\sum_{k=0}^{n}\mathcal{M}_k v_{kj}=0\quad \forall j=1..r \tag{3}$$

Eq. (2) is written in terms of mass concentration ρ_k of species k with respect to the porous material. This quantity can be related to the molar concentration by dividing it by the molar mass of the species k: $c_k=\rho_k/\mathcal{M}_k$, expressed in (mol m^{-3}).