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Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 4. Species transport fundamentals

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Abstract

This work is the fourth in a series of papers on the thermodynamically constrained averaging theory (TCAT) approach for modeling flow and transport phenomena in multiscale porous medium systems. The general TCAT framework and the mathematical foundation presented in previous works are built upon by formulating macroscale models for conservation of mass, momentum, and energy, and the balance of entropy for a species in a phase volume, interface, and common curve. In addition, classical irreversible thermodynamic relations for species in entities are averaged from the microscale to the macroscale. Finally, we comment on alternative approaches that can be used to connect species and entity conservation equations to a constrained system entropy inequality, which is a key component of the TCAT approach. The formulations detailed in this work can be built upon to develop models for species transport and reactions in a variety of multiphase systems.

Keywords: TCAT; Classical irreversible thermodynamics; Averaged thermodynamics; Species conservation equations; Model formulation

1. Introduction

This paper is the fourth in a series of efforts intended to yield complete, rigorous, closed models that describe transport phenomena in multiscale porous medium systems using the thermodynamically constrained averaging theory (TCAT) approach. The first paper [18] provides an overview of the general TCAT approach, which is built on averaged conservation and thermodynamic equations that constrain an entropy inequality. The second paper provides the mathematical fundamentals and theorems that are used to generate needed macroscale equations [25]. The third paper illustrates the application of the method for single-fluid-phase, single-species flow in a porous medium [19]. In the present work, we develop additional fundamental components of the theory to enable the subsequent building of rigorous, closed models for multispecies systems.

The composition of a phase is of central importance for modeling many porous medium systems. Example applications include saltwater intrusion; contaminant fate, transport, and remediation; irrigation and fertilization; aquifer storage and recovery of treated drinking water; and analysis of the effects of nuclear waste disposal. Models used to describe such systems are typically based upon the advective–dispersive equation, assuming a Fickian form of the dispersion process [11]. These models are typically posited directly at the macroscale and are not usually thermodynamically constrained. It is also commonplace for the variables that appear in such macroscale equations to lack precise definitions and connections to microscale quantities.

Of further significance is the general consensus that heterogeneity at the macroscale, typical of most natural systems, leads to the limited usefulness of the advective–dispersive equation for many problems of interest (e.g.

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Nomenclature

Roman letters

b	entropy source density
$\mathbf{C}$	Greens' deformation tensor
$\mathbf{d}$	rate of strain tensor
E	internal energy density
E_{T}	total energy density
$\mathcal{E}$	the set of entities
$\mathcal{E}_{\mathrm{C}}$	the set of common curve entities
$\mathcal{E}_{\mathrm{I}}$	the set of interface entities
$\mathcal{E}_{\mathrm{P}}$	the set of phase volume entities
$\mathcal{E}_{\mathrm{Pt}}$	the set of common point entities
$\mathscr{E}$	conservation of energy equation
$\mathbb{E}$	internal energy
$\mathcal{E}_{\mathrm{c}}$	connected set of entities
$\mathbf{e}$	unit vector tangent to a common curve and oriented positive outward
$e_{i\iota}$	microscale intra-entity internal energy transfer rate from all other species in entity ι to the i species per unit measure of the ι entity
$e_{\mathrm{T}i\iota}$	total microscale energy transferred intra-entity from all other species in entity ι to the i species per unit measure of the ι entity
$e_{\mathrm{T}}^{i\iota}$	total microscale energy transferred intra-entity from all other species in entity ι to the i species per unit measure of the ι entity
F	thermodynamic functional to be minimized
f	general variable
$\mathbf{f}$	general vector variable
$\mathbf{f}'$	general microscale vector tangent to an interface
$\mathbf{f}''$	general microscale vector tangent to a common curve
$\mathbf{g}$	acceleration vector due to an external force, such as gravity
h	heat source density
$\mathbf{I}$	identity tensor
$\mathbf{I}'$	surface identity tensor
$\mathcal{J}$	index set of entities
$\mathcal{J}_{\mathrm{C}}$	index set of common curve entities
$\mathcal{J}_{\mathrm{Cs}}$	index set of common curve entities that include an intersection with the solid phase volume
$\mathcal{J}_{\mathrm{C/s}}$	index set of common curve entities that do not include an intersection with the solid phase volume
$\mathcal{J}_{\mathrm{c}}$	index set of connected entities
$\mathcal{J}_{\mathrm{f}}$	index set of fluid-phase volumes
$\mathcal{J}_{\mathrm{I}}$	index set of interface entities
$\mathcal{J}_{\mathrm{Is}}$	index set of interface entities that include an intersection with the solid phase volume
$\mathcal{J}_{\mathrm{I/s}}$	index set of interface entities that do not include an intersection with the solid phase volume
$\mathcal{J}_{\mathrm{P}}$	index set of phase volume entities
$\mathcal{J}_{\mathrm{Pt}}$	index set of common point entities

$\mathcal{J}_{\mathrm{Pt}\iota}$	index set of all microscale points in the REV that describes Ω_ι
$\mathcal{J}_{\mathrm{Pts}}$	index set of common point entities that include an intersection with the solid phase volume entity
$\mathcal{J}_{\mathrm{Pt/s}}$	index set of common point entities that do not include and intersection the solid phase volume entity
$\mathcal{J}_{\mathrm{s}}$	index set of species
$\mathcal{J}_{\mathrm{s}\iota}$	index set of species in entity ι
j_{s}	solid-phase Jacobian
K_E	macroscale kinetic energy per unit mass due to microscale velocity fluctuations
$\mathbb{M}$	mass
M	variational constant subject to mass conservation constraint
$\mathcal{M}$	conservation of mass equation
$\overset{i\kappa\to i\iota}{M}$	transfer of mass of species i in the κ entity to the i species in the ι entity per unit volume per unit time
$\overset{i\kappa\to i\iota}{M_{E_i}}$	transfer of energy from the κ entity to the ι entity due to inter-entity mass transfer of species i per unit volume per unit time
$\overset{i\kappa\to i\iota}{\mathbf{M}_{v_i}}$	transfer of momentum from the κ entity to the ι entity due to inter-entity mass transfer of species i per unit volume per unit time
$\overset{i\kappa\to i\iota}{M_{\eta_i}}$	transfer of entropy from the κ entity to the ι entity due to inter-entity mass transfer of species i per unit volume per unit time
$\mathbf{n}_\iota$	outward unit normal vector from entity ι
$\mathcal{P}$	conservation of momentum equation
$\mathscr{P}_i$	general microscale property
p	fluid pressure
$\mathbf{p}_{i\iota}$	microscale intra-entity momentum transfer rate from all other species in entity ι to the i species per unit measure of the entity
$\mathbf{p}^{\overline{\overline{i\iota}}}$	macroscale intra-entity momentum transfer rate from all other species in entity ι to the i species per unit measure of the entity
$\overset{j\kappa\to i\iota}{Q}$	transfer of energy from species in the κ entity to the i species in the ι entity resulting from heat transfer and deviation from mean processes per unit volume per unit time
$\mathbf{q}$	non-advective heat flux density vector
$r_{i\iota}$	microscale intra-entity reaction rate resulting in the production of species i in entity ι from all other species per unit measure of the entity
$r^{i\iota}$	macroscale intra-entity reaction rate resulting in the production of species i in entity ι from all other species per unit measure of the entity
$\mathcal{S}$	entropy balance equation
$\mathbb{S}$	entropy
$\mathscr{S}$	set of all species