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Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 1. Motivation and overview

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Abstract

We give several examples of weaknesses in classical, empirically derived models of transport phenomena in porous medium systems. We also place recent attempts to develop improved multiscale porous medium models using averaging theory in context and note deficiencies in these approaches. These deficiencies are found to arise in part from the manner in which thermodynamics is introduced into a constrained entropy inequality, which is used to guide the formation of closed models. Because of this, we briefly examine several established thermodynamic approaches and outline a framework to develop macroscale models that retain consistency with microscale physics and thermodynamics. This framework will be detailed and applied in future papers in this series.

Keywords: Porous media; Modeling; Thermodynamics; Averaging theory

1. Introduction

The study of hydrologic systems is considered mature by some [69]. Models of porous medium systems are applied routinely in practice and for a wide range of applications. Many classical models have been reduced to textbook form and routinely appear, seemingly as matter-of-fact statements of the physics of transport phenomena in porous medium systems [3,43]. This is not only the case for single-fluid-phase flow under low Reynolds number conditions, but is also increasingly a common occurrence for multiple-fluid-phase flow, species transport and reaction, and energy transport [15,65,80]. One could argue that hydrologic analyses have led to classical models, deemed to be definitive; and simulators based upon these models exist for the corresponding applications.

Classical models have become so established that concerted efforts are undertaken routinely to account for parameter uncertainty [49] and to produce stochastic solutions of low-order moments to these models [17,25,32,79]. While originally focused on single-fluid-phase flow, stochastic approaches are increasingly being extended to solute-transport and reactions, and to multiple-fluid-phase systems [1,18,24,81]. To be sure, natural systems are indeed stochastic in nature, and meaningful analysis of natural systems will benefit from stochastic approaches for the foreseeable future. However, the foundation of such stochastic analyses is the accuracy of the underlying mathematical description of the physical processes in the problem of concern.

An alternative viewpoint is that the study of hydrologic systems is far from mature [62]. Specifically,

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Nomenclature

Roman letters

$\mathscr{E}$	conservation of energy equation
$\mathbb{E}$	internal energy
E	internal energy per unit volume
$\mathbf{I}$	internal variable vector
$\mathbf{J}$	flux vector
M	mass
$\mathscr{M}$	conservation of mass equation
N	number of chemical species
$\mathscr{P}$	conservation of momentum equations
p	fluid pressure
$\mathbb{S}$	entropy
$\mathscr{S}$	entropy equation
t	time
V	volume
$\mathbf{X}$	vector of independent variables
$\mathbf{x}$	position vector

Greek letters

ϵ^{α}	volume fraction of the α phase
η	entropy per unit volume
θ	temperature
Λ	entropy production rate
λ	Lagrange multiplier
$\boldsymbol{\lambda}$	vector of Lagrange multipliers
μ	chemical potential
ρ	mass density
ω	mass fraction

Subscripts and superscripts

$\mathscr{E}$	energy equation qualifier
i	species qualifier
$\mathscr{M}$	mass equation qualifier
$\mathscr{P}$	momentum equation qualifier
t	temporal derivative qualifier for Lagrange multipliers
w	wetting phase qualifier
$\mathbf{x}$	spatial derivative qualifier for Lagrange multipliers
α	entity qualifier

Acronyms

CIT	classical irreversible thermodynamics
EI	entropy inequality
EIT	extended irreversible thermodynamics
ET	equilibrium thermodynamics
RET	rational extended thermodynamics
REV	representative elementary volume
RT	rational thermodynamics
TCAT	thermodynamically constrained averaging theory
TIV	theory of internal variables

classical models of porous medium systems need further extension and revision to reach ultimate, or even functional, utility and may contain significant representational errors in some cases. Even for cases where the numerical solution is precise and the parameters are specified, model errors may result for two fundamental reasons: (1) the representation of the physics is inadequate, or (2) the parameters that appear in the model are not clearly defined and easily measurable. We believe both of these types of errors routinely occur in the modeling of porous medium systems.

Deficiencies in porous medium models have been noted in the past, and sustained efforts have been undertaken to develop a sound theoretical base upon which a rigorous set of new models can be constructed [36,42,44,53,58,70,74,76]. While significant progress has been made, the conceptual and mathematical difficulties associated with these formulations and technical issues with model closures have slowed the maturation into simulators, deployment, and verification of a new generation of well-defined models. However, the evolution of theoretical tools, mathematical machinery, and recent conceptual insights have, in principle, removed barriers to progress. We believe that substantive advances beyond the formulations in classical models are now possible.

The overall goal of this manuscript is to introduce a systematic framework for producing macroscale models of transport phenomena in porous medium systems that are consistent with microscale, or pore scale, representations of transport phenomena and thermodynamic constraints. The specific objectives are to:

- note examples of weaknesses in both classical models and previous averaging based approaches to modeling porous medium systems;
- highlight the critical role of thermodynamics and detail available theories that may be of use in porous medium model formulation;
- detail a consistent and flexible framework to guide the formulation of models to describe transport phenomena in porous medium systems;
- illustrate how the new framework can be used to derive thermodynamically consistent models; and
- comment on some open issues remaining with the current theoretical work and some potentially fruitful future endeavors.

Although the emphasis here is on porous media, the framework applies to any development of larger scale equations based on physical and thermodynamic processes. Subsequent efforts in the present series of papers will detail the mathematical machinery required, provide details on applications of the framework presented herein to a range of porous medium systems, and compare and contrast a set of new models with classical models.

2. Background

The purposes of this section are (1) to give examples of deficiencies in classical models of porous medium systems; (2) to place the last three decades of work on the development of averaging methods to describe transport phenomena in porous media in context and highlight the open issues; (3) to note the critical role of thermodynamics in constraining models to describe transport phenomena in porous media; and (4) to evaluate available classes of thermodynamic theories that may be used.

2.1. Deficiencies with classical models

Classical approaches to modeling transport phenomena in porous media e.g., [10,29,30,77] have become so common that we run the risk of overlooking their deficiencies, inconsistencies, and potential errors. The formulation of the classical model for single-fluid-phase flow includes writing a conservation of mass equation for the fluid phase; employing an equation of state relating the fluid pressure, temperature, composition, and density; imposing a linear compressibility model for the solid phase related to fluid pressure; and invoking Darcy's law to relate the specific discharge vector to the gradient in pressure and gravitational forces. For multiphase flow, a similar approach is taken with the exceptions that equations are written for each fluid phase; fluid saturations are related to the fluid pressures using empirical, hysteretic relations involving equilibrium states and neglecting transient behavior; and an extended version of Darcy's law is used, which typically includes relative permeabilties that are nonlinear and hysteretic functions of fluid saturations e.g., [61]. The single phase approach has its roots in the empirical observations of Darcy [26,27] in regard to one-dimensional flow in a column packed with homogeneous sand. The multiphase approach is an attempt to retain the simple structure of the Darcian equation even in more complex systems while accounting for the physics of interfaces between phases by allowing model parameters to take on values that depend on system state variables and history.

The situation for species transport is similar. Conservation of mass equations are written typically for each chemical species in each phase; dispersion is accounted for using either a classical Fickian model or a representation of the effect of sub-scale velocity variations; closure relations are used to express species reactions and exchange of mass between phases; and the phase velocities are calculated from Darcy equations. Increasingly, the focus is on complex sets of biogeochemical processes and multiple species systems, which require sets of species transport equations [9,78].

For most classical flow and transport models, conservation of energy is omitted by virtue of isothermal conditions; and constraints implied by the second law of thermodynamics are almost universally neglected. The classical approach to modeling transport phenomena in porous medium systems leads to several problems. These include: lack of a rigorous connection with pore scale physics; inadequate definition of variables; implicit approximations concerning system behavior; and lack of a structured framework for model refinement, extension, and simplification.

Common notions such as temperature and pressure, and even more complex concepts such as capillary pressure and fluid wettability, are well understood at the pore scale, also called the microscale. However, a rigorous connection of these quantities, and pore-scale physics in general, to the macroscale, or porous medium continuum scale, at which classical porous medium models are formulated is lacking. For example, if the microscale pressure is not constant within a macroscale region under conditions of no flow, the selection of a representative macroscale pressure that describes the thermodynamic state of that region is not obvious. Also, it is unclear as to which property's gradient is balanced by gravitational effects [41].

The absence of cross-scale consistency is a result of formulation approaches that by-pass the microscale and instead propose conservation equations and closure relations directly at the macroscale. When microscale physics is not a part of the macroscale formulation procedure, correspondence of physical descriptions between scales is not attained. A consequence of this circumstance is that macroscale closure relations must be invented directly at the macroscale to account for phenomena that are, in some cases, well-understood at the microscale. An example of this situation is fluid wettability as measured by the contact angle between fluid interfaces and the solid phase at the pore scale. Wettability is well known to affect dramatically behavior of multiphase flow at the macroscale, but does not appear in classical models of flow at that scale.

The lack of a rigorous connection between the microscale and the macroscale thus has two serious consequences. First, although macroscale equations are written in terms of nominal macroscale quantities, these quantities are ill-defined or defined too vaguely to guide measurements designed to confirm macroscale descriptions of the system physics. Second, processes observable and studied at the microscale that are known to influence system behavior are neglected explicitly at the macroscale, perhaps in the interest of model simplicity, with their effects buried in highly-variable, non-unique coefficients. For macroscale models to develop to the point where the influence of scale is apparent and subject to both simulation and experimental study and verification, precise definitions of model variables is required. By careful analysis, the macroscale variables appearing in currently employed classical models can be shown to relate to a variety of averages of microscale quantities. Some are spatial averages, some mass weighted averages, and still others can be shown to be averages obtained using other weighting functions. Other macroscale variables can be shown to be truncated approximations to averages of microscale quantities.

Standard modeling approaches include implicit approximations that result from the closure relations used to produce solvable systems. While such approaches may provide useful models for some cases, the implicit nature of the assumptions causes difficulty in assessing model errors and proposing corrective actions to reduce those errors. Examples of this situation occur in assessing when deviations from Darcy's law for single-fluid-phase flow lead to significant errors and in determining alternative closure approximations superior to Darcy's law [53]. More generally, the classical approach of using a modified form of Darcy's law instead of a formal conservation of momentum equation for multiphase flow obscures potentially important physical phenomena—such as viscous coupling between different fluids and the transient nature of relations among fluid pressures, saturations, and entrapment—which are increasingly being understood as important in some cases [4,68].

Even if one understands a classical model to be deficient, the usual approach of formulating models in conjunction with a common set of *ad hoc* closures directly at the macroscale does not provide a rigorous means to examine modeling assumptions or suggest any directions of inquiry that could lead to more accurate models. Ideally, a consistent and comprehensive theory would exist to guide model formulation and simplification which would allow for natural, well-specified approaches to both model simplification and extensions. Such a theory does not currently exist. The absence of a strong theoretical foundation for current models certainly limits options and paths for improvement. Such a limited situation is at odds with any claim of maturity of the field.

2.2. Averaging theory

Some researchers have attempted to develop a rigorous framework for formulating macroscale models that are consistent with smaller-scale representations of transport phenomena [6,11,12,23,38,44–46,50,63,76]. We use the term "averaging theory" to denote efforts based upon procedures that are designed to produce systematically macroscale quantities expressed as integral expressions involving microscale quantities and that yield and close conservations equations at the macroscale. The motivation behind such approaches is the achievement of a correspondence between well-described microscale physics and the model formulation and closure of less-well-described macroscale physics. Success in these efforts will overcome, at least, some of the deficiencies of classical models.

A number of the components of models based on averaging theory have been examined with varying degrees of rigor in an effort to arrive at a closed, consistent set of macroscale equations. We will indicate these components here, albeit briefly.

2.2.1. REV notions

One of the most useful conceptualizations that has permeated the development of a macroscale view of porous medium systems is the idea of a Representative Elementary Volume, or REV [7]. This concept is very similar to the microscale approach whereby a system is viewed as a continuum with each "point" deriving its properties from the large collection of molecules associated with that point. In fact, the point is a very small region in time and space. The number of molecules within the region is considered to be so large that variations in a property, such as mass density, are negligible for small changes in the size and duration of measurement of the sampling device. In essence, the objective in making this definition is to identify measurement regions such that the value of a quantity measured can be meaningfully reported without having to stipulate the size of the sample examined.

The REV, as applied to a macroscopic formulation, makes use of a representative region of a porous medium, large enough to include all phases present. The region is assumed to be of sufficient size that the values of averages that characterize a phase are independent of that size. Further, the size of the REV is considered to have a characteristic length scale that is much smaller than the system length scale such that gradients of macroscale quantities within the system are meaningful. However, since this REV includes multiple phases, interfaces, common curves, and common points, geometric densities must also be defined that stipulate, for example, the fraction of the REV occupied by a particular phase or the amount of interfacial area between two phases that exists within the volume. In practical terms, the transition from the microscale to a macroscale point eliminates distributions of function values within a phase in favor of average values of those distributions over a portion of that phase. For example, the velocity distribution of a phase within the pores is replaced in favor of an average volumetric flow over a cross-sectional area. Certainly, this macroscale velocity is conceptually easier to compute, especially in light of the fact that the actual distribution of the pore space is typically unknown. However, in practice, this simplicity is countered by the need to deal with the geometric densities and the need to obtain closure relations in terms of the macroscale variables.

The REV approach is sometimes criticized because it is invoked without proving the existence of the REV for the system under study and without determining that the REV employed is appropriate for all quantities being studied. In some instances when a porous medium exhibits fractal behavior, or when larger scale heterogeneities preclude the identification of an REV, approaches that depend upon a set of discrete and separable length scales fail [23]. Thus, the common assumption of the existence of discrete, separable length scales is a key premise which affects the applicability of models developed. However, even in cases when an REV does not exist, explicit definition of macroscale variables in terms of microscale quantities can be retained, allowing for the development of larger scale variables whose dependence on the size of the averaging volume employed can be investigated.

2.2.2. Averaging theorems

Important tools for the transformation of the conservation equations from the microscale to the macroscale are averaging theorems [2,5,39,71,75]. These equations convert averages of derivatives of microscale quantities into derivatives of macroscale averages. These equations are similar in form and utility to the well-known transport and divergence theorems that facilitate the interchange of the order of integration and differentiation of a function. The forms of the averaging theorems developed in the 1960s [2,70,75] are useful for dealing with phases that occupy portions of three-dimensional space. These theorems involve the transformation of the integral of a derivative of a function over a phase within an REV to a derivative of an integral of the function over the phase plus an integral of the function over the interface between the phase and the other phases within the averaging volume.

Recognition of the fact that it was not possible to account rigorously for capillary pressure without examining the physics of the interface between fluids led to the derivation of averaging theorems for surfaces and, additionally, for common curves [36,40]. These theorems, besides being useful for deriving macroscale surface and common curve conservation equations from their microscale counterparts, also suggest appropriate definitions of some macroscale properties in terms of their microscale antecedents.

2.2.3. Alternative approaches

The most common approach to conversion of the microscale conservation equations to the macroscale is integration of the mass, momentum, and energy equations over an REV. However, an alternative, that has some conceptual attractions, is to use a localization approach [38]. Conservation equations for an entity within the system are written in terms of microscale variables integrated over the entire domain. The averaging approach involves first obtaining point microscale equations by shrinking the domain to a microscopic point and then averaging the resulting microscale equations up to the macroscale. A localization approach may be used to obtain macroscale equations directly by shrinking the domain of scrutiny to a macroscale volume. Then application of localization theorems, which are simply alternate forms of averaging theorems, provides the macroscale equations. Certainly, these two different approaches lead to the same macroscale conservation equations, as they must, but the mathematical and conceptual steps to those equations are different.

We note, also, that averaging over small regions of time may also be included in the approaches to obtaining macroscale equations. However, since time is continuous and the entities each occupy all of time within an increment of time studied, averaging over time only alters the interpretation of macroscale quantities but not the form of the macroscale equations.

In addition to averaging over macroscale regions, some investigators have employed weighting functions intended to account for the sampling characteristics of measurement instruments [2,22,66]. Also, theorems have been proposed that allow for the averaging volumes to vary in size and shape with position and time [21,33]. Further, the fact that the averaging volume at a point may be different for different quantities has been considered [22]. However, in practice, none of these more complex formulations has been employed in model applications.

2.2.4. Multiple-scale approaches

The philosophy behind the development of macroscale equations opens the door to a range of conceptualizations of porous medium systems. For example, if the porous medium is fractured, fluid in the fractures can be considered to be a different phase from the fluid in the small pores. Then the averaging approach leads to separate conservation equations for the fluids in the pores and in the fractures. Closure relations are needed to describe the transfer of fluid between these two regions, but the different dynamics in the two scales of pore sizes are accounted for separately.

It has been pointed out previously that the microscale approach makes use of a set of equations formulated at a scale smaller than the pore diameter in a porous medium. These equations may be averaged up to the macroscale.

These macroscale equations can be averaged up again to an even larger scale, if desired. Indeed a hierarchy of length scales can be considered to account for large scale heterogeneities and inclusions [67]. To formulate equations at a large scale, one may simply develop the equations directly from the microscale or else formulate intermediate scale equations that are sequentially obtained from a smaller scale. Ideally, the equations obtained at the large scale using these two different approaches will be identical. However, this identity depends on the closure relations being identical. In fact, closure relations are only approximations to material behavior. In some instances this behavior can be best approximated by averaging closure relations up from a smaller scale rather than simply hypothesizing the relations at the large scale. Averaging of closure relations can be employed in conjunction with numerical simulation when the system is of a simple structure. It is also employed typically without considering the impact of thermodynamics and without careful successive change in scale of the thermodynamic functions. Direct hypothesis of closure relations at the largest scale considered is attractive in that errors made in smaller scale closure forms are not carried to the large scale.

2.2.5. Constrained closure relations

The averaged equations contain quantities, such as the stress tensor, the frictional interaction between phases, and the heat conduction vector, that must be approximated by constitutive relations. Although some researchers develop closure relations based on expected system behavior or through mapping between scales [76], another approach is to propose closure relations consistent with the second law of thermodynamics [13,37,38,46]. One particularly challenging part of the latter approach is formulating the second law constraint at a scale consistent with the scale of the governing conservation equations. In practice, this aspect of the problem has received little attention. Although an entropy inequality has been obtained from averaging, the determination of the functional dependence of macroscale entropy on macroscale properties has not been developed in a manner that ensures consistency with microscale thermodynamics. It is possible to provide the formulation of the thermodynamics in a general form that allows for either averaging of microscale thermodynamics or direct thermodynamic postulation at the macroscale; the averaging approach is more conceptually satisfying [35] but has not been used to develop complete porous medium models.

2.2.6. Conservation about areas, common curves, and common points

This subsection points out one of the most important developments in efforts to model flow in porous medium systems at the macroscale. In fact, the issue of conservation equations for entities other than phases does not arise when modeling a single fluid in the absence of a porous medium because there are no interfaces, common curves, or common points. The roots of formulations to model porous medium systems lie in the Darcy experiments that are concerned with the movement of a single fluid phase in packed column. Thus extension of the experimental results to systems that contain surfaces between fluid phases, common curves where three phases come together, and common points where four phases meet involves adventuresome speculation. The properties of the interfaces and the distributions of the fluid phases within the pore space are important features that impact the system dynamics such that models based on specification of phase properties only are insufficient. Rigorous modeling of the dynamics of transition regions between phases requires that the physics of capillary pressure sustained across interfaces and the spreading pressure at common lines be incorporated into the equation set. Additionally, the evolution of the interface between phases is an important factor in system dynamics. Therefore, the inclusion of the conservation equations for mass, momentum, and energy of interfaces, common curves, and common points provides the opportunity to develop a complete system model [38,42]. Even if some aspects of this complete model are subsequently deemed to be too complex to include in a particular application or are thought to have insignificant impact on the behavior of a study system, the assumptions made to arrive at a reduced equation set will be explicit and provide opportunities to evaluate the important features of the full model.

2.2.7. Consistent thermodynamics and additional approximate equations for closure

The change of scale of the conservation equations from the microscale to the macroscale can be accomplished by direct application of averaging theorems. This transformation is unique after one decides on the phases, species, interfaces, common curves, and common points that will be modeled. However, closure of the equations requires constitutive forms; and their development continues to be a most difficult challenge. The closure has two elements. First, equations of evolution of the geometric densities, such as volume fractions and interfacial area densities, must be formed. These densities are not subject to conservation equations but, instead, must be considered from just a mathematical perspective. For example, a volume changes in response to the extent of the movement of its boundary; the extent of an area changes due to deformation of the surface as well as from changes in the location of the bounding curve of the area. We emphasize that unique relations do not exist among geometric densities in a system. What we need, however, are equations that indicate how these densities evolve from one configuration to the next. Equations that describe these evolutions are not, generally, available [60]. However, some approximate relations have been developed and can be employed in system models [34,42]. Then, if better geometric evolution relations are found, these can be used as replacements.

The second ingredient of a successful approach to closure is the proper formulation of the system thermodynamics at the macroscale. Classical thermodynamics relates to the study of systems at equilibrium. Since we are dealing with dynamic processes, we are forced to deal with an extension of thermodynamics to systems that vary in time and space. At the microscale, a number of approaches to extend thermodynamics have been employed [51,59]. At the macroscale, the use of thermodynamics has been limited to forms postulated at that scale. Although postulation of macroscale thermodynamic dependences leads to closed equations through some elegant mathematics, at least two problems exist with this approach. First, the physical interpretation and procedures for measurement of the quantities in the equations are not clear. Second, these REV scale thermodynamics may not be consistent with the postulates and relations of classical thermodynamics developed at a smaller scale. If, instead, a macroscale thermodynamic approach is based on averaging of microscale thermodynamic equations, macroscale quantities are uniquely defined in terms of microscale counterparts and can be related to physical experiments across scales. Furthermore, consistency of the thermodynamic framework between scales will be assured. While preliminary work has been done that introduces these notions [35], complete models based upon this approach have yet to be formulated. Ideally, a rigorous framework to guide the formulation of a wide range of models based upon these concepts can be developed.

2.2.8. *Elements of a complete, consistent theory*

The information in the preceding subsections can be melded to develop a complete and consistent theory for flow and transport in porous media. The development of the theory requires mathematical tools that allow the equations and the thermodynamics to be formulated consistently and in such a way that the variables have physical, measurable meaning. The modeler still has the somewhat daunting task of deciding whether elements such as films, fracture flow, common curve physics, number of chemical constituents, etc. should be included in the model. Once the elements to be included are selected, then the governing equations and thermodynamics can be formulated. The mathematical, experimental, and computational effort needed to advance such a consistent set of rigorous models is certainly significant; and many open scientific issues must be resolved. Nevertheless, an approach ensuring consistency across scales and physically meaningful variables provides a robust foundation for the development of mature models.

2.3. *Thermodynamics*

Several theoretical approaches to the general field of thermodynamics exist, including the following: equilibrium thermodynamics (ET), classical irreversible thermodynamics (CIT), rational thermodynamics (RT), extended irreversible thermodynamics (EIT), rational extended thermodynamics (RET), and the theory of internal variables (TIV). Because thermodynamics plays a central role in the formation of thermodynamically constrained averaging theory models of concern in this work, it is worthwhile to consider briefly these various classes of thermodynamics. As will be discussed, several of these classes may be used to formulate consistent models that describe transport phenomena in porous medium systems. Some of these approaches have been used to produce unclear and ambiguous models. This discussion will serve as a foundation to support our further exposition on topics for which thermodynamics plays a central role. Table 1 presents a summary of various classes of thermodynamic approaches that are described, in turn, in the sections that follow. The intent of this table is to provide general notions for the theories listed. For simplicity, the general functional form indicated is restricted to a single-species phase entity occupying a volume. More complete discussions may be found in the indicated references for each approach. Some of these theories can be extended to other types of entities (interfaces, common curves, and common points) and such extensions are needed for rigorous

Table 1
Thermodynamic approaches

Abbreviation	Description	Functional form	Reference
ET	Equilibrium thermodynamics	$\mathbb{E} = \mathbb{E}(\mathbb{S}, V, M)$, for Ω	[8,16]
CIT	Classical irreversible thermodynamics	$E(\mathbf{x},t) = E[\eta(\mathbf{x},t), \rho(\mathbf{x},t)]$	[28]
RT	Rational thermodynamics	$E(\mathbf{x},t) = E[\eta(\mathbf{x},t), \rho(\mathbf{x},t), \ldots]$	[19,31,64,72]
EIT	Extended irreversible thermodynamics	$E(\mathbf{x},t) = E[\eta(\mathbf{x},t), \rho(\mathbf{x},t), \mathbf{J}]$	[51,52,55]
RET	Rational extended thermodynamics	$E(\mathbf{x},t) = E[\eta(\mathbf{x},t), \rho(\mathbf{x},t), \mathbf{J}, \ldots]$	[51,59]
TIV	Theory of internal variables	$E(\mathbf{x},t) = E[\eta(\mathbf{x},t), \rho(\mathbf{x},t), \mathbf{I}]$	[56,59]

models of multiphase porous medium systems. Enlightening discussions of the theories can be found in the literature (e.g., [51] and [59]).

2.3.1. Equilibrium thermodynamics (ET)

In developing ET, Gibbs' purpose was to cultivate a methodology by which equilibrium properties of thermodynamic systems can be characterized [54]. Absolute temperature and entropy are assumed to be defined and to exist. Critical to ET, applied to homogeneous volume phases, is the fundamental relation, typically [8,16]

$$\mathbb{S} = \mathbb{S}(\mathbb{E}, V, M) \tag{1}$$

or its inverted form

$$\mathbb{E} = \mathbb{E}(\mathbb{S}, V, M) \tag{2}$$

where $\mathbb{S}$ is the entropy of the system, $\mathbb{E}$ is the internal energy, V is the volume, and M is the mass. All of the above are extensive variables considered to be constant throughout the system, which is at equilibrium. Legendre transforms allow for the interchanging of extensive variables with intensive variables such as temperature, θ, pressure, p, and chemical potential, μ. While Gibbs' classic approach is extremely useful, it is limited in that it applies strictly only to homogeneous equilibrium situations. It provides information about differences between equilibrium states, but it provides no information about the rate of change from one state to another and no information about the system properties while the change is occurring.

2.3.2. Classical irreversible thermodynamics (CIT)

CIT is an extension of equilibrium thermodynamics generalized for application to irreversible processes. This approach has been expounded upon with insight and rigor by De Groot and Mazur [28] and provides for extension of the Gibbsian formulation to near-equilibrium dynamic systems. The fundamental functional dependence of the internal energy is postulated exactly as in equilibrium thermodynamics. However, critical to CIT, and the quality that distinguishes it from ET, is the local equilibrium hypothesis.

This hypothesis states that the local and instantaneous relations between the thermal and mechanical properties of a physical system are the same as for a uniform system at equilibrium. Essentially, to satisfy this hypothesis, a system is broken up into subsystems small enough that the ET formulation may be considered valid within any particular subsystem at any instant of time. The local equilibrium hypothesis has two important implications. First, all of the variables defined in the ET formulation remain significant and well-defined. Second, equilibrium relationships between thermodynamic state variables remain valid outside equilibrium provided they are stated locally at each instant in time. The ET postulate of Eq. (2) is made to apply at a microscale point by expressing the extensive variables on a per unit mass basis or, as in Table 1, per unit volume.

Subsequently, the assumption is made that the rate of entropy production for each subsystem is non-negative, which facilitates the derivation of relationships between driving forces, such as temperature differences between subsystems and fluxes. In the development of these relations using CIT, the system under consideration is assumed to have no memory. Therefore the flux at a particular instant depends only on the driving forces at that instant. Furthermore, the relationship between the fluxes and the driving forces is taken to be linear [16].

The CIT approach has been used with great success for the situation where each subsystem is a microscale point. However, after averaging to the macroscale, the direct application of the procedure, especially the preservation of the energy functional form on macroscopic variables, is suspect. The local equilibrium hypothesis in terms of macroscale variables can break down in the presence of gradients within the averaging region, and the definitions of temperature, pressure, and potential are not obvious.

2.3.3. Rational thermodynamics (RT)

Rational thermodynamics is another class of microscale thermodynamic approaches. Initially developed by Coleman [19], Eringen [31], Noll [64], Truesdell [72], this approach has proven to be a useful component of methods for deriving constitutive equations [51]. The method is mathematically rigorous and is built on principles that lead to certain mathematical forms for the energy and constitutive functions [31]. Although the principles have some mathematical appeal, Maugin [59] has pointed out that they are actually only working hypotheses while Vavruch [73] claims they are more accurately called useful rules. These rules include the following:

- equipresence—if an independent variable is present in one of the constitutive equations, it will, a priori, be present in all; and
- memory—present effects are dictated by the past as well as the present values of the independent variables.

Operationally, equipresence dictates that each dependent variable will be a function of all of the system's independent variables, except when the presence of the variable contradicts some law of physics or material symmetry. It leads to a postulated form of functional dependence of internal energy that is far more complex than the ET form and seemingly unrelated. Memory further requires that the dependent variables be functions of both past and present values of the independent variables.

In the case of flow in porous media, these two hypotheses impose some generality that is seemingly needlessly complicated. A somewhat simplified approximation that relieves some of the mathematical tedium has been put forth [48]. Maugin [59] also states that RT assumes notions that are precisely defined in ET to exist in any dynamic state. In RT, absolute temperature and entropy are considered primitive concepts and are believed to hold far from equilibrium; but they have no precise physical interpretation or physical relation to their ET counterparts. Materials are allowed to have a memory, and the concept of local equilibrium is not necessarily enforced.

RT is the thermodynamic approach most widely used in considering macroscale porous medium systems [14,37,46]. The problem of lack of correspondence between microscale entropy and temperature between ET and RT is compounded when the RT hypotheses are made at the macroscale such that this approach can be physically unsatisfying. For example, the use of derivatives of energy with respect to saturation as the definition of capillary pressure e.g. as reviewed in [47] and the appearance of three different mathematical definitions of pressure [14] are indications that the mathematical elegance of the RT approach is achieved while sacrificing the ability to relate easily terms appearing in derived conservation and constitutive equations to experimental measurements and observations.

2.3.4. Extended irreversible thermodynamics (EIT)

EIT is a relatively recent approach to microscale thermodynamics that extends the local equilibrium assumption employed with CIT by also allowing internal energy to depend on the local dissipative fluxes, denoted generically in Table 1 as **J** [51]. At equilibrium these fluxes will be zero. Thus at equilibrium, or when the dependence on these fluxes is small, the EIT formulation is identical to CIT. The range of applicability of non-equilibrium thermodynamics is considered to be extended by this formulation over that obtained with CIT because memory as well as non-local and non-linear effects are incorporated into the formulation through the extended dependence of energy on fluxes. The extension of this approach to the macroscale may be fruitful if the relation between microscopic and macroscopic variables can be established.

2.3.5. Rational extended thermodynamics (RET)

The EIT approach of including dependence of internal energy on dissipative fluxes has been combined with RT to obtain this method. The RT approach provides the general framework for the development of constitutive equations using RET. However, rather than the variables of interest being functions of the entire history, the space of independent variables is enlarged such that the history is no longer necessary [51]. General dependences that invoke the rule of equipresence and make other assumptions are postulated for variables of interest. A non-equilibrium entropy is employed and assumed to be a regular and continuous function of the full set of independent variables. In RET, the second law of thermodynamics is not assumed to take the form of the Clausius–Duhem inequality; and the entropy flux is not assumed to be given by the ratio of the heat flux to the temperature [51]. The heat flux itself is considered to be an independent variable, in contrast to RT where the heat flux is given by a constitutive relation. The entropy is expressed as a function of the heat flux, a key difference between RT and RET. RET suffers from the same problems as RT in regard to the meaning and measurability of the entropy and temperature functions. Likewise, extension of the method to the macroscale further obfuscates the physical meaning of the thermodynamic variables.

2.3.6. Theory of internal variables (TIV)

The TIV approach [56,59] has been developed to model systems that have internal structure. This approach makes use of the traditional intensive variables of ET in the formulation of the energy, but also adds some additional variables of state, the internal variables, which we denote as **I**. The classic intensive variables are considered controllable or observable while the newly introduced independent variables are not. Rather, these internal variables of state describe the internal structure hidden from the observer. Appropriate selection of these internal variables will depend heavily on the scale at which the system is being observed. This expansion of the list of variables at the microscale has some similarities to systematic transformation of CIT to a macroscale wherein internal variables relating to the geometric properties arise naturally.

2.3.7. Macroscale thermodynamics

All of the preceding approaches to thermodynamics have been applied at the microscale to obtain useful results. Thus they all have potential for application at the macroscale. However, at the macroscale the local equilibrium assumption does not apply in general; thus the specification of the functional dependence of energy is more complicated. For example, the local equilibrium assumption allows for temperature to be defined at a microscale point even when a system is not at global equilibrium. However, a macroscale "point" actually contains all the material in the REV centered at that point. Thus, specification of a macroscale temperature does not account for temperature gradients that may exist within the REV and therefore provides limited thermodynamic information. Furthermore, the temperatures of two different phases at the macroscale may be different even though, from a microscale perspective, the local equilibrium assumption would apply. Similar considerations apply to other intensive variables, such as pressure and chemical potential. Therefore to extend the applicability of any microscale thermodynamic approach, a method is needed that transforms the approach systematically from the microscale to the macroscale.

Recently, a macroscale thermodynamic formulation has been developed that is consistent with the microscale for a multiphase flow system along the lines of CIT [35]. When microscale thermodynamics are averaged, additional terms arise in the thermodynamic expressions that must be accounted for. Some of these terms relate to the geometric densities such that the macroscale thermodynamics takes on some of the attributes of TIV. However some additional terms arise that account for heterogeneity of the intensive variables within the averaging volume. These terms do not appear in the RT approach, the method that has been used heretofore for porous medium systems, so that consistency between microscale and macroscale perspectives cannot be established. Averaging of microscale thermodynamics provides an approach to develop macroscale closure relations that are consistent across scales.

3. Thermodynamically constrained averaging theory (TCAT)

3.1. Overview

We propose a thermodynamically constrained averaging theory (TCAT) approach as a systematic methodology that can be used to formulate porous medium models based upon rigorous averaging starting from microscale continuum conservation principles in conjunction with an appropriate microscale thermodynamic formulation. The TCAT approach involves the following steps:

- an entropy inequality (EI) expression for the entire system of concern is generated;
- an appropriate set of mass, momentum, and energy conservation equations is formulated at the desired scale for all relevant entities (volumes, areas, common curves, and common points) based upon clearly defined averages of microscale quantities;
- an appropriate microscale thermodynamic theory is averaged up to the desired scale, and differential forms of internal energy dependence for spatial and temporal derivatives are generated;
- the EI is augmented using the products of Lagrange multipliers with conservation equations and with differential, consistent-scale thermodynamic equations;
- the set of Lagrange multipliers is determined to select the combination of conservation equations that describes the physics of interest and to eliminate time derivatives from the augmented EI producing the constrained EI;
- geometric identities and approximations are applied to the constrained EI to eliminate additional remaining time derivatives as needed;
- the resultant simplified EI is used to guide the formulation of general forms of closure approximations consistent with the second law of thermodynamics; and
- microscale and macroscale modeling and experimentation are used to advance appropriate forms of closure relations.

The TCAT approach is intended to be a broad framework for generating consistent, closed models of transport phenomena in porous medium systems, as well as systems composed of any mixture of phases, at scales ranging from the microscale to the megascale. The resultant models are based upon rigorously defined spatial and, perhaps, temporal averages of microscale quantities. Transport phenomena of interest include mass, momentum, and energy transport for both entire entities, such as volumes, interfaces, common curves, and common points, and individual species within a set of entities. The spatial scales of concern include a continuum of length scales. This continuum consists of the following four members: (1) the microscale, the minimum scale at which the laws of continuum mechanics apply; (2) the macroscale or porous medium continuum scale; (3) the mesoscale or a scale over which macroscopic properties are heterogeneous in some regular or stochastic pattern; and (4) the megascale or scale of the system of concern.

The TCAT approach uses Lagrange multipliers, based loosely on [57], to constrain a system EI using conservation equations. Broadly, the Lagrange multipliers are selected to eliminate material time derivatives from the equation so that the entropy generation is related to dissipative fluxes. The approach involves generalizations in that conservation equations for species in phases, interfaces, common curves, and common points are all accounted for in a single framework. Additionally, thermodynamic relations are postulated at the small continuum scale. Since the scale of all equations is transformed systematically, ambiguity about the meaning of quantities at larger scales is avoided and consistency between the definitions of quantities at different scales is assured. In the sections that follow, we present general examples of the TCAT approach at two different spatial scales: the microscale and the macroscale. As mentioned above, the framework is applicable in general across a continuum of length and time scales and is mathematically consistent regardless of the scale chosen.

3.2. Microscale formulation

We consider here the general case of species i in entity α, where the entity may refer to a phase, an interface, or a common curve. Let the microscale mass balance equation be indicated as

$$\mathscr{M}_{i\alpha} = 0 \tag{3}$$

which describes the time rate of change of the mass of species i per unit region of entity and unit time. The terms in the equation include the rate of accumulation, flux, and generation terms. For simplicity here, and consistent with the idea that this manuscript provides only an overview, the precise forms of the conservation equations are not given. We simply state that conservation equations can be obtained at the scale of interest.

The momentum vector equation is given as

$$\mathscr{P}_{i\alpha} = 0 \tag{4}$$

which expresses the time rate of change of momentum and has dimensions of momentum of species i per unit region of entity and unit time.

The total energy conservation equation is represented as

$$\mathscr{E}_{i\alpha} = 0 \tag{5}$$

This form expresses the time rate of change of the sum of internal, potential, and kinetic energy and has dimensions of total energy of species i per unit region of entity. Each of the conservation equations contains terms that account for rates of accumulation of the property of interest within the entity, advection, a non-advective flux, surface and body sources, and rates of production.

Additionally, an entropy conservation equation for a species in an entity may be derived using general conservation principles. However, entropy is conceptually different from the strictly conserved quantities of mass, momentum, and energy because the production term for each species is unspecified. This characteristic seemingly makes the equation of little use. However, some advantage is achieved by summing the species entropy equations over all species, equating the remainder of the equation to the production term, and noting that inequality resulting from the second law of thermodynamics is of the form

$$\sum_i \mathscr{S}_{i\alpha} = \Lambda_\alpha \geqslant 0 \tag{6}$$

This equation has dimensions of entropy per unit region of entity and unit time. This relation applies to a "point" which, at the microscale, is "occupied" by all the species comprising the continuum at that location.

At the microscale, the conservation equations may be considered as constraints on entropy production in that entropy cannot be produced by any mechanism that would require violation of these basic laws. Thus the conservation equations may be indicated as constraints by making use of Lagrange multipliers such that the point entropy inequality must satisfy:

$$\sum_i \mathscr{S}_{i\alpha} + \sum_i \lambda_{\mathscr{E}_{i\alpha}} \mathscr{E}_{i\alpha} + \sum_i \boldsymbol{\lambda}_{\mathscr{P}_{i\alpha}} \cdot \boldsymbol{\mathscr{P}}_{i\alpha} + \sum_i \lambda_{\mathscr{M}_{i\alpha}} \mathscr{M}_{i\alpha} = \Lambda_\alpha \geqslant 0 \tag{7}$$

This equation contains material time derivatives of entropy; internal, kinetic, and potential energy; momentum; and mass. Because the time derivatives that appear in this relation can be either positive or negative, reduction of the equation to a form that provides insight into the forms of the dissipative fluxes requires that these time derivatives be eliminated. This is achieved by requiring the coefficients of the independent time derivatives to be zero. This is accomplished by selecting the Lagrange multipliers such that they eliminate these time derivatives. For example, the time derivatives of velocity are eliminated by judicious choice of the Lagrange multiplier for the momentum equation, $\boldsymbol{\lambda}_{\mathscr{P}_{i\alpha}}$, that multiplies the time derivative of velocity in that equation in light of the Lagrange multiplier for the energy equation, $\lambda_{\mathscr{E}_{i\alpha}}$, that multiples a time derivative of velocity that arises in the kinetic energy term. The time derivatives of energy, entropy, and mass appear in only one of the conservation equations and therefore will survive the purging of time derivatives unless some additional relation can be provided that expresses their interdependence. This relation of interdependence is obtained from thermodynamic considerations and serves as yet one more constraint to be incorporated into Eq. (7).

Eq. (1) provides an equilibrium thermodynamic relation for a phase over an entire system Ω. It is important to realize that such an expression applies at equilibrium only and not during a transition or in transient cases or when there are gradients in the variables. A time derivative of this equation is formally meaningless. However, our interests, and the equations we are working with, involve dynamic processes. To model such processes, it is common to assume implicitly that the laws of thermodynamics can be applied locally. This assumption is known as the local equilibrium hypothesis, and it assumes that a system can be considered to be an assembly of subsystems for which the rules of equilibrium thermodynamics apply. The local equilibrium assumption is a component of the CIT theory, for example. Thus rather than imposing Eq. (1) on an entire system as a whole, such an equation is considered to apply at each point in the system with the relation expressed in terms of the extensive quantities per unit mass or per unit entity region. Time derivatives and spatial gradients of these quantities are then allowed to exist within the system.

For example, if Eq. (2) is expressed per unit volume for a point within a phase, it becomes

$$E = E(\eta, \rho) \tag{8}$$

Note that the functional dependence indicated is very simple. If energy density depends on time, this is accounted for through the dependence of entropy and mass densities on time. Similarly spatial variation of energy is accounted for through the dependence of entropy and mass densities on position. In more general cases when the system is far enough from equilibrium that the local equilibrium assumption does not apply, it may be useful to also include dependence on other quantities that would be zero for a total system at equilibrium but are non-zero for dynamic systems. For example, dependence of the entropy on a heat conduction vector may be postulated; such a situation would require thermodynamics of the EIT or RET class. The objective of this paper is not to determine or specify any specific thermodynamic functional dependence or to restrict the analysis just to those cases where the local equilibrium assumption applies. Rather, the objective is to outline a method of derivation of closed conservation equations in instances when some thermodynamic functional dependence is employed. Therefore, we express the microscale entropy per unit region of species i in entity α as

$$E_{i\alpha} = E_{i\alpha}(\mathbf{X}_{i\alpha}) \tag{9}$$

where $\mathbf{X}_{i\alpha}$ is the vector of independent variables on which the energy per region of entity of species i in entity α may depend. Then the equation for the partial time derivative of energy is

$$\frac{\partial E_{i\alpha}}{\partial t} - \frac{\partial E_{i\alpha}}{\partial \mathbf{X}_{i\alpha}} \cdot \frac{\partial \mathbf{X}_{i\alpha}}{\partial t} = 0 \tag{10}$$

If the entity α is a surface, common curve, or point, the partial time derivative is taken holding surface, curve, or point coordinates, respectively, constant. Similarly, a gradient with the appropriate dimensionality may be obtained as

$$\nabla E_{i\alpha} - \nabla \mathbf{X}_{i\alpha} \cdot \frac{\partial E_{i\alpha}}{\partial \mathbf{X}_{i\alpha}} = 0 \tag{11}$$

where ∇ is the three-, two-, or one-dimensional gradient operator depending on whether α represents a volume, interface, or common curve type of entity, respectively. Of course, there is no gradient operator for a common point entity.

As an example of Eq. (11), if the entity is a phase w that is composed of a single species with energy density depending only on entropy and mass densities then the gradient of energy is related to the gradient of the independent variables according to

$$\nabla E_w - \frac{\partial E_w}{\partial \eta_w} \nabla \eta_w - \frac{\partial E_w}{\partial \rho_w} \nabla \rho_w = 0 \tag{12}$$

The thermodynamic constraints express relations among variables that are useful in determining the values of the Lagrange multipliers. Eqs. (10) and (11) are applied as constraints to Eq. (7)

$$\begin{aligned} &\sum_i \mathscr{S}_{i\alpha} + \sum_i \lambda_{\mathscr{E}_{i\alpha}} \mathscr{E}_{i\alpha} + \sum_i \boldsymbol{\lambda}_{\mathscr{P}_{i\alpha}} \cdot \boldsymbol{\mathscr{P}}_{i\alpha} \\ &\quad + \sum_i \lambda_{\mathscr{M}_{i\alpha}} \mathscr{M}_{i\alpha} + \sum_i \lambda_{t_{i\alpha}} \left(\frac{\partial E_{i\alpha}}{\partial t} - \frac{\partial E_{i\alpha}}{\partial \mathbf{X}_{i\alpha}} \cdot \frac{\partial \mathbf{X}_{i\alpha}}{\partial t} \right) \\ &\quad + \sum_i \boldsymbol{\lambda}_{\mathbf{X}_{i\alpha}} \cdot \left(\nabla E_{i\alpha} - \nabla \mathbf{X}_{i\alpha} \cdot \frac{\partial E_{i\alpha}}{\partial \mathbf{X}_{i\alpha}} \right) = \Lambda_\alpha \geqslant 0 \end{aligned} \tag{13}$$

For this microscale equation, the selection of the Lagrange multipliers determines which entity is under study and the types of closure relations that can be obtained.

As an example of the application of Eq. (13), consider a fluid phase, w, that is composed of N chemical species. Although it is possible to examine this system using a full set of equations for each species, consider the simplification where the mass of each species is modeled while the momentum and energy of the phase as a whole is of interest. For this situation, Eq. (13) reduces to

$$\begin{aligned} &\mathscr{S}_w + \lambda_{\mathscr{E}_w} \mathscr{E}_w + \boldsymbol{\lambda}_{\mathscr{P}_w} \cdot \boldsymbol{\mathscr{P}}_w + \sum_{i=1}^N \lambda_{\mathscr{M}_{iw}} \mathscr{M}_{iw} \\ &\quad + \lambda_{t_w} \left(\frac{\partial E_w}{\partial t} - \frac{\partial E_w}{\partial \mathbf{X}_w} \cdot \frac{\partial \mathbf{X}_w}{\partial t} \right) \\ &\quad + \boldsymbol{\lambda}_{\mathbf{X}_w} \cdot \left(\nabla E_w - \nabla \mathbf{X}_w \cdot \frac{\partial E_w}{\partial \mathbf{X}_w} \right) = \Lambda_w \geqslant 0 \end{aligned} \tag{14}$$

where

$$\mathscr{S}_w = \sum_{i=1}^N \mathscr{S}_{iw} \tag{15}$$

$$\lambda_{\mathscr{E}_{iw}} = \lambda_{\mathscr{E}_w}, \quad i = 1, \ldots, N \tag{16}$$

$$\mathscr{E}_w = \sum_{i=1}^N \mathscr{E}_{iw} \tag{17}$$

$$\boldsymbol{\lambda}_{\mathscr{P}_{iw}} = \boldsymbol{\lambda}_{\mathscr{P}_w}, \quad i = 1, \ldots, N \tag{18}$$

$$\boldsymbol{\mathscr{P}}_w = \sum_{i=1}^N \boldsymbol{\mathscr{P}}_{iw} \tag{19}$$

$$E_w = \sum_{i=1}^N E_{iw} \tag{20}$$

$$\lambda_{t_{iw}} = \lambda_{t_w}, \quad i = 1, \ldots, N \tag{21}$$

$$\boldsymbol{\lambda}_{\mathbf{X}_{iw}} = \boldsymbol{\lambda}_{\mathbf{X}_w}, \quad i = 1, \ldots, N \tag{22}$$

Additionally, for this system, a common selection of the independent variables on which the energy density depends, based on the local equilibrium assumption, would be the entropy density and the mass density of each of the chemical species such that

$$\mathbf{X}_w = \{\eta_w, \rho_w \omega_{iw}\}, \quad i = 1, \ldots, N \tag{23}$$

where ρ_w is the density of phase w and ω_{iw} is the mass fraction of species i in phase w. When this selection is made, the following conditions are also obtained from standard thermodynamic approaches (e.g., CIT)

$$E_w = \eta_w\theta_w + \sum_{i=1}^{N}(\rho_w\omega_{iw}\mu_{iw}) - p_w \tag{24}$$

where p_w is the pressure, θ_w is the temperature defined by

$$\theta_w = \left(\frac{\partial E_w}{\partial \eta_w}\right)_{\rho_w\omega_{iw}} \tag{25}$$

and μ_{iw} is the chemical potential for species i defined as

$$\mu_{iw} = \left(\frac{\partial E_w}{\partial \rho_w\omega_{iw}}\right)_{\rho_w\omega_{jw},\eta_w} \tag{26}$$

In Eq. (25), $\rho_w\omega_{iw}$ is constant for all i such that the total mass per volume and composition are constant. In Eq. (26), $\rho_w\omega_{jw}$ is constant for all j not equal to i such that the relative concentrations of all species to each other, except for species i, is held constant.

The general formulation given by Eq. (13) and the subsequent definitions are used with a systematic procedure such as the Coleman and Noll method [20] to obtain closure relations for some quantities appearing in the conservation equations. The expressions requiring closure include the diffusion vector that appears in the species balance equation, the stress tensor in the momentum equation, and the non-advective heat flux in the energy equation. Equations of state are also needed to make the system of equations solvable.

One final note that may help explain the workings of this development is that if one applied the condition $\lambda_{\mathscr{M}_{iw}} = \lambda_{\mathscr{M}_w}$ for all i, the separate species conservation equations in Eq. (13) would collapse to a sum that is equal to the mass conservation equation for the w phase. Although such a formulation is allowable, it would not be possible to extract information about the functional form of the diffusion vector. Only the behavior of the phase as a whole would be described by the closure relations. Thus the Lagrange multipliers have a multiple role in TCAT. First, they indicate the detail of a model of an entity, either including or excluding mass, momentum, and energy equations on a species basis and even on an entity basis. Second, their inclusion to constrain the entropy inequality with mass, momentum, and energy conservation conditions ensures that the entropy inequality applies to actual processes. Third, their selection in conjunction with the postulated extension of equilibrium thermodynamic relations to the dynamic state facilitates the elimination of time derivatives such that the entropy production rate density, Λ_α, is related entirely to terms in the conservation equations describing body and surface sources as well as generation terms (i.e., the terms other than those originating from temporal derivatives). This approach allows for derivation of functional forms of the source terms that require closure.

3.3. Macroscale formulation

The macroscale formulation involves a change in scale such that the properties of continuum "points" are obtained from a much larger collection of molecules than the microscale description. Some sort of averaging procedure is done that involves a region in the neighborhood of a microscale point. The average values obtained are then associated with the point of interest. In this fashion, continuum descriptions are generated that have larger scale time and space characteristics. The time-averaged momentum equation that describe turbulent flow, ultimately with the aid of constitutive approximations for the Reynolds stresses, is an example of averaging in time. Simulation of flow and contaminant variations along a river channel using equations that have been integrated over the river cross-section, and perhaps averaged over a time interval, also involves macroscale forms of mass and momentum conservation equations. Macroscale simulation of flow and transport in porous media employs averaging around a point such that the conservation equations are expressed as functions of time and all three dimensions in space.

Here, we will consider this last kind of averaging such that an integration region in space is occupied by a number of entities such that they are intermixed. Thus, the macroscale perspective does not recognize phases as being adjacent to each other but models them as being present at a "point" and occupying various fractions of that point. Likewise, the exact placement of the interfaces between phases is not known at the macroscale. Alternatively, the amount of area per volume is considered as well as macroscale measures of the orientation of the interfaces within the averaging region. Similar considerations apply to the common curves and common points. With this averaging perspective, we include integration over a river cross section, for example, as a special case in which one phase occupies the complete averaging region and the scale of averaging in two of the dimensions is on the same order as the system dimension. Thus, the formalism advocated is applicable to a wide range of problems. Indeed, if the region of averaging is of microscale dimensions, the subsequent framework becomes equivalent to that of Section 3.2.

For the macroscale formulation applied to porous medium systems, the conservation equations for an entity are averaged by integration over the space of the entity within an REV. Thus, at each point, conservation equations for macroscale properties of phases, surfaces, common curves, and common points are obtained. Let the macroscopic mass balance equation be expressed analogously to its microscale precursor using superscripts rather than subscripts. In entity α, the macroscale mass balance equation for species i is indicated as

$$\mathscr{M}^{i\alpha} = 0 \tag{27}$$

Regardless of the entity being considered, this equation has dimensions of mass per unit volume and unit time. For example, if one integrates the mass conservation equation for a species within a surface contained in an REV over that surface and then divides by the volume of the REV, the mass conservation equation will have units of mass per time and volume. This approach to obtaining macroscale equations is operationally simpler than averaging and dividing by the associated area because it allows the entity equations obtained to be directly added together to obtain a full conservation equation for a species at a macroscale point.

The vector macroscale momentum equation for species i has dimensions of momentum of species i in entity α per unit volume and unit time and is given as

$$\boldsymbol{\mathscr{P}}^{i\alpha} = 0 \tag{28}$$

The total energy conservation equation models the rate of change of internal, potential, and kinetic energy of species i in entity α and has dimensions of energy per unit volume of REV and time according to

$$\mathscr{E}^{i\alpha} = 0 \tag{29}$$

Eqs. (27)–(29) account for rates of accumulation of the properties of interest at the macroscale point due to the presence of an entity, its interaction with other entities within the region and the advection, non-advective transport, surface and body sources, and rates of production of the properties. The additional condition that the rate of production of entropy at any point must be non-negative accounts for the fact that the properties of the material at a point are made up of contributions from all entities as well as from all species. Therefore, the entropy inequality at a macroscale point is

$$\sum_{\alpha} \sum_{i} \mathscr{S}^{i\alpha} = \Lambda \geqslant 0 \tag{30}$$

At the macroscale, the conservation equations are again considered to be constraints that limit mechanisms of entropy production. Since all entities and species are present at a point, conservation equation constraints are enforced using Lagrange multipliers such that

$$\sum_{\alpha} \sum_{i} \mathscr{S}^{i\alpha} + \sum_{\alpha} \sum_{i} \lambda_{\mathscr{E}}^{i\alpha} \mathscr{E}^{i\alpha} + \sum_{\alpha} \sum_{i} \boldsymbol{\lambda}_{\mathscr{P}}^{i\alpha} \cdot \boldsymbol{\mathscr{P}}^{i\alpha} + \sum_{\alpha} \sum_{i} \lambda_{\mathscr{M}}^{i\alpha} \mathscr{M}^{i\alpha} = \Lambda \geqslant 0 \tag{31}$$

Although this equation indeed constrains the entropy inequality by subjecting it to conservation equations, these constraints may only be utilized to advantage if the proper system thermodynamics are imposed. This need gives rise to additional complications.

Specification of thermodynamics for a macroscale formulation is not obvious. Consider a rather simple case where cold water is poured over very hot rocks. Microscale modeling of this system would consider temperature gradients within each phase and would also identify a temperature for each point in the phases even though the system is not at equilibrium. Definition of a temperature at the interface between the phases would be complex and, perhaps, could be avoided by use of some two domain heat transfer relation that only requires specification of the temperatures near the interface. Local equilibrium hypotheses could be used to advantage in modeling this system. However, if we consider a macroscale point containing rocks, water, and a gas phase composed of air and water vapor, the macroscale temperatures of the three phases will be different. Furthermore, microscale temperature gradients that exist within each phase suggest that the macroscale temperature does not convey the full richness of processes occurring in the system. The macroscale temperature for a phase is some average of the microscale temperatures. The idea of temperature as a measure of equilibrium is diminished, as is the actual meaning of the macroscale temperature as a quantity to be directly measured. The microscale thermodynamic internal energy function may be employed and exploited thermodynamically under the assumption of local equilibrium and systematic extensions to that assumption. However, the local equilibrium assumption is not as robust for macroscale systems particularly when the time and space dimensions defining the macroscale of interest are large enough that variation of microscale properties within the averaging region may be significant.

In the face of this adversity, the rational thermodynamic approach moves boldly forward and hypothesizes dependences of the macroscale internal energy on a selected set of macroscale variables. The actual definitions of these variables that would lead to them being measured is disregarded. Furthermore, the requirement that a macroscale thermodynamic formulation should become equivalent to a microscale thermodynamic formulation when its time and length scales are reduced is not considered. Essentially, the RT approach borrows some elements from the microscale, but makes additional postulates on an "as needed" basis to arrive at mathematically consistent and useful formulations. Measurement of the parameters that appear in the equations as they arise from their mathematical definitions is implicitly abandoned in favor of using values that actually describe the physical systems of interest.

This seemingly harsh assessment is not intended to deny the success that rational thermodynamics has enjoyed, especially in microscale formulations. However, a macroscale thermodynamic formulation must lead to a system description that involves measurable, or at least well-defined, parameters and that is consistent with the microscale model.

To foster these desired traits, we use the TCAT approach to macroscale modeling. This approach employs an averaging procedure to transfer whatever microscale thermodynamic formulation one wishes to employ to the macroscale. Thus, efficiencies and deficiencies of a microscale model are preserved, but no new deficiencies are introduced. The mechanics of this conversion have been introduced previously [35] and will be employed for systems of varying complexity in subsequent papers. The effect of this transformation is to obtain a macroscale internal energy per volume with dependence on an expanded set of macroscale variables in comparison to the number of variables on which the microscale form depends. Alternatively, this dependence may be expressed analogously to the microscale form with some additional terms arising in expressions for the derivatives of the macroscale energy.

Here the thermodynamic formulation employed will make use of the internal energy of species i in the α entity per unit of averaging volume as

$$E^{i\bar{\bar{\alpha}}} = E^{i\bar{\bar{\alpha}}}\left(\mathbf{X}^{i\alpha}\right) \tag{32}$$

In general, the set $\mathbf{X}^{i\alpha}$ consists of macroscopic counterparts to $\mathbf{X}_{i\alpha}$ as well as some additional variables. Note that nothing in this specification precludes the use of a direct macroscale RT specification of dependence of energy on macroscale variables. Indeed, any macroscale postulation of thermodynamic behavior may be employed in the formalism. The TCAT approach, however, obtains the thermodynamic dependence through systematic transformation of variables from the microscale to the macroscale.

The time derivative and gradient of the macroscale internal energy are obtained, respectively, as

$$\frac{\partial E^{i\bar{\bar{\alpha}}}}{\partial t} - \frac{\partial E^{i\bar{\bar{\alpha}}}}{\partial \mathbf{X}^{i\alpha}} \cdot \frac{\partial \mathbf{X}^{i\alpha}}{\partial t} = 0 \tag{33}$$

and

$$\nabla E^{i\bar{\bar{\alpha}}} - \nabla \mathbf{X}^{i\alpha} \cdot \frac{\partial E^{i\bar{\bar{\alpha}}}}{\partial \mathbf{X}^{i\alpha}} = 0 \tag{34}$$

Although these two equations appear to be similar to their microscale counterparts, Eqs. (10) and (11), there is one important conceptual difference. The transformation to the macroscale by integration over entities within an REV changes all variables such that they are defined in three-dimensional space, not only on the corresponding entity space. For example, a microscale surface property is defined only on that surface such that its gradient is a two dimensional function. A macroscale surface property is obtained as the amount associated with a macroscale volume. Thus the partial time derivative in Eq. (33) and the gradient in Eq. (34) are both applied to functions that depend on time and three macroscale space dimensions.

The thermodynamic conditions as given by Eqs. (33) and (34) are applied as constraints to Eq. (31) yielding

$$\begin{aligned}
&\sum_{\alpha}\sum_{i}\mathscr{S}^{i\alpha} + \sum_{\alpha}\sum_{i}\lambda_{\mathscr{E}}^{i\alpha}\mathscr{E}^{i\alpha} + \sum_{\alpha}\sum_{i}\boldsymbol{\lambda}_{\mathscr{P}}^{i\alpha}\cdot\boldsymbol{\mathscr{P}}^{i\alpha} \\
&\quad + \sum_{\alpha}\sum_{i}\lambda_{\mathscr{M}}^{i\alpha}\mathscr{M}^{i\alpha} + \sum_{\alpha}\sum_{i}\lambda_{t}^{i\alpha}\left(\frac{\partial E^{i\bar{\bar{\alpha}}}}{\partial t} - \frac{\partial E^{i\bar{\bar{\alpha}}}}{\partial \mathbf{X}^{i\alpha}}\cdot\frac{\partial \mathbf{X}^{i\alpha}}{\partial t}\right) \\
&\quad + \sum_{\alpha}\sum_{i}\boldsymbol{\lambda}_{\mathbf{x}}^{i\alpha}\cdot\left(\nabla E^{i\bar{\bar{\alpha}}} - \nabla\mathbf{X}^{i\alpha}\cdot\frac{\partial E^{i\bar{\bar{\alpha}}}}{\partial \mathbf{X}^{i\alpha}}\right) = \Lambda \geqslant 0
\end{aligned} \tag{35}$$

Both of the vector Lagrange multipliers in this equation are three dimensional. Additionally, when the transformation of the microscale thermodynamics to the macroscale is performed systematically, some of the derivative terms in the thermodynamic expressions may be replaced by integral expressions. This situation will be explored in subsequent papers.

An interesting conceptual point is the fact that by the TCAT approach in which the macroscale thermodynamics are averaged from the microscale, Eq. (35) may be obtained as the average of Eq. (13) written for each of the entities and summed together if the Lagrange multipliers are treated as constants for the averaging process. This highlights the fact that the conservation equations and thermodynamic relations are consistent between scales in that the fully averaged constrained entropy inequality at the larger scale is just the average of the smaller scale form. In all previous macroscale formulations, the conservation equations are averaged between scales to retain consistency, but the thermodynamic formulations are independent thus making it impossible to make direct comparisons of terms.

The general expression given in Eq. (35) provides the largest number of independent constraints that are available from conservation and thermodynamic equations. In theory, some additional constraints can be formulated from relations involving geometric variables that arise in the averaging process. For example, the sum of the partial mass entity spaces of the species within each entity must be 1. Also, the sum of the volume fractions within the averaging volume must be 1. These straightforward conditions can be added as constraints to Eq. (35). More complex are conditions involving the evolution of the size of the volume fractions, the interfacial areas per volume, and the common curve lengths per volume. In general these conditions are not known [60] but some approximate expressions can be written for the near equilibrium situation [42]. For convenience, these approximate relations will be applied to the entropy inequality subsequent to the determination of the Lagrange multipliers in Eq. (35). The reason for this postponement is that the geometric relations are only approximate, and it will be useful to have an expression not influenced by these approximations. Then, if better approximations become available, it will be relatively easy to employ them.

Typically, when studying a system, use of separate energy equations for each species in each entity is avoided as being excessively complex. Combining the energy equations for the species makes it unnecessary to examine partial energy entities for each species. Only the partial mass energies for the entities need to be modeled. This relaxation of the constraints is obtained by requiring for all species i

$$\lambda_{\mathscr{E}}^{i\alpha} = \lambda_{\mathscr{E}}^{\alpha} \tag{36}$$

$$\lambda_{t}^{i\alpha} = \lambda_{t}^{\alpha} \tag{37}$$

$$\boldsymbol{\lambda}_{\mathbf{x}}^{i\alpha} = \boldsymbol{\lambda}_{\mathbf{x}}^{\alpha} \tag{38}$$

With these conditions imposed, Eq. (35) becomes

$$\sum_{\alpha}\mathscr{S}^{\alpha} + \sum_{\alpha}\lambda_{\mathscr{E}}^{\alpha}\mathscr{E}^{\alpha} + \sum_{\alpha}\sum_{i}\boldsymbol{\lambda}_{\mathscr{P}}^{i\alpha}\cdot\boldsymbol{\mathscr{P}}^{i\alpha} + \sum_{\alpha}\sum_{i}\lambda_{\mathscr{M}}^{i\alpha}\mathscr{M}^{i\alpha} + \sum_{\alpha}\lambda_{t}^{\alpha}\left(\frac{\partial E^{\bar{\bar{\alpha}}}}{\partial t} - \frac{\partial E^{\bar{\bar{\alpha}}}}{\partial \mathbf{X}^{\alpha}}\cdot\frac{\partial \mathbf{X}^{\alpha}}{\partial t}\right) + \sum_{\alpha}\boldsymbol{\lambda}_{\mathbf{x}}^{\alpha}\cdot\left(\nabla E^{\bar{\bar{\alpha}}} - \nabla\mathbf{X}^{\alpha}\cdot\frac{\partial E^{\bar{\bar{\alpha}}}}{\partial \mathbf{X}^{\alpha}}\right) = \Lambda \geqslant 0 \tag{39}$$

where the macroscale entropy equation, energy equation, and internal energy for an entity are defined, respectively, by

$$\mathscr{S}^{\alpha} = \sum_{i}\mathscr{S}^{i\alpha} \tag{40}$$

$$\mathscr{E}^{\alpha} = \sum_{i}\mathscr{E}^{i\alpha} \tag{41}$$

and

$$E^{\bar{\bar{\alpha}}} = \sum_{i}E^{i\bar{\bar{\alpha}}} \tag{42}$$

As an example of the expression for the macroscale thermodynamic equations for $E^{\bar{\bar{\alpha}}}$, consider a phase w with the microscale internal energy defined by Eq. (24). If the TCAT approach is employed such that this equation is averaged over the w phase within an averaging volume similarly to the procedures in [35], the macroscale expression for the energy is

$$E^{\bar{\bar{w}}} = \eta^{\bar{\bar{w}}}\theta^{\bar{w}} + \sum_{i=1}^{N}(\rho^{w}\epsilon^{w}\omega^{i\bar{w}}\mu^{i\bar{w}}) - \epsilon^{w}p^{w} \tag{43}$$

where

$$E^{\bar{\bar{w}}} = \frac{1}{V}\int_{\Omega_w} E_w\,\mathrm{d}\mathbf{r} \tag{44}$$

$$\eta^{\bar{\bar{w}}} = \frac{1}{V}\int_{\Omega_w} \eta_w\,\mathrm{d}\mathbf{r} \tag{45}$$

$$\epsilon^{w}\rho^{w} = \frac{1}{V}\int_{\Omega_w} \rho_w\,\mathrm{d}\mathbf{r} \tag{46}$$

$$\omega^{i\bar{w}} = \frac{1}{\rho^{w}\epsilon^{w}}V\int_{\Omega_w} \rho_w\omega_{iw}\,\mathrm{d}\mathbf{r} \tag{47}$$

$$\epsilon^{w} = \frac{1}{V}\int_{\Omega_w} \mathrm{d}\mathbf{r} \tag{48}$$

$$\theta^{\bar{w}} = \frac{1}{\eta^{\bar{\bar{w}}}V}\int_{\Omega_w} \eta_w\theta_w\,\mathrm{d}\mathbf{r} \tag{49}$$

$$\mu^{i\bar{w}} = \frac{1}{\rho^{w}\epsilon^{w}\omega^{i\bar{w}}V}\int_{\Omega_w} \rho_w\omega_{iw}\mu_{iw}\,\mathrm{d}\mathbf{r} \tag{50}$$

$$\epsilon^{w}p^{w} = \frac{1}{V}\int_{\Omega_w} p_w\,\mathrm{d}\mathbf{r} \tag{51}$$

Note the subtle point that the macroscale temperature and chemical potential obtained using TCAT are defined as weighted averages of microscale counterparts, whereas the definitions of these quantities at the microscale, as given in Eqs. (25) and (26), are obtained through partial derivatives of the internal energy. Definitions similar in form to the microscale definitions, but in terms of macroscale quantities, are proposed if one uses the RT approach. However, the precise meaning and measurability of these quantities based on RT is unclear.

Additionally, the derivative of the macroscale internal energy based on Eq. (43) is

$$\mathrm{d}E^{\bar{\bar{w}}} = \theta^{\bar{w}}\,\mathrm{d}\eta^{\bar{\bar{w}}} + \sum_{i=1}^{N}\mu^{i\bar{w}}\,\mathrm{d}(\rho^{w}\epsilon^{w}\omega^{i\bar{w}}) - p^{w}\,\mathrm{d}\epsilon^{w} + \eta^{\bar{\bar{w}}}\,\mathrm{d}\theta^{\bar{w}} + \sum_{i=1}^{N}(\rho^{w}\epsilon^{w}\omega^{i\bar{w}})\,\mathrm{d}\mu^{i\bar{w}} - \epsilon^{w}\,\mathrm{d}p^{w} \tag{52}$$

Further manipulation of the thermodynamic expression obtained by using the thermodynamics obtained with TCAT leads to the following relation:

$$\eta^{\bar{\bar{w}}}\,\mathrm{d}\theta^{\bar{w}} + \sum_{i=1}^{N}(\rho^{w}\epsilon^{w}\omega^{i\bar{w}})\,\mathrm{d}\mu^{i\bar{w}} - \epsilon^{w}\,\mathrm{d}p^{w} = -\frac{1}{V}\int_{\Omega_w}\eta_w[\mathrm{d}(\theta_w - \theta^{\bar{w}})]\mathrm{d}\mathbf{r} - \sum_{i}\left(\frac{1}{V}\int_{\Omega_w}\rho_w\omega_{iw}[\mathrm{d}(\mu_{iw} - \mu^{i\bar{w}})]\mathrm{d}\mathbf{r}\right) + \frac{1}{V}\int_{\Omega_w}[\mathrm{d}(p_w - p^{w})]\mathrm{d}\mathbf{r} \tag{53}$$

If microscale point values are constant within an REV such that the average temperature, chemical potentials, and pressure are equal to those point values, the three integrals on the right side of Eq. (53) are zero. The form of the equation is identical to the microscale

Gibbs-Duhem equation. Additionally, in this case, the last three terms in Eq. (52) will drop out; and the equation has a similar form as the microscale equation based upon a CIT approach. However, in general, the deviations of microscale values from their macroscale averages introduce the additional terms in the TCAT approach. Although these terms may seem to be undesirable, in fact they are important in assuring consistency between scales.

This outline of the macroscale formulation is intended to be an introduction to the use of macroscale formulations in modeling. The full exposition of the utility of the method must be postponed until the development of all the mathematical tools has been presented. Several points related to the richness of the methods for developing model equations at larger scales and the degree of refinement of the models are mentioned briefly here. Specification of the Lagrange multipliers provides constraints that indicate the detail of the conservation equations to be employed in constraining the entropy inequality. Setting the multipliers of a conservation equation type, such as energy, to be equal for all species in an entity eliminates the ability to obtain closure relations for the governing equations on a species basis, but also reduces the data required to support the model equations. Additionally, the Lagrange multipliers may be used to exclude an entity from the model description. Additional constraints on the behavior of the system, such as incompressibility or geometric information, may be added to the form here via Lagrange multipliers. Systematic and unambiguous change of scale of variables must be performed to enhance understanding and to allow for information transfer between scales. In particular, the thermodynamic forms at the macroscale have historically not received research attention commensurate with their importance.

4. Discussion

Current modeling of porous medium systems is plagued with inconsistencies and ill-defined variables. In part, at least, this is due to the traditional roots of porous medium flow equations, even for complex systems, in the classic experimental work of Darcy for the simplest of single fluid phase porous media. Additionally, the absence of a careful transformation of all microscale quantities in a formulation to the scale of interest has contributed to this problem and hindered progress.

The procedure outlined here provides a systematic path to continuum scale models for non-isothermal, multiphase, multispecies porous medium systems across a range of space and time scales with the common point of origination being the microscale, or pore scale. The TCAT approach outlined and shown by example ensures the desired consistency and provides a framework for the development of models across a range of complexities.

The TCAT, and previous developments upon which it is based, provides a basis for a systematic development of a hierarchical set of porous medium models of varying complexity. To be sure, this formulation approach involves detailed, technical calculations, and in some cases some new mathematical machinery. Future work will report these details and the resulting new closed models that result from application of the TCAT approach. Of course, these models must be compared with both classical formulations and detailed computational or laboratory experiments to evaluate fully the value they add to our physical understanding and simulation abilities.

The preceding should not be construed to suggest that all porous medium formulation problems are within reach. We believe that many unresolved issues exist that will require substantial, creative effort to produce a mature level of understanding. As an example, we note three areas in which significant work remains to be done: thermodynamic approaches, multiple fluid phase models, and stochastic models.

We have shown how thermodynamics can be systematically included in porous medium model formulations starting from the microscale. However, we consider the appropriate form of the thermodynamics upon which one should base a given model an open issue. CIT is a starting point, but may not be the final word. Detailed work and comparisons among competing theories should be investigated for a range of models and systems.

While the TCAT approach provides a framework to address complex multiphase, multispecies porous medium models, we believe that many significant unresolved problems exist with such systems. For example, this framework will result in non-traditional closure relations. Reasonable forms of these closure relations need to be deduced so that they are consistent with the theory and observations. Once a suitable form of the closure relations has been determined, issues related to parameter value identification will also need to be resolved. Further, multiple fluid phase porous medium systems that occur in nature involve complex physical interactions and processes that are not completely understood. Among the most challenging are accounting for the influence of disconnected fluid phases, of film flow, and of mixed wettability systems. Much work remains to resolve fully these issues.

Natural systems are stochastic in nature and the strict assumptions of an REV and clearly separable length scales may not be met for many systems. When such instances occur, it will be necessary to modify the TCAT approach to include these more complex conditions. Such modifications appear possible, but significant detailed calculations remain to assess fully the impact of such conditions on the resultant models. We do believe, however, that this is a more satisfying approach than building stochastic models based upon the implicit, and sometimes questionable, assumption that a classical model provides a satisfactory description of the system physics.

Lastly, while the focus of this work is primarily on the formulation of macroscale models of multiphase porous medium systems, the TCAT approach is in principle much more general than this. The TCAT approach can be used to formulate consistent multiphase porous medium models at the microscale, mesoscale, or megascale, or time-averaged models as well. Even more generally, since most natural and engineered systems are a subset of the complex systems considered explicity in this work, models for such systems also may be formulated based upon the TCAT approach.

5. Conclusions

Several observations form the basis of this work and serve as the motivation for careful analyses to be presented in subsequent papers:

- classical porous medium models suffer from inconsistencies manifested as model variables and parameters that are not rigorously defined and, hence, cannot be consistently measured;
- averaging theory developed and applied over the last two decades has resolved some of the problems with classical models, but it too has led to some ill-defined variables and inconsistencies;
- a key step in averaging theory is the introduction of thermodynamics into a system entropy inequality, and improvements in this step are needed to eliminate many of the problems with existing models;
- we advocate the use of thermodynamic expressions averaged from microscale thermodynamics as an appropriate source of information needed to form a useful system entropy inequality expression; and
- a framework based upon established and new notions, which we call the thermodynamically constrained averaging theory (TCAT) approach, is outlined and is applicable to a wide range of problems.

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