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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.

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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. 7–9]. However, we draw a distinction between the formulation of macroscale models and the upscaling of these macromodels to an even larger scale where the form of the model, and precise meaning of the parameters, should not be expected to be consistent with the underlying macroscale model [26]. Thus multiple levels and types of upscaling are ultimately of concern for many situations of interest.

The TCAT approach ensures a precise connection to both microscale quantities and thermodynamic constraints, which are in turn used to guide the development of macroscale closure relations. The TCAT approach differs in another important respect from typical model formulation approaches: it includes specific conservation and balance equations for interfaces and common curves. Given the importance of problems that involve composition, the extension of the TCAT framework to compositional macroscale systems is a reasonable next step in the evolution of this model formulation approach. This extension will require conservation and balance equations for species in entities and averaged thermodynamic relations, which have not yet appeared in the literature.

The overall goal of this work is to advance components needed to formulate TCAT-based macroscale models to describe compositional multispecies, multiphase porous medium systems. The specific objectives of this work are: (1) to develop species conservation and balance equations for phase volumes, interfaces, and common curves; (2) to formulate macroscale thermodynamic relations for compositional systems based upon averaged microscale relations; (3) to outline a flexible constraint approach for connecting conservation equations to a system entropy inequality to yield a range of different models; and (4) to discuss ways in which the fundamental tools developed in this work can be utilized in the formulation of closed macroscale models of compositional multiphase porous medium systems.

2 System Definition

We define multispecies, multiphase systems using set notation. This allows for the development of general conservation and balance equations and compact formulations of certain forms of the entropy inequality used in the TCAT approach. As with previous work in this series [19], we describe the set of entities ε as the regions within the domain Ω, which can include phase volumes, interfaces, common curves, and common points. The full set of entities is given by

$$\varepsilon = \left\{ \Omega_\iota \middle| \iota \in I \right\} \tag{1}$$

where I is the index set of entity qualifiers or identifiers. Qualifiers are super-scripts (for macroscale quantities) and subscripts (for microscale quantities) that denote an entity of interest. Entities consist of phase volumes, interfaces, common curves, and common points. In some instances, it is convenient to consider only the members of one of these types of entities. To facilitate this, the qualifiers identifying one type of entity lie in the index set of phase volume qualifiers, I_P; interface qualifiers, I_I; common curve qualifiers, I_C; or common point qualifiers, I_Pt. The individual entity types can be combined such that $I = I_\mathrm{P} \cup I_\mathrm{I} \cup I_\mathrm{C} \cup I_\mathrm{Pt}$. For example, for a system composed of three phases, denoted as w, n, and s

$$I_\mathrm{P} = \{w,n,s\} \tag{2}$$

$$I_\mathrm{I} = \{wn,ws,ns\} \tag{3}$$

$$I_\mathrm{C} = \{wns\} \tag{4}$$

$$I_\mathrm{Pt} = \{\} \tag{5}$$

The members of these sets are used as qualifiers (subscripts for microscale quantities and superscripts for macroscale quantities) with a quantity of interest to associate that quantity with a particular entity (phase, interface, common curve, or common point).

The connected entity set is also an important concept as it defines all the entities in contact with a particular entity Ω_ι, such as the interface entities that bound a particular phase entity. This set is defined by

$$\varepsilon_{\mathrm{c}\iota} = \left\{ \Omega_\kappa \middle| (\overline{\Omega}_\iota \cap \overline{\Omega}_\kappa \neq \phi) \wedge \overline{\Omega}_\iota \neq \overline{\Omega}_\kappa), \forall \Omega_\kappa \in \varepsilon \right\} \tag{6}$$

where the closure of the entities is defined as $\overline{\Omega}_\iota = \Omega_\iota \cup \Gamma_\iota, \Gamma_\iota$ is the boundary of Ω_ι, and $I_{\mathrm{c}\iota}$ is the index set corresponding to $\varepsilon_{\mathrm{c}\iota}$ so $\varepsilon_{\mathrm{c}\iota} = \{\Omega_\kappa | \kappa \in I_{\mathrm{c}\iota}\}$. $\varepsilon_{\mathrm{c}\iota}$ is the set of entities that form an internal boundary for entity Ω_ι.

For compositional systems, it is necessary to describe the species present in the system, which we define as the set S with index set I_S. Correspondingly, the set of species in entity Ω_ι is S_ι with index set $I_{S\iota}$. It follows that $\mathrm{S} = \cup_{\iota \in I} S_\iota$ and $I_S = \cup_{\iota \in I} I_{S\iota}$.

3 Conservation and Balance Equations

Conservation of mass, momentum, and energy and balance of entropy equations have been derived for phase volumes, interfaces, and common curves based upon averaging of microscale equations and localization approaches [17]. In the averaging approach, microscale equations are typically integrated over a representative region in space and simplified using transport and divergence theorems. Such a procedure can be applied for each entity type and quantity of concern. Both significant manipulation and care are required if precise definitions of all variables in terms of microscale quantities is a desired result; such a connection is a goal of this work. The sections that follow detail the formulation of a full set of macroscale conservation and balance equations for species in entities. These conservation and balance equations are building blocks needed to formulate complete, closed, macroscale models. These models are general in form and under-determined, which is indicative of the closure problem that the TCAT approach is used to resolve.

3.1 Energy for a Phase Volume

For reasons that will become clear in the following section, we first consider the conservation of energy for a species in a phase volume. The approach to be employed is to start from the accepted microscale conservation of energy equation for a species and average this equation to the macroscale. Then the macroscale equation is simplified using available theorems to yield a final, general conservation equation.

The point microscale conservation of energy equation for a species i in phase volume entity ι may be written as

$$\begin{aligned}&\frac{\partial}{\partial t}\left(E_{i\iota}+\tfrac{1}{2}\rho_\iota\omega_{i\iota}\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}\right)+\nabla\cdot\left[\left(E_{i\iota}+\tfrac{1}{2}\rho_\iota\omega_{i\iota}\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}\right)\mathbf{v}_{i\iota}\right]\\ &\quad-\nabla\cdot(\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota})-\rho_\iota\omega_{i\iota}\mathbf{g}_{i\iota}\cdot\mathbf{v}_{i\iota}-h_{i\iota}-e_{Ti\iota}=0,\quad\text{for }\iota\in I_P\end{aligned}\tag{7}$$

for

$$e_{Ti\iota}=e_{i\iota}+\mathbf{v}_{i\iota}\cdot\mathbf{p}_{i\iota}+\frac{\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}}{2}r_{i\iota}\tag{8}$$

where $E_{i\iota}$ is the internal energy density (the internal energy of species i in entity ι per volume of entity ι), t is time, ρ_ι is the mass density (the mass of entity ι per volume of entity ι), $\omega_{i\iota}$ is the species i mass fraction (the mass of species i per total mass of entity ι), $\mathbf{v}_{i\iota}$ is the velocity vector for species i in entity ι, $\mathbf{t}_{i\iota}$ is the stress tensor associated with species i in entity ι, $\mathbf{q}_{i\iota}$ is the heat flux vector associated with species i in entity ι, $\mathbf{g}_{i\iota}$ is an acceleration vector impacting species i in entity ι due to an external force (e.g., gravity), $h_{i\iota}$ is the heat source density associated with species i in entity ι, $e_{Ti\iota}$ is the total energy density gained by species i within entity ι due to internal energy exchange, work due to the presence of all other species that exist in entity ι, and chemical reactions. These intra-entity exchange processes are accounted for, respectively, by the three terms on the right of Eq. (8). The fact that the phase and species qualifiers are subscripts denotes that the quantities being considered are microscale quantities.

Eq. (7) can be put into total energy form by relating the acceleration potential to the acceleration vector and performing some straightforward manipulations. With this as our goal, the relation between the acceleration vector, $\mathbf{g}_{i\iota}$, and its potential, $\psi_{i\iota}$, can be expressed as

$$\rho_\iota\omega_{i\iota}\mathbf{g}_{i\iota}\cdot\mathbf{v}_{i\iota}=-\rho_\iota\omega_{i\iota}\nabla\psi_{i\iota}\cdot\mathbf{v}_{i\iota}\tag{9}$$

A sum of three time derivatives that is equal to zero by the product rule may be added to the left side of this equation to yield

$$\frac{\partial(\rho_\iota\omega_{i\iota}\psi_{i\iota})}{\partial t}-\psi_{i\iota}\frac{\partial(\rho_\iota\omega_{i\iota})}{\partial t}-\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\rho_\iota\omega_{i\iota}\mathbf{g}_{i\iota}\cdot\mathbf{v}_{i\iota}=-\rho_\iota\omega_{i\iota}\nabla\psi_{i\iota}\cdot\mathbf{v}_{i\iota}\tag{10}$$

Rewriting the right side of this equation by application of the product rule, we obtain

$$\begin{aligned}&\tfrac{\partial(\rho_\iota\omega_{i\iota}\psi_{i\iota})}{\partial t}-\psi_{i\iota}\tfrac{\partial(\rho_\iota\omega_{i\iota})}{\partial t}-\rho_\iota\omega_{i\iota}\tfrac{\partial\psi_{i\iota}}{\partial t}+\rho_\iota\omega_{i\iota}\mathbf{g}_{i\iota}\cdot\mathbf{v}_{i\iota}=\\ &\quad-\nabla\cdot(\rho_\iota\omega_{i\iota}\psi_{i\iota}\mathbf{v}_{i\iota})+\psi_{i\iota}\nabla\cdot(\rho_\iota\omega_{i\iota}\mathbf{v}_{i\iota})\end{aligned}\tag{11}$$

The microscale mass conservation equation for a species in a phase volume is

$$\frac{\partial(\rho_\iota\omega_{i\iota})}{\partial t}+\nabla\cdot(\rho_\iota\omega_{i\iota}\mathbf{v}_{i\iota})-r_{i\iota}=0\tag{12}$$

Combination of Eq. (11) and Eq. (12) gives

$$\rho_\iota\omega_{i\iota}\mathbf{g}_{i\iota}\cdot\mathbf{v}_{i\iota}=-\frac{\partial(\rho_\iota\omega_{i\iota}\psi_{i\iota})}{\partial t}+\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}-\nabla\cdot(\rho_\iota\omega_{i\iota}\psi_{i\iota}\mathbf{v}_{i\iota})+\psi_{i\iota}r_{i\iota}\tag{13}$$

which may be substituted into Eq. (7) to give a total energy equation

$$\begin{aligned}&\frac{\partial}{\partial t}\left(E_{i\iota}+\tfrac{1}{2}\rho_\iota\omega_{i\iota}\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}+\rho_\iota\omega_{i\iota}\psi_{i\iota}\right)\\ &\quad+\nabla\cdot\left[\left(E_{i\iota}+\tfrac{1}{2}\rho_\iota\omega_{i\iota}\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}+\rho_\iota\omega_{i\iota}\psi_{i\iota}\right)\mathbf{v}_{i\iota}\right]-\nabla\cdot(\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota})\\ &\quad-h_{i\iota}-e_{Ti\iota}-\psi_{i\iota}r_{i\iota}-\rho_\iota\omega_{i\iota}\tfrac{\partial\psi_{i\iota}}{\partial t}=0,\quad\text{for }\iota\in I_{\mathrm{P}}\end{aligned}\tag{14}$$

or

$$\begin{aligned}&\tfrac{\partial E_{Ti\iota}}{\partial t}+\nabla\cdot(E_{Ti\iota}\mathbf{v}_{i\iota})-\nabla\cdot(\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota})-h_{i\iota}\\ &\quad-e_{Ti\iota}-\psi_{i\iota}r_{i\iota}-\rho_\iota\omega_{i\iota}\tfrac{\partial\psi_{i\iota}}{\partial t}=0,\quad\text{for }\iota\in I_{\mathrm{P}}\end{aligned}\tag{15}$$

where

$$E_{Ti\iota}=E_{i\iota}+\frac{1}{2}\rho_\iota\omega_{i\iota}\mathbf{v}_{i\iota}\cdot\mathbf{v}_{i\iota}+\rho_\iota\omega_{i\iota}\psi_{i\iota} \tag{16}$$

Our objective is to upscale Eq. (15) from the microscale to the macroscale to obtain a conservation of energy equation for a species in a phase volume. There are multiple approaches to accomplish this objective. We will average Eq. (15) directly to the macroscale using the averaging operator defined by [25]

$$\langle\mathscr{P}_i\rangle_{\Omega_\iota,\Omega_\kappa,W}=\frac{\int\limits_{\Omega_\iota}W\mathscr{P}_i\mathrm{d}\mathbf{r}}{\int\limits_{\Omega_\kappa}W\mathrm{d}\mathbf{r}} \tag{17}$$

where $\mathscr{P}_i$ is a property to be averaged to the macroscale, the subscripts on the operator correspond to the domains of integration, and the weighting function, respectively, and $\Omega_\iota,\Omega_\kappa \in \varepsilon_P \cup \varepsilon_I \cup \varepsilon_C$. If the weighting function subscript is omitted, it is assumed to be equal to unity.

To extend Eq. (17) to cases in which $\Omega_\iota \in \varepsilon_{Pt}$ and/or $\Omega_\kappa \in \varepsilon_{Pt}$, the integrals over a common point domain are replaced by discrete sums, for example

$$\int\limits_{\Omega_\iota}W\mathscr{P}_i\mathrm{d}\mathbf{r}\equiv\sum_{l\in I_{\mathrm{Pt}\iota}}W\mathscr{P}_i\Big|_{\Omega_{\iota l}} \tag{18}$$

where $I_{\mathrm{Pt}\iota}$ is the index set of all microscale points in the representative elementary volume (REV) that describes Ω_ι, and $\Omega_{\iota l}$ is a single qualified point such that $\Omega_\iota = \cup_{l\in I_{\mathrm{Pt}\iota}} \Omega_{\iota l}$.

We will encounter four types of macroscale variables: intrinsic averages of the form

$$f^\iota=\langle f_\iota\rangle_{\Omega_\iota,\Omega_\iota} \tag{19}$$

mass averages of the form

$$f^{\bar{\iota}}=\langle f_\iota\rangle_{\Omega_\iota,\Omega_\iota,\rho_\iota} \tag{20}$$

species mass averages of the form

$$f^{\overline{i\iota}}=\langle f_\iota\rangle_{\Omega_\iota,\Omega_\iota,\rho_\iota\omega_{i\iota}} \tag{21}$$

and double-barred averages such as $f^{\bar{\bar{\iota}}}$, which require a special definition for each occurrence due to their non-standard form. In the preceding definition equations, f is considered a general property; and superscripted quantities with specific adornments denote the specific type of averaged macroscale quantities.

Application of the averaging operator defined by Eq. (17) to Eq. (15) gives

$$\begin{aligned}&\langle\frac{\partial E_{Ti\iota}}{\partial t}\rangle_{\Omega_\iota,\Omega}+\langle\nabla\cdot(E_{Ti\iota}\mathbf{v}_{i\iota})-\nabla\cdot(\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota})\rangle_{\Omega_\iota,\Omega}\\&\quad-\langle h_{i\iota}+e_{Ti\iota}+\psi_{i\iota}r_{i\iota}+\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\rangle_{\Omega_\iota,\Omega}=0,\quad\text{for }\iota\in I_{\mathrm{P}}\end{aligned} \tag{22}$$

Eq. (22) is an expression involving integrals of differential quantities, which in general are not easily measurable quantities. Instead, we wish to derive macroscale conservation equations that involve conservation of macroscale quantities averaged from the microscale. Put another way, we wish to reverse the order of integration and differentiation to yield more accessible models that are still exact statements of conservation principles. To accomplish this goal, we rely upon available theorems [1,21,27], namely

Theorem 1 (D[3,(3,0),0])

$$\langle \nabla \cdot \mathbf{f}_\iota \rangle_{\Omega_\iota,\Omega} = \nabla \cdot \langle \mathbf{f}_\iota \rangle_{\Omega_\iota,\Omega} + \sum_{\kappa \in I_{c\iota}} \langle \mathbf{n}_\iota \cdot \mathbf{f}_\iota \rangle_{\Omega_\kappa,\Omega} \tag{23}$$

Theorem 2 (T[3,(3,0),0])

$$\left\langle \frac{\partial f_\iota}{\partial t} \right\rangle_{\Omega_\iota,\Omega} = \frac{\partial}{\partial t} \langle f_\iota \rangle_{\Omega_\iota,\Omega} - \sum_{\kappa \in I_{c\iota}} \langle \mathbf{n}_\iota \cdot \mathbf{v}_\kappa f_\iota \rangle_{\Omega_\kappa,\Omega} \tag{24}$$

where $\mathbf{n}_\iota$ is the outward normal vector from phase volume ι and $\mathbf{n}_\iota \cdot \mathbf{v}_\kappa$ is both the normal component of the velocity of the κ interface and the normal component of the velocity of the material in the κ interface. The summation in these equations indicates that the surface integrations are performed over all interfaces between the ι phase and all other phases that come into contact with the ι phase (i.e., the interfaces which form the members of the connected set $I_{c\iota}$).

Evaluating some of the averaging operators in Eq. (22), applying Theorems 1 and 2, and rewriting the product of the acceleration potential and reactions in macroscale mass-averaged form, we obtain

$$\begin{aligned}
&\frac{\partial E_T^{\overline{\overline{i\iota}}}}{\partial t} + \nabla \cdot \langle (E_{Ti\iota} \mathbf{v}_{i\iota} - \mathbf{t}_{i\iota} \cdot \mathbf{v}_{i\iota} - \mathbf{q}_{i\iota}) \rangle_{\Omega_\iota,\Omega} - \epsilon^\iota h^{i\iota} - \epsilon^\iota e_T^{i\iota} \\
&\quad - \epsilon^\iota \psi^{\overline{i\iota}} r^{i\iota} - \left\langle \left(\psi_{i\iota} - \psi^{\overline{i\iota}} \right) r_{i\iota} \right\rangle_{\Omega_\iota,\Omega} - \left\langle \rho_\iota \omega_{i\iota} \frac{\partial \psi_{i\iota}}{\partial t} \right\rangle_{\Omega_\iota,\Omega} \\
&\quad - \sum_{\kappa \in I_{c\iota}} \langle \mathbf{n}_\iota \cdot [E_{Ti\iota} (\mathbf{v}_\kappa - \mathbf{v}_{i\iota}) + \mathbf{t}_{i\iota} \cdot \mathbf{v}_{i\iota} + \mathbf{q}_{i\iota}] \rangle_{\boldsymbol{\Omega}_\kappa,\boldsymbol{\Omega}} = 0, \quad \text{for } \iota \in I_{\mathrm{P}}
\end{aligned} \tag{25}$$

where

$$E_T^{\overline{\overline{i\iota}}} = \langle E_{Ti\iota} \rangle_{\Omega_\iota,\Omega} \tag{26}$$

$$\varepsilon^\iota e_T^{i\iota} = \langle e_{Ti\iota} \rangle_{\Omega_\iota,\Omega} \tag{27}$$

$$\varepsilon^\iota r^{i\iota} = \langle r_{i\iota} \rangle_{\Omega_\iota,\Omega} \tag{28}$$

Note that the total energy may be written as

$$E_T^{\overline{\overline{i\iota}}} = \left\langle E_{i\iota} + \frac{1}{2} \rho_\iota \omega_{i\iota} \mathbf{v}_{i\iota} \cdot \mathbf{v}_{i\iota} + \rho_\iota \omega_{i\iota} \psi_{i\iota} \right\rangle_{\Omega_\iota,\Omega} \tag{29}$$

which may be expanded to

$$E_T^{\overline{\overline{i\iota}}} = \left\langle E_{i\iota} + \frac{1}{2} \rho_\iota \omega_{i\iota} \left[\mathbf{v}^{\overline{i\iota}} + \left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}} \right) \right] \cdot \left[\mathbf{v}^{\overline{i\iota}} + \left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}} \right) \right] \right\rangle_{\Omega_\iota,\Omega} + \langle \rho_\iota \omega_{i\iota} \psi_{i\iota} \rangle_{\Omega_\iota,\Omega} \tag{30}$$

and simplified to

$$E_T^{\overline{\overline{i\iota}}} = \varepsilon^\iota E^{i\iota} + \varepsilon^\iota \rho^\iota \omega^{\overline{i\iota}} \left(\frac{\mathbf{v}^{\overline{i\iota}} \cdot \mathbf{v}^{\overline{i\iota}}}{2} + K_E^{\overline{\overline{i\iota}}} + \psi^{\overline{i\iota}} \right) \tag{31}$$

where

$$K_E^{\overline{\overline{i\iota}}} = \frac{1}{2} \left\langle \left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}} \right) \cdot \left(\mathbf{v}_{i\iota} - \mathbf{v}^{\overline{i\iota}} \right) \right\rangle_{\Omega_\iota,\boldsymbol{\Omega}_\iota,\rho_\iota \omega_{i\iota}} \tag{32}$$

Now consider the divergence term in Eq. (25), which can be expanded to

$$\begin{aligned}&\nabla\cdot\langle(E_{Ti\iota}\mathbf{v}_{i\iota}-\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}-\mathbf{q}_{i\iota})\rangle_{\Omega_\iota,\Omega}=\\&\quad\nabla\cdot\left\langle\left[\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}+\left(\frac{E_{Ti\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\right]\rho_\iota\omega_{i\iota}\left[\mathbf{v}^{\overline{i\iota}}+\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\right\rangle_{\Omega_\iota,\Omega}\\&\quad-\nabla\cdot\left\langle\left\{\mathbf{t}_{i\iota}\cdot\left[\mathbf{v}^{\overline{i\iota}}+\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]+\mathbf{q}_{i\iota}\right\}\right\rangle_{\Omega_\iota,\Omega}\end{aligned}\tag{33}$$

or

$$\begin{aligned}&\nabla\cdot\langle(E_{Ti\iota}\mathbf{v}_{i\iota}-\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}-\mathbf{q}_{i\iota})\rangle_{\Omega_\iota,\Omega}=\\&\nabla\cdot\left\langle\left[\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\rho_\iota\omega_{i\iota}\mathbf{v}^{\overline{i\iota}}+\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\right\rangle_{\Omega_\iota,\Omega}\\&+\nabla\cdot\left\langle\left(\frac{E_{Ti\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\rho_\iota\omega_{i\iota}\mathbf{v}^{\overline{i\iota}}\right\rangle_{\Omega_\iota,\Omega}\\&+\nabla\cdot\left\langle\left(\frac{E_{Ti\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}\\&-\nabla\cdot\left\langle\left\{\mathbf{t}_{i\iota}\cdot\left[\mathbf{v}^{\overline{i\iota}}+\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]+\mathbf{q}_{i\iota}\right\}\right\rangle_{\Omega_\iota,\Omega}\end{aligned}\tag{34}$$

Note that

$$\left\langle\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}=0\tag{35}$$

$$\left\langle\left(\frac{E_{Ti\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\rho_\iota\omega_{i\iota}\mathbf{v}^{\overline{i\iota}}\right\rangle_{\Omega_\iota,\Omega}=0\tag{36}$$

which allows for

$$\begin{aligned}&\nabla\cdot\langle(E_{Ti\iota}\mathbf{v}_{i\iota}-\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}-\mathbf{q}_{i\iota})\rangle_{\Omega_\iota,\Omega}=\\&\quad\nabla\cdot\left(E_T^{\overline{\overline{i\iota}}}\mathbf{v}^{\overline{i\iota}}\right)+\nabla\cdot\left\langle\left[\left(\frac{E_{Ti\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\right\rangle_{\Omega_\iota,\Omega}\\&\quad-\nabla\cdot\left(\varepsilon^\iota\mathbf{t}^{i\iota}\cdot\mathbf{v}^{\overline{i\iota}}+\varepsilon^\iota\mathbf{q}^{i\iota}\right)-\nabla\cdot\left\langle\mathbf{t}_{i\iota}\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}\end{aligned}\tag{37}$$

The fluctuation product term may be expanded as

$$\begin{aligned}&\nabla\cdot\left\langle\left[\left(\frac{E_{Ti\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\right\rangle_{\Omega_\iota,\Omega}=\\&\quad\nabla\cdot\left\langle\left\{\frac{E_{i\iota}}{\rho_\iota\omega_{i\iota}}+\frac{1}{2}\left[\mathbf{v}^{\overline{i\iota}}+\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\cdot\left[\mathbf{v}^{\overline{i\iota}}+\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\right\}\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}\\&\quad+\nabla\cdot\left\langle\left(\psi_{i\iota}-\frac{E^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}-\frac{\mathbf{v}^{\overline{i\iota}}\cdot\mathbf{v}^{\overline{i\iota}}}{2}-K_E^{\overline{\overline{i\iota}}}-\psi^{\overline{i\iota}}\right)\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}\end{aligned}\tag{38}$$

and simplified to

$$\begin{aligned}&\nabla\cdot\left\langle\left[\left(\frac{E_{Ti\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\right\rangle_{\Omega_\iota,\Omega}=\\&\quad\nabla\cdot\left\langle\left[\frac{E_{i\iota}}{\rho_\iota\omega_{i\iota}}+\mathbf{v}^{\overline{i\iota}}\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)+\frac{1}{2}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}\\&\quad+\nabla\cdot\left\langle\left(\psi_{i\iota}-\frac{E^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}-K_E^{\overline{\overline{i\iota}}}-\psi^{\overline{i\iota}}\right)\rho_\iota\omega_{i\iota}\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega}\end{aligned}\tag{39}$$

Combining Eq. (25), Eq. (37), and Eq. (39) yields

$$\begin{aligned}&\frac{\partial E_T^{\overline{\overline{i\iota}}}}{\partial t}+\nabla\cdot\left(E_T^{\overline{\overline{i\iota}}}\mathbf{v}^{\overline{i\iota}}-\varepsilon^\iota\mathbf{t}^{\overline{\overline{i\iota}}}\cdot\mathbf{v}^{\overline{i\iota}}-\varepsilon^\iota\mathbf{q}^{\overline{\overline{i\iota}}}\right)-\varepsilon^\iota h^{i\iota}-\varepsilon^\iota e_T^{i\iota}\\&-\varepsilon^\iota\psi^{\overline{i\iota}}r^{i\iota}-\langle\left(\psi_{i\iota}-\psi^{\overline{i\iota}}\right)\ r_{i\iota}\rangle_{\Omega_\iota,\Omega}-\langle\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\rangle_{\Omega_\iota,\Omega}\\&-\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot[\,E_{Ti\iota}(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})+\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota}]\rangle_{\Omega_\kappa,\Omega}=0\end{aligned}\tag{40}$$

where

$$\varepsilon^\iota\mathbf{t}^{\overline{\overline{i\iota}}}=\varepsilon^\iota\mathbf{t}^{\overline{\overline{i\iota}}}-\langle\rho_\iota\omega_{i\iota}\,(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})\,(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})\rangle_{\Omega_\iota,\Omega}\tag{41}$$

and

$$\begin{aligned}\varepsilon^\iota\mathbf{q}^{\overline{\overline{i\iota}}}=\varepsilon^\iota\mathbf{q}^{i\iota}&-\langle\left(\frac{E_{i\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E^{\overline{i\iota}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\quad\rho_\iota\omega_{i\iota}\quad(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})\rangle_{\Omega_\iota,\Omega}\\&-\langle\left[\frac{1}{2}(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})\cdot(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})-K_E^{\overline{\overline{i\iota}}}\right]\quad\rho_\iota\omega_{i\iota}\quad(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})\rangle_{\Omega_\iota,\Omega}\\&-\langle\left(\psi_{i\iota}-\psi^{\overline{i\iota}}\right)\quad\rho_\iota\omega_{i\iota}\quad(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})-\mathbf{t}_{i\iota}\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\rangle_{\Omega_\iota,\Omega}\end{aligned}\tag{42}$$

The summation term in Eq. (40) that accounts for the exchange of energy across the connected set of entities can be put in a more convenient form. For the phase volume being considered here, the connected entity set involves interfaces between the phase being considered and all other phases with which it may come into contact. Energy may be transfered due to mass exchange, interfacial stress, and heat transfer. Interfacial stress also results in a transfer of momentum across an interface. Mass exchange across an interface also gives rise to interfacial contributions to both momentum and mass exchange. Because of the repeated appearance of certain exchange terms, it is desirable to seek a notational form that conveniently allows for the reuse of key quantities.

Expansion of the boundary exchange terms from Eq. (40) gives

$$\begin{aligned}&\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot[\,E_{Ti\iota}\,(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})+\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota}]\rangle_{\Omega_\kappa,\Omega}=\\&\quad\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\rho_\iota\omega_{i\iota}\quad\left[\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}+\left(\frac{E_{Ti\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\right](\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\left\{\mathbf{t}_{i\iota}\cdot\left[\mathbf{v}^{\overline{i\iota}}+(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})\right]+\mathbf{q}_{i\iota}\right\}\rangle_{\Omega_\kappa,\Omega}\end{aligned}\tag{43}$$

Part of the first term on the right side of Eq. (43)) can be expressed as a product of a macroscopic quantity and a mass exchange term across an interface giving

$$\begin{aligned}&\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot[\,E_{Ti\iota}\,(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\,+\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota}]\rangle_{\Omega_\kappa,\Omega}=\\&\quad\sum_{\kappa\in I_{c\iota}}\left(\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\langle\mathbf{n}_\iota\cdot\rho_\iota\omega_{i\iota}\,(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\rho_\iota\omega_{i\iota}\left(\frac{E_{Ti\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\left\{\mathbf{t}_{i\iota}\cdot[\,\mathbf{v}^{\overline{i\iota}}+(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})]+\mathbf{q}_{i\iota}\right\}\rangle_{\Omega_\kappa,\Omega}\end{aligned}\tag{44}$$

Expanding the total energy in the second term on the right side of this equation gives

$$\begin{aligned}
&\sum_{\kappa\in I_{c\iota}}\langle \mathbf{n}_\iota\cdot[E_{Ti\iota}\,(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})+\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota}]\rangle_{\Omega_\kappa,\Omega}=\\
&\quad\sum_{\kappa\in I_{c\iota}}\left(\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\quad\langle\mathbf{n}_\iota\cdot\rho_\iota\omega_{i\iota}\,(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\rho_\iota\omega_{i\iota}\quad\left(\frac{E_{i\iota}}{\rho_\iota\omega_{i\iota}}+\psi_{i\iota}-\frac{E^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}-\psi^{\overline{i\iota}}\right)(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_k,\Omega}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\left\{\frac{\rho_\iota\omega_{i\iota}}{2}\left[\mathbf{v}^{\overline{i\iota}}+(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})\right]\cdot\left[\mathbf{v}^{\overline{i\iota}}+(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})\right]\right\}(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\
&\quad-\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_i\cdot\rho_\iota\omega_{i\iota}\quad\left(\frac{\mathbf{v}^{\overline{i\iota}}\cdot\mathbf{v}^{\overline{i\iota}}}{2}+K_E^{\overline{\overline{i\iota}}}\right)(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\left\{\mathbf{t}_{i\iota}\cdot[\mathbf{v}^{\overline{i\iota}}+(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}})]+q_{i\iota}\right\}\rangle_{\Omega_\kappa,\Omega}
\end{aligned}\tag{45}$$

Simplifying Eq. (45)) yields

$$\begin{aligned}
&\sum_{\kappa\in I_{c\iota}}\langle \mathbf{n}_\iota\cdot[E_{Ti\iota}(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})+\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota}]\rangle_{\Omega_\kappa,\Omega}=\\
&\quad\sum_{\kappa\in I_{c\iota}}\left(\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\quad\langle\mathbf{n}_\iota\cdot\rho_\iota\omega_{i\iota}\,(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\rho_\iota\omega_{i\iota}\quad\left(\frac{E_{i\iota}}{\rho_\iota\omega_{i\iota}}+\psi_{i\iota}-\frac{E^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}-\psi^{\overline{i\iota}}\right)\quad(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_k,\Omega}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\left\{\frac{\rho_\iota\omega_{i\iota}}{2}\left[2\mathbf{v}^{\overline{i\iota}}\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)+\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\right\}(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\
&\quad-\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_i\cdot\rho_\iota\omega_{i\iota}K_E^{\overline{\overline{i\iota}}}(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\left\{\mathbf{t}_{i\iota}\cdot\left[\mathbf{v}^{\overline{i\iota}}+\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]+\mathbf{q}_{i\iota}\right\}\rangle_{\Omega_\kappa,\Omega}
\end{aligned}\tag{46}$$

Rearranging Eq. (46) to separate out a macroscale multiple of the momentum exchange terms gives

$$\begin{aligned}
&\sum_{\kappa\in I_{c\iota}}\langle \mathbf{n}_\iota\cdot[E_{Ti\iota}\,(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})+\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota}]\rangle_{\Omega_\kappa,\Omega}=\\
&\quad\sum_{\kappa\in I_{c\iota}}\left(\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\quad\langle\mathbf{n}_\iota\cdot\rho_\iota\omega_{i\iota}\,(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\left[\mathbf{t}_{i\iota}+\rho_\iota\omega_{i\iota}\,(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\rangle_{\Omega_k,\Omega}\cdot\mathbf{v}^{\overline{i\iota}}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\rho_\iota\omega_{i\iota}\quad\left(\frac{E_{i\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}+\psi_{i\iota}-\psi^{\overline{i\iota}}\right)\quad(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_i\cdot\left\{\rho_\iota\omega_{i\iota}\quad\left[\frac{\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)}{2}-K_E^{\overline{\overline{i\iota}}}\right]\right\}\quad(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\langle\mathbf{n}_\iota\cdot\left[\mathbf{t}_{i\iota}\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)+\mathbf{q}_{i\iota}\right]\rangle_{\Omega_\kappa,\Omega}
\end{aligned}\tag{47}$$

Since Eq. (47) contains macroscale products of mass and momentum exchange terms, we can introduce the shorthand notation

$$\sum_{\kappa\in I_{c\iota}}\langle \mathbf{n}_\iota\cdot[E_{Ti\iota}(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})+\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota}]\rangle_{\Omega_\kappa,\Omega}=\sum_{\kappa\in I_{c\iota}}\left[\left(\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\overset{i\kappa\to i\iota}{M}+\sum_{j\in I_s}\left(\overset{j\kappa\to i\iota}{\mathbf{T}}\cdot\mathbf{v}^{\overline{i\iota}}+\overset{j\kappa\to i\iota}{Q}\right)\right] \tag{48}$$

where

$$\overset{i\kappa\to i\iota}{M}=\langle\rho_\iota\omega_{i\iota}\mathbf{n}_\iota\cdot(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega},\quad \text{for}\quad \dim\Omega_\iota>\dim\Omega_\kappa \tag{49}$$

$$\begin{aligned}\overset{j\kappa\to i\iota}{\mathbf{T}}&=\langle \underset{j\kappa\to i\iota}{Z_T}\,\mathbf{n}_\iota\cdot\mathbf{t}_{i\iota}\rangle_{\Omega_\kappa,\Omega}\\&+\delta_{ij}\langle\mathbf{n}_i\cdot\left[\rho_\iota\omega_{i\iota}(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right]\rangle_{\Omega_\kappa,\Omega},\quad\text{for}\quad\dim\Omega_\iota>\dim\Omega_\kappa\end{aligned} \tag{50}$$

and

$$\begin{aligned}\overset{j\kappa\to i\iota}{Q}&=\langle\underset{j\kappa\to i\iota}{z_Q}\,\mathbf{n}_\iota\cdot\mathbf{q}_{i\iota}\rangle_{\Omega_\kappa,\Omega}+\langle\underset{j\kappa\to i\iota}{z_T}\,\mathbf{n}_\iota\cdot\mathbf{t}_{i\iota}\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\rangle_{\Omega_\kappa,\Omega}\\&+\delta_{ij}\langle\rho_\iota\omega_{i\iota}\left(\frac{E_{i\iota}}{\rho_\iota\omega_{i\iota}}-\frac{E^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}+\psi_{i\iota}-\psi^{\overline{i\iota}}\right)\mathbf{n}_\iota\cdot(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega}\\&+\delta_{ij}\langle\left\{\rho_\iota\omega_{i\iota}\left[\frac{\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\cdot\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)}{2}-K_E^{\overline{\overline{i\iota}}}\right]\right\}\mathbf{n}_\iota\cdot(\mathbf{v}_\kappa-\mathbf{v}_{i\iota})\rangle_{\Omega_\kappa,\Omega},\\&\text{for }\dim\Omega_\iota>\dim\Omega_\kappa\end{aligned} \tag{51}$$

$\overset{i\kappa\to i\iota}{M}$ represents mass exchange from the κ entity to the *i* species in the ι entity per unit volume per unit time, $\overset{j\kappa\to i\iota}{\mathbf{T}}$ represents momentum transfer from species in the κ entity to the *i* species and ι entity due to stress and deviation from mean processes per unit volume per unit time; $\overset{j\kappa\to i\iota}{Q}$ represents transfer of energy from species in the κ entity to the *i* species in the ι entity resulting from heat energy and deviation from mean processes per unit volume per unit time, and δ_{ij} is the Kronecker delta function. Additionally, when $\dim\Omega_\iota>\dim\Omega_\kappa$

$$\underset{j\kappa\to i\iota}{z_T}=\underset{j\kappa\to i\iota}{z_Q}=\delta_{ij} \tag{52}$$

These definitions of $\underset{j\kappa\to i\iota}{z_T}$ and $\underset{j\kappa\to i\iota}{z_Q}$ always apply when ι is a phase volume entity, and these quantities represent the fractional contribution of stress and heat energy transfer from species in the κ entity that impacts the *i* species in the ι entity. We will examine the conditions on these coefficients for ι referring to an interface or common curve subsequently.

Thus the total energy equation for a species in a phase volume becomes

$$\begin{aligned}&\frac{\partial E_T^{\overline{\overline{i\iota}}}}{\partial t}+\nabla\cdot\left(E_T^{\overline{\overline{i\iota}}}\mathbf{v}^{\overline{i\iota}}-\varepsilon^\iota\mathbf{t}^{\overline{\overline{i\iota}}}\cdot\mathbf{v}^{\overline{i\iota}}-\varepsilon^\iota\mathbf{q}^{\overline{i\iota}}\right)-\varepsilon^\iota h^{\overline{\overline{i\iota}}}\\&-\varepsilon^\iota\left(e_T^{i\iota}+\psi^{\overline{i\iota}}r^{i\iota}\right)-\langle\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\rangle_{\Omega_\iota,\Omega}\\&-\sum_{\kappa\in I_{c\iota}}\left[\left(\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\overset{i\kappa\to i\iota}{M}+\sum_{j\in I_s}\left(\overset{j\kappa\to i\iota}{\mathbf{T}}\cdot\mathbf{v}^{\overline{i\iota}}+\overset{j\kappa\to i\iota}{Q}\right)\right]=0,\quad\text{for }\iota\in I_{\mathrm{P}}\end{aligned} \tag{53}$$

where

$$\varepsilon^\iota h^{\overline{\overline{i\iota}}}=\varepsilon^\iota h^{i\iota}+\langle\left(\psi_{i\iota}-\psi^{\overline{i\iota}}\right)r_{i\iota}\rangle_{\Omega_\iota,\Omega} \tag{54}$$

or in material derivative form

$$\begin{aligned}\varepsilon^{i\iota} = {} & \frac{\mathrm{D}^{\overline{i\iota}} E_T^{\overline{\overline{i\iota}}}}{\mathrm{D}t} + E_T^{\overline{\overline{i\iota}}} \mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I} - \nabla\cdot\left(\varepsilon^\iota \mathbf{t}^{\overline{\overline{i\iota}}}\cdot\mathbf{v}^{\overline{i\iota}} + \varepsilon^\iota \mathbf{q}^{\overline{\overline{i\iota}}}\right) - \varepsilon^\iota h^{\overline{\overline{i\iota}}} \\ & - \varepsilon^\iota\left(e_T^{\overline{\overline{i\iota}}} + \psi^{\overline{i\iota}} r^{i\iota}\right) - \left\langle \rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\right\rangle_{\Omega_\iota,\Omega} \\ & - \sum_{\kappa\in I_{c\iota}} \left[\left(\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\overset{i\kappa\to i\iota}{M} + \sum_{j\in I_s}\left(\overset{j\kappa\to i\iota}{\mathbf{T}}\cdot\mathbf{v}^{\overline{i\iota}} + \overset{j\kappa\to i\iota}{Q}\right)\right] = 0, \quad \text{for } \iota\in I_{\mathrm{P}}\end{aligned} \tag{55}$$

where the material derivative is

$$\frac{\mathrm{D}^{\overline{i\iota}}}{\mathrm{D}t} = \frac{\partial}{\partial t} + \mathbf{v}^{\overline{i\iota}}\cdot\nabla \tag{56}$$

and the rate of strain tensor is defined as

$$\mathbf{d}^{\overline{\overline{i\iota}}} = \frac{1}{2}\left[\nabla\mathbf{v}^{\overline{i\iota}} + \left(\nabla\mathbf{v}^{\overline{i\iota}}\right)^{\mathrm{T}}\right] \tag{57}$$

3.2 Mass and Momentum for a Phase Volume

Continuum mechanical equations must satisfy the axiom of objectivity, which means that all velocities must be referenced to a common frame of reference. Conservation equations must remain valid under a change in the reference velocity. Here we develop the macroscale mass and momentum conservation equations for a phase volume following the approach in [22] that was applied to microscale equations.

If we adjust all velocities in Eq. (55) by subtracting a constant reference velocity **V** then we obtain

$$\begin{aligned}& \frac{\mathrm{D}^{\overline{i\iota}}\left[\varepsilon^\iota E^{i\iota} + \varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\left(\frac{\left(\mathbf{v}^{\overline{i\iota}}-\mathbf{V}\right)\cdot\left(\mathbf{v}^{\overline{i\iota}}-\mathbf{V}\right)}{2} + K_E^{\overline{\overline{i\iota}}} + \psi^{\overline{i\iota}}\right)\right]}{\mathrm{D}t} \\ & + \left[\varepsilon^\iota E^{i\iota} + \varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\left(\frac{\left(\mathbf{v}^{\overline{i\iota}}-\mathbf{V}\right)\cdot\left(\mathbf{v}^{\overline{i\iota}}-\mathbf{V}\right)}{2} + K_E^{\overline{\overline{i\iota}}} + \psi^{\overline{i\iota}}\right)\right] \quad \mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I} \\ & - \nabla\cdot\left[\varepsilon^\iota\mathbf{t}^{\overline{\overline{i\iota}}}\cdot\left(\mathbf{v}^{\overline{i\iota}} - \mathbf{V}\right) + \varepsilon^\iota\mathbf{q}^{\overline{\overline{i\iota}}}\right] - \varepsilon^\iota h^{\overline{\overline{i\iota}}} \\ & - \left\langle e_{Ti\iota} + \left(\frac{\mathbf{v}^{\overline{i\iota}}\cdot\mathbf{v}^{\overline{i\iota}}}{2} - \mathbf{v}_{i\iota}\cdot\mathbf{V} + \frac{\mathbf{V}\cdot\mathbf{V}}{2}\right) \quad r_{i\iota} + \mathbf{v}_{i\iota}\cdot\mathbf{p}_{i\iota} - \mathbf{V}\cdot\mathbf{p}_{i\iota}\right\rangle_{\Omega_\iota,\Omega} \\ & - \varepsilon^\iota\psi^{\overline{i\iota}} r^{\overline{i\iota}} - \left\langle\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t} - \rho_\iota\omega_{i\iota}\nabla\psi_{i\iota}\cdot\mathbf{V}\right\rangle_{\Omega_\iota,\Omega} \\ & - \sum_{\kappa\in I_{c\iota}}\left(\frac{E^{i\iota}}{\rho^\iota\omega^{\overline{i\iota}}} + \frac{\left(\mathbf{v}^{\overline{i\iota}} - \mathbf{V}\right)\cdot\left(\mathbf{v}^{\overline{i\iota}} - \mathbf{V}\right)}{2} + K_E^{\overline{\overline{i\iota}}} + \psi^{\overline{i\iota}}\right)\overset{i\kappa\to i\iota}{M} \\ & - \sum_{\kappa\in I_{c\iota}}\sum_{j\in I_s}\left[\overset{j\kappa\to i\iota}{\mathbf{T}}\cdot\left(\mathbf{v}^{\overline{i\iota}} - \mathbf{V}\right) + \overset{j\kappa\to i\iota}{Q}\right] = 0\end{aligned} \tag{58}$$

Expanding terms and combining quantities such that terms as they originally appeared in Eq. (55) are evident gives

$$\begin{aligned}
&\frac{\mathrm{D}^{\overline{i\iota}}\left[\varepsilon^{\iota}E^{i\iota}+\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\left(\frac{\mathbf{v}^{\overline{i\iota}}\cdot\mathbf{v}^{\overline{i\iota}}}{2}+K_{E}^{\overline{\overline{i\iota}}}+\psi^{\overline{i\iota}}\right)\right]}{\mathrm{D}t}\\
&\quad-\mathbf{V}\cdot\frac{\mathrm{D}^{\overline{i\iota}}\left(\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\mathbf{v}^{\overline{i\iota}}\right)}{\mathrm{D}t}+\left(\frac{\mathbf{V}\cdot\mathbf{V}}{2}\right)\frac{\mathrm{D}^{\overline{i\iota}}\left(\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\right)}{\mathrm{D}t}\\
&\quad+\left[\varepsilon^{\iota}E^{i\iota}+\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\left(\frac{\mathbf{v}^{\overline{i\iota}}\cdot\mathbf{v}^{\overline{i\iota}}}{2}+K_{E}^{\overline{\overline{i\iota}}}+\psi^{\overline{i\iota}}\right)\right]\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}\\
&\quad-\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\mathbf{V}\cdot\mathbf{v}^{\overline{i\iota}}\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}+\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\left(\frac{\mathbf{V}\cdot\mathbf{V}}{2}\right)\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}\\
&\quad-\nabla\cdot\left(\varepsilon^{\iota}\mathbf{t}^{\overline{\overline{i\iota}}}\cdot\mathbf{v}^{\overline{i\iota}}+\varepsilon^{\iota}\mathbf{q}^{\overline{\overline{i\iota}}}\right)+\nabla\cdot\left(\varepsilon^{\iota}\mathbf{t}^{\overline{\overline{i\iota}}}\right)\cdot\mathbf{V}-\varepsilon^{\iota}h^{\overline{\overline{i\iota}}}\\
&\quad-\left\langle e_{Ti\iota}+\left(\frac{\mathbf{v}^{\overline{i\iota}}\cdot\mathbf{v}^{\overline{i\iota}}}{2}-\mathbf{v}_{i\iota}\cdot\mathbf{V}+\frac{\mathbf{V}\cdot\mathbf{V}}{2}\right)r_{i\iota}+\mathbf{v}_{i\iota}\cdot\mathbf{p}_{i\iota}-\mathbf{V}\cdot\mathbf{p}_{i\iota}\right\rangle_{\Omega_{\iota},\Omega}\\
&\quad-\varepsilon^{\iota}\psi^{\overline{i\iota}}r_{i\iota}-\left\langle\rho_{\iota}\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}-\rho_{\iota}\omega_{i\iota}\nabla\psi_{i\iota}\cdot\mathbf{V}\right\rangle_{\Omega_{\iota},\Omega}\\
&\quad-\sum_{\kappa\in I_{c\iota}}\left(\frac{E^{i\iota}}{\rho^{\iota}\omega^{i\bar{\iota}}}+\frac{\mathbf{v}^{\overline{i\iota}}\cdot\mathbf{v}^{\overline{i\iota}}}{2}+K_{E}^{\overline{\overline{i\iota}}}+\psi^{\overline{i\iota}}\right)\overset{i\kappa\to i\iota}{M}\\
&\quad+\sum_{\kappa\in I_{c\iota}}\mathbf{V}\cdot\mathbf{v}^{\overline{i\iota}}\overset{i\kappa\to i\iota}{M}-\sum_{\kappa\in I_{c\iota}}\frac{\mathbf{V}\cdot\mathbf{V}}{2}\overset{i\kappa\to i\iota}{M}\\
&\quad-\sum_{\kappa\in I_{c\iota}}\sum_{j\in I_{s}}\left(\overset{j\kappa\to i\iota}{\mathbf{T}}\cdot\mathbf{v}^{\overline{i\iota}}+\overset{j\kappa\to i\iota}{Q}\right)+\sum_{\kappa\in I_{c\iota}}\sum_{j\in I_{s}}\overset{j\kappa\to i\iota}{\mathbf{T}}\cdot\mathbf{V}=0
\end{aligned}\tag{59}$$

The vector **V** can be made a factor in collecting terms such that Eq. (59) can be written in the form

$$\varepsilon^{i\iota}-\mathbf{V}\cdot P^{i\iota}+\frac{\mathbf{V}\cdot\mathbf{V}}{2}\mathscr{M}^{i\iota}=0\tag{60}$$

where $\varepsilon^{i\iota}$, $\boldsymbol{P}^{i\iota}$, and $\mathfrak{M}^{i\iota}$ are each independent of **V**. Since **V** is an arbitrary constant vector, the null vector is a valid choice. This implies $\varepsilon^{i\iota} = 0$, which we also know to be the case because this condition is identical to the conservation of energy equation as given by Eq. (55). With this condition imposed, Eq. (60) reduces to

$$-\mathbf{V}\cdot\left(P^{i\iota}-\frac{\mathbf{V}}{2}\mathscr{M}^{i\iota}\right)=0\tag{61}$$

Since **V** is an arbitrary vector, it can be chosen to be non-zero and orthogonal to $\boldsymbol{P}^{i\iota}$. Satisfaction of Eq. (61) then requires $\mathfrak{M}^{i\iota} = 0$. Making use of this constraint, we see that since **V** need not be orthogonal to $\boldsymbol{P}^{i\iota}$, $\boldsymbol{P}^{i\iota}$ itself must also equal **0**.

These considerations imply a species conservation of momentum equation of the form

$$\begin{aligned}
P^{i\iota}=&\frac{\mathrm{D}^{\overline{i\iota}}\left(\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\mathbf{v}^{\overline{i\iota}}\right)}{\mathrm{D}t}+\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\mathbf{v}^{\overline{i\iota}}\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}-\nabla\cdot\left(\varepsilon^{\iota}\mathbf{t}^{\overline{\overline{i\iota}}}\right)\\
&-\varepsilon^{\iota}r^{i\iota}\mathbf{v}^{\overline{i\iota}}-\varepsilon^{\iota}\mathbf{p}^{\overline{\overline{i\iota}}}-\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\mathrm{g}^{\overline{i\iota}}-\sum_{\kappa\in I_{c\iota}}\left(\overset{i\kappa\to i\iota}{M}\mathbf{v}^{\overline{i\iota}}+\sum_{j\in I_{s}}\overset{j\kappa\to i\iota}{\mathbf{T}}\right)=0
\end{aligned}\tag{62}$$

and a species conservation of mass equation of the form

$$\mathscr{M}^{i\iota}=\frac{\mathrm{D}^{\overline{i\iota}}\left(\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\right)}{\mathrm{D}t}+\varepsilon^{\iota}\rho^{\iota}\omega^{i\bar{\iota}}\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}-\varepsilon^{\iota}r^{i\iota}-\sum_{\kappa\in I_{c\iota}}\overset{i\kappa\to i\iota}{M}=0\tag{63}$$

where

$$\varepsilon^{\iota}\mathbf{p}^{\overline{\overline{i\iota}}}=\left\langle\mathbf{p}_{i\iota}+\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)r_{i\iota}\right\rangle_{\Omega_{\iota},\Omega}\tag{64}$$

3.3 Entropy for Phase Volume

A microscale balance of entropy equation for a species in a phase volume may be written as

$$\frac{\partial\eta_{i\iota}}{\partial t}+\nabla\cdot(\eta_{i\iota}\mathbf{v}_{i\iota})-\nabla\cdot\varphi_{i\iota}-b_{i\iota}=\Lambda_{i\iota} \tag{65}$$

where $\eta_{i\iota}$ is the entropy of species i in the ι entity per unit volume, $\varphi_{i\iota}$ is the non-advective entropy flux vector associated with species i in entity ι, $b_{i\iota}$ is the entropy source for species i in entity ι, and $\Lambda_{i\iota}$ is the entropy production rate associated with species i in entity ι. Since the entropy balance equation will be expressed in terms of the system for the applications of interest in this work, the contributions to entropy production for species i from other species are included in $\Lambda_{i\iota}$. This is a convention that leads to a shorter equation; we emphasize that the entropy balance subsequently employed is summed over all species and entities.

Application of the averaging operator to Eq. (65) gives

$$\left\langle\frac{\partial\eta_{i\iota}}{\partial t}\right\rangle_{\Omega_\iota,\Omega}+\langle\nabla\cdot(\eta_{i\iota}\mathbf{v}_{i\iota})-\nabla\cdot\varphi_{i\iota}-b_{i\iota}\rangle_{\Omega_\iota,\Omega}=\langle\Lambda_{i\iota}\rangle_{\Omega_\iota,\Omega} \tag{66}$$

Evaluating the averaging operator, applying Theorems 1 and 2, simplifying, and making use of the material derivative gives

$$\frac{\mathrm{D}^{\overline{i\iota}}\eta^{\overline{\overline{i\iota}}}}{\mathrm{D}t}+\eta^{\overline{\overline{i\iota}}}\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}-\nabla\cdot\left(\varepsilon^{\iota}\varphi^{\overline{\overline{i\iota}}}\right)-\varepsilon^{\iota}b^{i\iota}-\sum_{\kappa\in I_{c\iota}}\left(\overset{i\kappa\to i\iota}{M}\frac{\eta^{\overline{\overline{i\iota}}}}{\varepsilon^{\iota}\rho^{\iota}\omega^{\overline{i\iota}}}+\sum_{j\in I_s}\overset{j\kappa\to i\iota}{\Phi}\right)=\Lambda^{\overline{\overline{i\iota}}} \tag{67}$$

where

$$\varepsilon^{\iota}\varphi^{\overline{\overline{i\iota}}}=\left\langle\varphi_{i\iota}-\eta_{i\iota}\quad\left(\mathbf{v}_{i\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_\iota,\Omega} \tag{68}$$

and

$$\overset{j\kappa\to i\iota}{\Phi}=\langle\underset{j\kappa\to i\iota}{z_{\Phi}}\ \mathbf{n}_\iota\cdot\varphi_{i\iota}\rangle_{\Omega_\kappa,\Omega}+\delta_{ij}\left\langle\rho_\iota\omega_{i\iota}\left(\frac{\eta_{i\iota}}{\rho_\iota\omega_{i\iota}}-\frac{\eta^{\overline{\overline{i\iota}}}}{\varepsilon^{\iota}\rho^{\iota}\omega^{\overline{i\iota}}}\right)\quad\mathrm{n}_\iota\cdot(\mathrm{v}_\kappa-\mathrm{v}_{i\iota})\right\rangle_{\Omega_\kappa,\Omega},$$
$$\text{for}\quad\dim\Omega_\iota>\quad\dim\quad\Omega_\kappa \tag{69}$$

The quantity $\overset{j\kappa\to i\iota}{\Phi}$ represents the transfer of entropy from the κ entity to the i species in the ι entity due to processes other than phase change per unit volume per unit time.

3.4 Interfaces, Common Curves, and Common Points

Because the TCAT approach includes entities other than phase volumes, such as interfaces, common curves, and common points, conservation and balance equations for species in these other entities are needed as well. These equations may be derived using different approaches. For example, one could start with the corresponding microscale conservation or balance equation for a species in an entity and average it up to the macroscale or use a localization approach [17]. Alternatively, one could average the microscale equation for a conservation of energy of a species in an entity to the macroscale, apply the axiom of objectivity, and deduce a conservation of mass and momentum equation from the species energy equation, as was done for phase volumes.

Following this latter approach, the microscale conservation of total energy for a species i in an interface ι is

$$\begin{aligned}&\frac{\partial' E_{Ti\iota}}{\partial t}+\nabla'\cdot\left(E_{Ti\iota}\mathbf{v}_{i\iota}\right)-\nabla'\cdot\left(\mathbf{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathbf{q}_{i\iota}\right)-h_{i\iota}\\&\quad-\left(e_{Ti\iota}+\psi_{i\iota}r_{i\iota}\right)-\rho_\iota\omega_{i\iota}\frac{\partial'\psi_{i\iota}}{\partial t}+\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{P}}}\mathbf{n}_\kappa\cdot E_{Ti\kappa}\left(\mathbf{v}_\iota-\mathbf{v}_{i\kappa}\right)\\&\quad+\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{P}}}\sum_{j\in I_{s\kappa}}\mathbf{n}_\kappa\cdot\left(\underset{j\kappa\to i\iota}{z_T}\mathbf{t}_{j\kappa}\cdot\mathbf{v}_{j\kappa}+\underset{j\kappa\to i\iota}{z_{\mathrm{Q}}}\mathbf{q}_{j\kappa}\right)\Big|_{\Omega_\iota}=0,\quad\text{for}\quad\iota\in I_{\mathrm{I}}\end{aligned}\tag{70}$$

where the del operator and partial time derivative in the surface are defined, respectively, as

$$\nabla'=\mathbf{I}'\cdot\nabla\tag{71}$$

$$\frac{\partial'}{\partial t}=\frac{\partial}{\partial t}+\mathbf{v}_\iota\cdot\left(\mathbf{I}-\mathbf{I}'\right)\cdot\nabla\tag{72}$$

where the surface unit tensor is $\mathbf{I}'=\mathbf{I}-\mathbf{n}_\alpha\mathbf{n}_\alpha$ for a surface defined by $\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta$, $\mathbf{n}_\alpha$ is the unit outward normal vector to Ω_α, $I_{s\kappa}$ is the index set of all species in the κ entity, $\underset{j\kappa\to i\iota}{z_T}$ represents the fraction of the stress energy transferred from the *j* species in the κ entity to the ι entity that impacts the *i* species in the ι entity, and $\underset{j\kappa\to i\iota}{z_Q}$ represents the fraction of the heat energy transferred to the *j* species in the κ entity to the ι entity that impacts the *i* species in the ι entity. Because stress energy and heat energy transfer are not confined to the same species in each entity and overall conservation must be preserved, it follows that

$$\sum_{i\in I_{s\iota}}\underset{j\kappa\to i\iota}{z_T}=\sum_{i\in I_{s\iota}}\underset{j\kappa\to i\iota}{z_Q}=1\tag{73}$$

We will apply the averaging operator given by Eq. (17) of the form $\langle\cdot\rangle_{\Omega_\iota,\Omega}$ for $\iota\in I_{\mathrm{I}}$, the index set of all interfaces, to Eq. (70). The result can be simplified using two averaging theorems for surfaces [16,21]

Theorem 3 (D[2,(3,0),0])

$$\langle\nabla'\cdot\mathbf{f}_\iota\rangle_{\Omega_\iota,\Omega}=\nabla\cdot\langle\mathbf{f}'_\iota\rangle_{\Omega_\iota,\Omega}+\langle\left(\nabla'\cdot\mathbf{n}_\alpha\right)\mathbf{n}_\alpha\cdot\mathbf{f}_\iota\rangle_{\Omega_\iota,\Omega}+\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{C}}}\langle\mathbf{n}_\iota\cdot\mathbf{f}_\iota\rangle_{\Omega_\kappa,\Omega}\tag{74}$$

and

Theorem 4 (T[2,(3,0),0])

$$\begin{aligned}&\langle\frac{\partial' f_\iota}{\partial t}\rangle_{\Omega_\iota,\Omega}=\frac{\partial}{\partial t}\langle f_\iota\rangle_{\Omega_\iota,\Omega}+\nabla\cdot\langle\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\mathbf{v}_\iota f_\iota\rangle_{\Omega_\iota,\Omega}\\&\quad-\langle\left(\nabla'\cdot\mathbf{n}_\alpha\right)\quad\mathbf{n}_\alpha\cdot\mathbf{v}_\iota f_\iota\rangle_{\Omega_\iota,\Omega}-\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{c}}}\langle\mathbf{n}_\iota\cdot\mathbf{v}_\kappa f_\iota\rangle_{\Omega_\kappa,\Omega}\end{aligned}\tag{75}$$

where $\iota\in I_{\mathrm{I}},\Omega_\iota=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta,\mathbf{n}_\alpha$ is the outward unit normal vector from phase volume Ω_α, $\mathbf{n}_\iota$ is the outward unit normal vector from the common curve bounding Ω_ι that is tangent to interface Ω_ι, and we employ the following definition

$$\mathbf{f}'_\iota=\mathbf{I}'\cdot\mathbf{f}_\iota=\mathbf{f}_\iota-\mathbf{n}_\alpha\mathbf{n}_\alpha\cdot\mathbf{f}_\iota\tag{76}$$

Performing a set of manipulations similar to those detailed for a phase volume we obtain the macroscale conservation of energy equation for species *i* in interface ι of the form

$$\begin{aligned}
\varepsilon^{i\iota}=&\frac{\mathrm{D}^{\overline{i\iota}}E_T^{\overline{\overline{i\iota}}}}{\mathrm{D}t}+E_T^{\overline{\overline{i\iota}}}\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}-\nabla\cdot\left(\varepsilon^{\iota}\mathbf{t}^{\overline{\overline{i\iota}}}\cdot\mathbf{v}^{\overline{\overline{i\iota}}}+\varepsilon^{\iota}\mathbf{q}^{\overline{\overline{i\iota}}}\right)-\varepsilon^{\iota}h^{\overline{\overline{i\iota}}}\\
&-\varepsilon^{\iota}\left(e_T^{i\iota}+\psi^{\overline{\overline{i\iota}}}r^{i\iota}\right)-\left\langle\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\right\rangle_{\Omega_\iota,\Omega}\\
&-\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{P}}}\left[\left(\frac{E_T^{\overline{\overline{i\kappa}}}}{\varepsilon^{\kappa}\rho^{\kappa}\omega^{\overline{i\kappa}}}\right)\overset{i\kappa\to i\iota}{M}+\sum_{j\in I_s}\left(\overset{j\kappa\to i\iota}{\mathbf{T}}\cdot\mathbf{v}^{\overline{j\kappa}}+\overset{j\kappa\to i\iota}{Q}\right)\right]\\
&-\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{C}}}\left[\left(\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^{\iota}\rho^{\iota}\omega^{\overline{i\iota}}}\right)\overset{i\kappa\to i\iota}{M}+\sum_{j\in I_s}\left(\overset{j\kappa\to i\iota}{\mathbf{T}}\cdot\mathbf{v}^{\overline{i\iota}}+\overset{j\kappa\to i\iota}{Q}\right)\right]=0,\quad\text{for}\quad\iota\in I_{\mathrm{I}}
\end{aligned}\tag{77}$$

where

$$\overset{i\kappa\to i\iota}{M}=-\langle\rho_\kappa\omega_{i\kappa}\mathbf{n}_\kappa\cdot(\mathbf{v}_\iota-\mathbf{v}_{i\kappa})\rangle_{\Omega_\iota,\Omega},\quad\text{for}\dim\Omega_\iota<\dim\Omega_\kappa\tag{78}$$

$$\begin{aligned}
\overset{j\kappa\to i\iota}{\mathbf{T}}=&-\langle\underset{j\kappa\to i\iota}{z_T}\mathbf{n}_\kappa\cdot\mathbf{t}_{j\kappa}\rangle_{\Omega_\iota,\Omega}\\
&-\delta_{ij}\langle\mathbf{n}_\kappa\cdot\left[\rho_\kappa\omega_{i\kappa}(\mathbf{v}_\iota-\mathbf{v}_{i\kappa})\left(\mathbf{v}_{i\kappa}-\mathbf{v}^{\overline{i\kappa}}\right)\right]\rangle_{\Omega_\iota,\Omega},\quad\text{for}\quad\dim\Omega_\iota<\dim\Omega_\kappa
\end{aligned}\tag{79}$$

and

$$\begin{aligned}
\overset{j\kappa\to i\iota}{Q}=&-\langle\underset{j\kappa\to i\iota}{z_Q}\mathbf{n}_\kappa\cdot\mathbf{q}_{j\kappa}\rangle_{\Omega_\iota,\Omega}-\langle\underset{j\kappa\to i\iota}{z_T}\mathbf{n}_\kappa\cdot\mathbf{t}_{j\kappa}\cdot\left(\mathbf{v}_{j\kappa}-\mathbf{v}^{\overline{j\kappa}}\right)\rangle_{\Omega_\iota,\Omega}\\
&-\delta_{ij}\langle\rho_\kappa\omega_{i\kappa}\left(\frac{E_{i\kappa}}{\rho_\kappa\omega_{i\kappa}}-\frac{E^{\overline{\overline{i\kappa}}}}{\varepsilon^{\kappa}\rho^{\kappa}\omega^{\overline{i\kappa}}}+\psi_{i\kappa}-\psi^{\overline{i\kappa}}\right)\mathbf{n}_\kappa\cdot(\mathbf{v}_i-\mathbf{v}_{i\kappa})\rangle_{\Omega_\iota,\Omega}\\
&-\delta_{ij}\langle\left\{\rho_\kappa\omega_{i\kappa}\left[\frac{\left(\mathbf{v}_{i\kappa}-\mathbf{v}^{\overline{i\kappa}}\right)\cdot\left(\mathbf{v}_{i\kappa}-\mathbf{v}^{\overline{i\kappa}}\right)}{2}-K_E^{\overline{\overline{i\kappa}}}\right]\right\}\mathbf{n}_\kappa\cdot(\mathbf{v}_\iota-\mathbf{v}_{i\kappa})\rangle_{\Omega_\iota,\Omega},\\
&\text{for}\quad\dim\Omega_\iota<\dim\Omega_\kappa
\end{aligned}\tag{80}$$

The definitions given by Eq. (78)–Eq. (80) can be compared to those given by Eq. (49)–Eq. (51), and two significant differences can be noted. First, a consistent convention is used in which the integration is performed about the lower dimensional entity and the conserved quantity being transferred is evaluated in the higher dimensional entity at the boundary. Second, because of the convention used, when the exchange of a conserved quantity involves an entity that is of greater dimension than the dimension that the overall conservation equation is being written for, then contributions to stress and heat energy must be accounted for due to the fractional effect of all species in the higher dimensional entity. For the interface case being considered here, the exchange terms between the phase volumes and the interface include such multiple species contributions, which are reflected in the above definitions. Specifically, this is accounted for by the $\underset{j\kappa\to i\iota}{z_T}$ and $\underset{j\kappa\to i\iota}{z_Q}$ terms, which do not reduce to δ_{ij} for this case.

The microscale conservation of total energy equation for a species i in a common curve ι is

$$\begin{aligned}
&\frac{\partial'' E_{Ti\iota}}{\partial t}+\nabla''\cdot(E_{Ti\iota}\mathbf{v}_{i\iota})-\nabla''\cdot(\mathrm{t}_{i\iota}\cdot\mathbf{v}_{i\iota}+\mathrm{q}_{i\iota})-h_{i\iota}\\
&\quad-(e_{Ti\iota}+\psi_{i\iota}r_{i\iota})-\rho_\iota\omega_{i\iota}\frac{\partial''\psi_{i\iota}}{\partial t}+\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{I}}}\mathrm{n}_\kappa\cdot E_{Ti\kappa}(\mathbf{v}_\iota-\mathbf{v}_{i\kappa})\\
&\quad+\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{I}}}\sum_{j\in I_s}\mathrm{n}_\kappa\cdot\left(\underset{j\kappa\to i\iota}{z_T}\mathrm{t}_{j\kappa}\cdot\mathbf{v}_{j\kappa}+\underset{j\kappa\to i\iota}{z_Q}\mathrm{q}_{j\kappa}\right)\Big|_{\Omega_\iota}=0,\quad\text{for }\iota\in I_{\mathrm{C}}
\end{aligned}\tag{81}$$

where

$$\nabla''=\mathbf{n}_\iota\mathbf{n}_\iota\cdot\nabla\tag{82}$$

$$\frac{\partial''}{\partial t}=\frac{\partial}{\partial t}+\mathbf{v}_\iota\cdot(\mathbf{I}-\mathbf{n}_\iota\mathbf{n}_\iota)\cdot\nabla \tag{83}$$

We will also apply the averaging operator given by Eq. (17) of the form $\langle\cdot\rangle_{\Omega_\iota,\Omega}$ for ι ∈ I_C, the index set of all common curves, to Eq. (81). The result will make use of the following two averaging theorems [21]

Theorem 5 (D[1,(3,0),0])

$$\begin{aligned}\langle\nabla''\cdot\mathbf{f}_\iota\rangle_{\Omega_\iota,\Omega}=&\nabla\cdot\langle\mathbf{f}_\iota\rangle_{\Omega_\iota,\Omega}-\nabla\cdot\langle(\mathbf{I}-\mathbf{n}_\iota\mathbf{n}_\iota)\cdot\mathbf{f}_\iota\rangle_{\Omega_\iota,\Omega}\\&-\langle\mathbf{n}_\iota\cdot\nabla''\mathbf{n}_\iota\cdot\mathbf{f}_\iota\rangle_{\Omega_\iota,\Omega}+\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{Pt}}}(\mathbf{e}_\iota\cdot\mathbf{f}_\iota)\big|_{\Omega_\kappa}\end{aligned} \tag{84}$$

and

Theorem 6 (T[1,(3,0),0])

$$\begin{aligned}\langle\frac{\partial''f_\iota}{\partial t}\rangle_{\Omega_\iota,\Omega}=&\frac{\partial}{\partial t}\langle f_\iota\rangle_{\Omega_\iota,\Omega}+\nabla\cdot\langle(\mathbf{I}-\mathbf{n}_\iota\mathbf{n}_\iota)\cdot\mathbf{v}_\iota f_\iota\rangle_{\Omega_\iota,\Omega}\\&+\langle\mathbf{n}_\iota\cdot\nabla''\mathbf{n}_\iota\cdot\mathbf{v}_\iota f_\iota\rangle_{\Omega_\iota,\Omega}-\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{Pt}}}(\mathbf{e}_\iota\cdot\mathbf{v}_\kappa f_\iota)\big|_{\Omega_\kappa}\end{aligned} \tag{85}$$

where ι ∈ I_C, **n**ι is the unit normal vector tangent to common curve Ω_ι, e_ι is the unit vector tangent to common curve Ω_ι oriented positive outward, and

$$\mathbf{f}''=\mathbf{n}_\iota\mathbf{n}_\iota\cdot\mathbf{f} \tag{86}$$

Performing a similar set of manipulations to those detailed for a phase and employed in analyzing an interface, we obtain the macroscale conservation of energy equation for species *i* in common curve ι of the form

$$\begin{aligned}\varepsilon^{i\iota}=&\frac{\mathrm{D}^{\overline{i\iota}}E_T^{\overline{\overline{i\iota}}}}{\mathrm{D}t}+E_T^{\overline{\overline{i\iota}}}\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}-\nabla\cdot\left(\varepsilon^\iota\mathbf{t}^{\overline{\overline{i\iota}}}\cdot\mathbf{v}^{\overline{i\iota}}+\varepsilon^\iota\mathbf{q}^{\overline{\overline{i\iota}}}\right)-\varepsilon^\iota h^{\overline{\overline{i\iota}}}\\&-\varepsilon^\iota\left(e_T^{i\iota}+\psi^{\overline{i\iota}}r^{i\iota}\right)-\langle\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\rangle_{\Omega_\iota,\Omega}\\&-\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{I}}}\left[\left(\frac{E_T^{\overline{\overline{i\kappa}}}}{\varepsilon^\kappa\rho^\kappa\omega^{\overline{i\kappa}}}\right)\overset{i\kappa\to i\iota}{M}+\sum_{j\in I_s}\overset{j\kappa\to i\iota}{\mathbf{T}}\cdot\mathbf{v}^{\overline{j\kappa}}+\overset{j\kappa\to i\iota}{Q}\right]\\&-\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{Pt}}}\left[\left(\frac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\overset{i\kappa\to i\iota}{M}+\sum_{j\in I_s}\left(\overset{j\kappa\to i\iota}{\mathbf{T}}\cdot\mathbf{v}^{\overline{i\iota}}+\overset{j\kappa\to i\iota}{Q}\right)\right]=0,\quad\text{for }\iota\in I_{\mathrm{C}}\end{aligned} \tag{87}$$

where analogous conventions to those used for exchange terms in Eq. (77) also apply to Eq. (87).

A comparison of Eq. (55), Eq. (77), and Eq. (87) reveals that these equations are of a similar form, differing only in the terms that involve the exchange of energy across the boundaries of the respective entities. With appropriate definitions, these equations can be put in the identical form given by

$$\begin{aligned}\varepsilon^{i\iota}=&\frac{\mathrm{D}^{\overline{i\iota}}E_T^{\overline{\overline{i\iota}}}}{\mathrm{D}t}+E_T^{\overline{\overline{i\iota}}}\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}-\nabla\cdot\left(\varepsilon^\iota\mathbf{t}^{\overline{\overline{i\iota}}}\cdot\mathbf{v}^{\overline{i\iota}}+\varepsilon^\iota\mathbf{q}^{\overline{\overline{i\iota}}}\right)-\varepsilon^\iota h^{\overline{\overline{i\iota}}}\\&-\varepsilon^\iota\left(e_T^{i\iota}+\psi^{\overline{i\iota}}r^{i\iota}\right)-\langle\rho_\iota\omega_{i\iota}\frac{\partial\psi_{i\iota}}{\partial t}\rangle_{\Omega_\iota,\Omega}\\&-\sum_{\kappa\in I_{c\iota}}\left[\overset{i\kappa\to i\iota}{M}_{E_i}+\sum_{j\in I_s}\left(\overset{j\kappa\to i\iota}{T}_{\upsilon_i}+\overset{j\kappa\to i\iota}{Q}\right)\right]=0,\quad\text{for}\quad\iota\in I\end{aligned} \tag{88}$$

where

$$\overset{i\kappa\to i\iota}{M}_{E_i}=\begin{cases}\left(\dfrac{E_T^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\overset{i\kappa\to i\iota}{M}, & \text{for}\quad \dim\kappa<\dim\iota\\ \left(\dfrac{E_T^{\overline{\overline{i\kappa}}}}{\varepsilon^\kappa\rho^\kappa\omega^{\overline{i\kappa}}}\right)\overset{i\kappa\to i\iota}{M}, & \text{for}\quad \dim\kappa>\dim\iota\end{cases}\tag{89}$$

$$\overset{j\kappa\to i\iota}{T}_{\upsilon_i}=\begin{cases}\mathbf{v}^{\overline{i\iota}}\cdot\overset{j\kappa\to i\iota}{\mathbf{T}}, & \text{for}\quad \dim\kappa<\dim\iota\\ \mathbf{v}^{\overline{j\kappa}}\cdot\overset{j\kappa\to i\iota}{\mathbf{T}}, & \text{for}\quad \dim\kappa>\dim\iota\end{cases}\tag{90}$$

These exchange terms hold in general for any set of entities, with the proviso that for exchanges that involve common points the averaging operator reduces to a discrete sum as described by Eq. (17) and Eq. (18).

Eq. (88) can be used along with the axiom of objectivity to derive momentum and mass conservation equations for interfaces and common curves in the same manner that Eq. (62)) and Eq. (63) were derived for phases. We obtain the general macroscale conservation of momentum equation for species *i* in entity ι

$$\begin{aligned}P^{i\iota}=&\frac{\mathrm{D}^{\overline{i\iota}}\left(\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\mathbf{v}^{\overline{i\iota}}\right)}{\mathrm{D}t}+\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\mathbf{v}^{\overline{i\iota}}\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}-\nabla\cdot\left(\varepsilon^\iota\mathbf{t}^{\overline{\overline{i\iota}}}\right)-\varepsilon^\iota r^{i\iota}\mathbf{v}^{\overline{i\iota}}-\varepsilon^\iota\mathbf{p}^{\overline{\overline{i\iota}}}\\&-\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}g^{\overline{i\iota}}-\sum_{\kappa\in I_{c\iota}}\left(\overset{i\kappa\to i\iota}{\mathbf{M}}_{\upsilon_i}+\sum_{j\in I_s}\overset{j\kappa\to i\iota}{\mathbf{T}}\right)=0,\quad\text{for }\iota\in I\end{aligned}\tag{91}$$

where

$$\overset{i\kappa\to i\iota}{\mathbf{M}}_{\upsilon_i}=\begin{cases}\overset{i\kappa\to i\iota}{M}\mathbf{v}^{\overline{i\iota}}, & \text{for}\quad \dim\kappa<\dim\iota\\ \overset{i\kappa\to i\iota}{M}\mathbf{v}^{\overline{i\kappa}}, & \text{for}\quad \dim\kappa>\dim\iota\end{cases}\tag{92}$$

and the general macroscale conservation of mass equation for species *i* in entity ι

$$\mathscr{M}^{i\iota}=\frac{\mathrm{D}^{\overline{i\iota}}\left(\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\right)}{\mathrm{D}t}+\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}-\varepsilon^\iota r^{i\iota}-\sum_{\kappa\in I_{c\iota}}\overset{i\kappa\to i\iota}{M}=0,\quad\text{for }\iota\in I\tag{93}$$

Eq. (91)–Eq. (92)) apply for species *i* in any general entity ι where ι refers to a phase, interface, or common curve. We assume that common points will be relatively unimportant for most applications and thus we ignore everything but the exchange terms for these entities. If one wished to develop full conservation equations for common points, additional averaging theorems would be employed to upscale from the microscale to the macroscale.

A general macroscale balance of entropy equation can be derived as well for species *i* in entity ι and is of the form

$$S^{i\iota}=\frac{\mathrm{D}^{\overline{i\iota}}\eta^{\overline{\overline{i\iota}}}}{\mathrm{D}t}+\eta^{\overline{\overline{i\iota}}}\mathbf{d}^{\overline{\overline{i\iota}}}:\mathbf{I}-\nabla\cdot\left(\varepsilon^\iota\varphi^{\overline{\overline{i\iota}}}\right)-\varepsilon^\iota b^{i\iota}-\sum_{\kappa\in I_{c\iota}}\left(\overset{i\kappa\to i\iota}{M}_{\eta_i}+\sum_{j\in I_s}\overset{j\kappa\to i\iota}{\Phi}\right)=\Lambda^{\overline{\overline{i\iota}}}\tag{94}$$

where

$$\overset{i\kappa\to i\iota}{M}_{\eta_i}=\begin{cases}\left(\dfrac{\eta^{\overline{\overline{i\iota}}}}{\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}}\right)\overset{i\kappa\to i\iota}{M}, & \text{for}\quad \dim\kappa<\dim\iota\\ \left(\dfrac{\eta^{\overline{\overline{i\kappa}}}}{\varepsilon^\kappa\rho^\kappa\omega^{\overline{i\kappa}}}\right)\overset{i\kappa\to i\iota}{M}, & \text{for}\quad \dim\kappa>\dim\iota\end{cases}\tag{95}$$

The same comments that were made regarding exchange terms for general conservation equations for common points apply to the balance of entropy for a set of common points.

4 Thermodynamics

4.1 Overview

In the TCAT approach, thermodynamic identities are used to connect the conservations equations to the entropy inequality, which is in turn used to guide the formulation of closed models. Choices exist for the form of the thermodynamics used to develop these identities [22,24]. These choices involve the type of thermodynamics used, which has been discussed previously. The simplest form of thermodynamics that is suitable to our needs is classical irreversible thermodynamics (CIT), described in [10], which was relied upon in deriving closed models for single-fluid-phase flow [19]. While several other choices exist [18], we will restrict our comments herein to CIT. If CIT proves to be inadequate for a system of concern and a more complicated thermodynamic basis is desired, then the notions considered in this section would need to be revisited.

The other choice that must be made is the specific form of the thermodynamics within a given type. Specifically, internal energy can be considered on either a species in an entity or an entity basis, which implies summation over all species. Even if the system consists of multiple species, either approach is still possible. For simplicity, we will restrict our consideration of multispecies systems to those cases in which entity-based expressions for internal energy are adequate. If this proves to be too restrictive, even if CIT is still appropriate, then relationships for the internal energy of individual species would need to be developed at the macroscale. This restriction on entity-based forms of internal energy has implications for the forms of the conservation of energy equation and the properties of the Lagrange multipliers used to augment the entropy inequality and produce a constrained entropy inequality. These considerations are discussed in §5.

With these choices in mind, we focus on two specific thermodynamical aspects that will be important in deriving TCAT models: (1) averaged macroscale expressions that relate material derivatives of internal energy to material derivatives of entropy, mass, and geometric measures for near equilibrium conditions; and (2) a set of thermodynamically based equalities that must hold at equilibrium. The following two sections detail these two classes of equalities and will be relied upon to produce closed multispecies, multiphase models in future work.

4.2 Material Derivatives of Internal Energy

A set of general macroscale expressions for the material derivative of the internal energy of an entity in a multispecies, multiphase system are needed to connect an appropriate set of conservation equations to the system entropy inequality for general TCAT models. The TCAT approach relies upon averaging the microscale thermodynamic relations to the macroscale. The general procedure to accomplish such a formulation was introduced by Gray [15] for single-species entities, while Gray and Schrefler [20] considered a single-species solid phase in detail. Gray and Miller [19] used these conditions to produce a closed TCAT model. What has not yet been accomplished is to average multispecies microscale CIT expressions to the macroscale, which is the current focus. Because the focus of foreseeable TCAT modeling work will be on developing models that do not require the species energy of an entity, we consider only the material derivative of internal energy for an entity. Furthermore, because we do not consider conservation equations for common points; we are only concerned with deriving expressions for phase volumes, interfaces, and common curves. Within phase volumes, different expressions are needed for fluids and solids, due to fundamental differences in the thermomechanical behavior of these two types of materials.

First, consider the microscale fundamental thermodynamic equation for a fluid phase volume [2,6,23]

$$\mathbb{E}_\iota=\mathbb{E}_\iota\left(\mathbb{S}_\iota,V_\iota,\mathbb{M}_{i\iota}\right)\quad\forall i\in I_{s\iota} \tag{96}$$

where $\mathbb{E}_\iota$ is the internal energy of the entity, $\mathbb{S}_\iota$ is the entropy of the entity, $\mathbb{M}$ is the mass, i is a species qualifier and ι specifies a fluid phase volume, or $\iota \in I_\mathrm{f}$ for I_f the index set of fluid phase volumes. Normalizing by the volume yields a fundamental equation of the form

$$E_\iota=E_\iota\left(\eta_\iota,\rho_\iota\omega_{i\iota}\right)\quad\forall i\in I_{s\iota} \tag{97}$$

For CIT the Euler equation for the fluid phase volume can be written at the microscale as

$$E_\iota=\theta_\iota\eta_\iota+\sum_{i\in I_{s\iota}}\rho_\iota\omega_{i\iota}\mu_{i\iota}-p_\iota \tag{98}$$

Applying the averaging operator to both sides of Eq. (98) gives

$$\langle E_\iota\rangle_{\Omega_\iota,\Omega}=\langle\theta_\iota\eta_\iota+\sum_{i\in I_{s\iota}}\rho_\iota\omega_{i\iota}\mu_{i\iota}-p_\iota\rangle_{\Omega_\iota,\Omega} \tag{99}$$

Evaluation of this averaging operator requires some care and multiple approaches are possible to separate the factors of terms containing products. We consider this expression term by term. First, we define the macroscale internal energy per unit volume to be

$$E^{\overline{\overline{\iota}}}=\varepsilon^\iota E^\iota=\langle E_\iota\rangle_{\Omega_\iota,\Omega} \tag{100}$$

which is the usual definition. Next consider the average of the product of temperature and entropy and define

$$\langle\theta_\iota\eta_\iota\rangle_{\Omega_\iota,\Omega}=\eta^{\overline{\overline{\iota}}}\langle\theta_\iota\rangle_{\Omega_\iota,\Omega_\iota,\eta_\iota}=\theta^{\overline{\overline{\iota}}}\eta^{\overline{\overline{\iota}}} \tag{101}$$

where

$$\eta^{\overline{\overline{\iota}}}=\varepsilon^\iota\eta^\iota=\langle\eta_\iota\rangle_{\Omega_\iota,\Omega} \tag{102}$$

$$\theta^{\overline{\overline{\iota}}}=\langle\theta_\iota\rangle_{\Omega_\iota,\Omega_\iota,\eta_\iota} \tag{103}$$

The average of the product of mass fraction, density, and chemical potential can be written as

$$\begin{aligned}\langle\rho_\iota\omega_{i\iota}\mu_{i\iota}\rangle_{\Omega_\iota,\Omega}\quad&=\langle\rho_\iota\omega_{i\iota}\rangle_{\Omega_\iota,\Omega}\,\langle\mu_{i\iota}\rangle_{\Omega_\iota,\Omega_\iota,\rho_\iota\omega_{i\iota}}\\&=\langle\rho_\iota\rangle_{\Omega_\iota,\Omega}\,\langle\omega_{i\iota}\rangle_{\Omega_\iota,\Omega_\iota,\rho_\iota}\,\langle\mu_{i\iota}\rangle_{\Omega_\iota,\Omega_\iota,\rho_\iota\omega_{i\iota}}\\&=\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\mu^{\overline{i\iota}}\end{aligned} \tag{104}$$

where

$$\varepsilon^\iota\rho^\iota=\langle\rho_\iota\rangle_{\Omega_\iota,\Omega} \tag{105}$$

$$\omega^{\overline{i\iota}}=\langle\omega_{i\iota}\rangle_{\Omega_\iota,\Omega_\iota,\rho_\iota} \tag{106}$$

$$\mu^{\overline{i\iota}}=\langle\mu_{i\iota}\rangle_{\Omega_\iota,\Omega_\iota,\rho_\iota\omega_{i\iota}} \tag{107}$$

Thus the derived macroscale form of the Euler equation for internal energy in a multispecies system becomes

$$E^{\overline{\overline{\iota}}}=\theta^{\overline{\overline{\iota}}}\eta^{\overline{\overline{\iota}}}+\sum_{i\in I_{s\iota}}\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\mu^{\overline{i\iota}}-\varepsilon^\iota p^\iota \tag{108}$$

In fact, the definitions of $\theta^{\bar{\bar{\iota}}}$ and $\mu^{\overline{i\iota}}$ were determined based on the objective of obtaining a form for Eq. (108) that is similar to microscale Eq. (98).

The differential of the Euler equation at the microscale may be obtained from Eq. (97) as

$$\mathrm{d}E_\iota = \theta_\iota \mathrm{d}\eta_\iota + \sum_{i \in I_{s\iota}} \mu_{i\iota} \mathrm{d}\left(\rho_\iota \omega_{i\iota}\right) \tag{109}$$

Comparison of this expression with that obtained as the differential of Eq. (98) provides the microscale Gibbs-Duhem equation

$$0 = \eta_\iota \mathrm{d}\theta_\iota + \sum_{i \in I_{s\iota}} \rho_\iota \omega_{i\iota} \mathrm{d}\mu_{i\iota} - \mathrm{d}p_\iota \tag{110}$$

Perfectly analogous manipulations to those used to obtain the last two equations are not, in general, possible at the macroscale. Eq. (97) expresses the dependence of the microscale energy function on the entropy density and the mass densities of each of the chemical species. Since these densities may not be constant within an averaging volume, a corresponding expression for macroscale energy as a function only of macroscale densities may not exist. When the variations of the macroscale densities within the averaging volume are negligible, the macroscale thermodynamic expressions for the differential of energy and for the Gibbs-Duhem equation will correspond, term by term, to their microscale counterparts. Here, we seek the more general forms of differentials of energy that allow for microscale variability of thermodynamic properties within an averaging volume.

The differential of the macroscale Euler equation (108) may be expressed as

$$\mathrm{d}E^{\bar{\bar{\iota}}} = \theta^{\bar{\bar{\iota}}} \mathrm{d}\eta^{\bar{\bar{\iota}}} + \sum_{i \in I_{s\iota}} \mu^{\overline{i\iota}} \mathrm{d}\left(\varepsilon^\iota \rho^\iota \omega^{i\bar{\iota}}\right) - p^\iota \mathrm{d}\varepsilon^\iota + \left\langle \eta_\iota \mathrm{d}\theta^{\bar{\bar{\iota}}} + \sum_{i \in I_{s\iota}} \rho_\iota \omega_{i\iota} \mathrm{d}\mu^{\overline{i\iota}} - \mathrm{d}p^\iota \right\rangle_{\Omega_\iota,\Omega} \tag{111}$$

Averaging Eq. (110) gives

$$0 = \left\langle \eta_\iota \mathrm{d}\theta_\iota + \sum_{i \in I_{s\iota}} \rho_\iota \omega_{i\iota} \mathrm{d}\mu_{i\iota} - \mathrm{d}p_\iota \right\rangle_{\Omega_\iota,\Omega} \tag{112}$$

Subtraction of Eq. (112) from Eq. (111) gives

$$\begin{aligned} \mathrm{d}E^{\bar{\bar{\iota}}} = {} & \theta^{\bar{\bar{\iota}}} \mathrm{d}\eta^{\bar{\bar{\iota}}} + \sum_{i \in I_{s\iota}} \mu^{\overline{i\iota}} \mathrm{d}\left(\varepsilon^\iota \rho^\iota \omega^{i\bar{\iota}}\right) - p^\iota \mathrm{d}\varepsilon^\iota \\ & + \left\langle \eta_\iota \mathrm{d}\left(\theta^{\bar{\bar{\iota}}} - \theta_\iota\right) + \sum_{i \in I_{s\iota}} \rho_\iota \omega_{i\iota} \mathrm{d}\left(\mu^{\overline{i\iota}} - \mu_{i\iota}\right) - \mathrm{d}\left(p^\iota - p_\iota\right) \right\rangle_{\Omega_\iota,\Omega} \end{aligned} \tag{113}$$

The differential here may be replaced by the general macroscale material derivative so that for a fluid phase-volume entity

$$\begin{aligned} \mathrm{T}^\iota = {} & \frac{\mathrm{D}^{\bar{\iota}} E^{\bar{\bar{\iota}}}}{\mathrm{D}t} - \theta^{\bar{\bar{\iota}}} \frac{\mathrm{D}^{\bar{\iota}} \eta^{\bar{\bar{\iota}}}}{\mathrm{D}t} - \sum_{i \in I_{s\iota}} \mu^{\overline{i\iota}} \frac{\mathrm{D}^{\bar{\iota}}\left(\varepsilon^\iota \rho^\iota \omega^{i\bar{\iota}}\right)}{\mathrm{D}t} + p^\iota \frac{\mathrm{D}^{\bar{\iota}} \varepsilon^\iota}{\mathrm{D}t} \\ & + \left\langle \eta_\iota \frac{\mathrm{D}^{\bar{\iota}}\left(\theta_\iota - \theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t} + \sum_{i \in I_{s\iota}} \rho_\iota \omega_{i\iota} \frac{\mathrm{D}^{\bar{\iota}}\left(\mu_{i\iota} - \mu^{\overline{i\iota}}\right)}{\mathrm{D}t} - \frac{\mathrm{D}^{\bar{\iota}}\left(p_\iota - p^\iota\right)}{\mathrm{D}t} \right\rangle_{\Omega_\iota,\Omega} = 0 \end{aligned} \tag{114}$$

If the system is spatially homogeneous at the microscale in θ_ι, $\mu_{i\iota}$, or p_ι, then the corresponding time derivative involving the difference between the microscale precursor and the macroscale average will vanish. Even if the system is not microscopically spatially homogeneous, the integral terms involving the time derivatives may be zero. In general however, these extra terms represent a difference between formulations based upon averaged microscale thermodynamics and formulations based upon thermodynamics posited directly at the macroscale. In many cases these terms may be negligible; in other instances, not.

Eq. (114) can be used directly when a single momentum equation is employed for the fluid phase. In that instance, $\mathbf{v}^{\overline{\iota}}$ is the phase velocity that is under consideration. However, if one chooses to formulate momentum equations for each species in the fluid phase, the velocities that appear in the momentum equation are $\mathbf{v}^{\overline{i\iota}}$. For this case, the velocities in the material derivatives must be the species velocities. We therefore will make use of the relation

$$\frac{\mathrm{D}^{\overline{\iota}}}{\mathrm{D}t}=\sum_{i\in I_{s\iota}}\left(\omega^{\overline{i\iota}}\frac{\partial}{\partial t}+\omega^{\overline{i\iota}}\mathrm{v}^{\overline{i\iota}}\cdot\nabla\right)=\sum_{i\in I_{s\iota}}\omega^{\overline{i\iota}}\frac{\mathrm{D}^{\overline{i\iota}}}{\mathrm{D}t} \tag{115}$$

to rearrange Eq. (114) to

$$\begin{aligned}\mathrm{T}^{\iota}=&\sum_{i\in I_{s\iota}}\omega^{\overline{i\iota}}\left(\frac{\mathrm{D}^{\overline{i\iota}}E^{\overline{\overline{\iota}}}}{\mathrm{D}t}-\theta^{\overline{\overline{\iota}}}\frac{\mathrm{D}^{\overline{i\iota}}\eta^{\overline{\overline{\iota}}}}{\mathrm{D}t}-\sum_{k\in I_{s\iota}}\mu^{\overline{k\iota}}\frac{\mathrm{D}^{\overline{i\iota}}\left(\varepsilon^{\iota}\rho^{\iota}\omega^{\overline{k\iota}}\right)}{\mathrm{D}t}+p^{\iota}\frac{\mathrm{D}^{\overline{i\iota}}\varepsilon^{\iota}}{\mathrm{D}t}\right)\\&+\sum_{i\in I_{s\iota}}\omega^{\overline{i\iota}}\left\langle\eta_{\iota}\frac{\mathrm{D}^{\overline{i\iota}}\left(\theta_{\iota}-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}+\sum_{k\in I_{s\iota}}\rho_{\iota}\omega_{k\iota}\frac{\mathrm{D}^{\overline{i\iota}}\left(\mu_{k\iota}-\mu^{\overline{k\iota}}\right)}{\mathrm{D}t}-\frac{\mathrm{D}^{\overline{i\iota}}(p_{\iota}-p^{\iota})}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}=0\end{aligned} \tag{116}$$

The material time derivative of the CIT formulation averaged from the microscale to the macroscale (ACIT) for a solid phase volume can be derived in a manner similar to that detailed for the fluid phase volume, and expressed in terms of products terms with deformation rate tensors or relative velocities using notions detailed in [20], giving

$$\begin{aligned}\mathrm{T}^{s}=&\frac{\mathrm{D}^{\overline{s}}E^{\overline{\overline{s}}}}{\mathrm{D}t}-\theta^{\overline{\overline{s}}}\frac{\mathrm{D}^{\overline{s}}\eta^{\overline{\overline{s}}}}{\mathrm{D}t}-\sum_{i\in I_{s\iota}}\mu^{\overline{is}}\frac{\mathrm{D}^{\overline{s}}(\varepsilon^{s}\rho^{s}\omega^{\overline{is}})}{\mathrm{D}t}\\&+\left\langle\eta_{s}\frac{\mathrm{D}^{\overline{s}}\left(\theta_{s}-\theta^{\overline{\overline{s}}}\right)}{\mathrm{D}t}+\sum_{i\in I_{s\iota}}\rho_{s}\omega_{is}\frac{\mathrm{D}^{\overline{s}}(\mu_{is}-\mu^{\overline{is}})}{\mathrm{D}t}\right\rangle_{\Omega_{s},\Omega}\\&-\sum_{\iota\in I_{cs}}\left\langle\left(\frac{\mathbf{C}_{s}}{j_{s}}:\sigma_{s}\right)(\mathbf{v}_{\iota}-\mathbf{v}_{s})\cdot\mathbf{n}_{s}\right\rangle_{\Omega_{\iota},\Omega}\\&-\left\langle\mathbf{n}_{s}\cdot\left[\frac{2}{j_{s}}\sigma_{s}:(\nabla_{X}\mathbf{x}\nabla_{X}\mathbf{x})\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right]\right\rangle_{\Omega_{ss},\Omega}\\&+\left\langle\left\{\nabla\cdot\left[\frac{2}{j_{s}}\sigma_{s}:(\nabla_{X}\mathbf{x}\nabla_{X}\mathbf{x})\right]-\nabla\sigma_{s}:\frac{C_{s}}{j_{s}}\right\}\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{s},\Omega}\\&+\varepsilon^{s}\sigma^{\overline{\overline{s}}}:\frac{\mathbf{C}^{s}}{j^{s}}\mathbf{I}:\mathbf{d}^{\overline{\overline{s}}}-\left\langle\frac{2}{j_{s}}\sigma_{s}:(\nabla_{X}\mathbf{x}\nabla_{X}\mathbf{x})\right\rangle_{\Omega_{s},\Omega}:\mathbf{d}^{\overline{\overline{s}}}\\&-\nabla\cdot\left\langle\left[\frac{2}{j_{s}}\sigma_{s}:(\nabla_{X}\mathbf{x}\nabla_{X}\mathbf{x})-\sigma_{s}:\frac{\mathbf{C}_{s}}{j_{s}}\mathbf{I}\right]\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{s}}\right)\right\rangle_{\Omega_{s},\Omega}=0\end{aligned} \tag{117}$$

where $\mathbf{C}_s$ is the Green's deformation tensor, j_s is the Jacobian, $\nabla_X\mathbf{x}$ is the deformation gradient [12] where $\mathbf{X}$ are the material coordinates and $\mathbf{x}$ are the spatial coordinates, the solid surface is denoted by $\Omega_{ss} = \{\Omega_\kappa, \forall\kappa \in I_{cs}\}$, and subscripts denote microscale quantities while superscripts denote macroscale quantities. The Lagrangian stress tensor $\boldsymbol{\sigma}_s$ is defined as a partial derivative of the internal energy with respect to the Green's deformation tensor. This particular stress tensor is equal to one half the second Piola-Kirchhoff stress tensor.

It will be reasonable to neglect dispersion within the solid phase so that the velocities of all species will be equal in that phase. Nevertheless, in general, when a momentum equation is to be formulated for each species, we will need the thermodynamic expression for the solid phase to be written in terms of species velocities rather than the phase velocity. This may be obtained from Eq. (117) as:

$$\begin{aligned}
\mathrm{T}^{s}=&\sum_{i\in I_{s\iota}}\omega^{i\overline{s}}\left(\frac{\mathrm{D}^{\overline{is}}E^{\overline{\overline{s}}}}{\mathrm{D}t}-\theta^{\overline{\overline{s}}}\frac{\mathrm{D}^{\overline{is}}\eta^{\overline{\overline{s}}}}{\mathrm{D}t}-\sum_{k\in I_{s\iota}}\mu^{\overline{ks}}\frac{\mathrm{D}^{\overline{is}}(\varepsilon^{s}\rho^{s}\omega^{k\overline{s}})}{\mathrm{D}t}\right)\\
&+\sum_{i\in I_{s\iota}}\omega^{i\overline{s}}\langle\eta_{s}\frac{\mathrm{D}^{\overline{is}}\left(\theta_{s}-\theta^{\overline{\overline{s}}}\right)}{\mathrm{D}t}+\sum_{k\in I_{s\iota}}\rho_{s}\omega_{ks}\frac{\mathrm{D}^{\overline{is}}\left(\mu_{ks}-\mu^{\overline{ks}}\right)}{\mathrm{D}t}\rangle_{\Omega_{s},\Omega}\\
&-\sum_{\iota\in I_{cs}}\sum_{i\in I_{s\iota}}\langle\left(\frac{\mathbf{C}_{s}}{j_{s}}:\sigma_{s}\right)\omega_{is}\left(\mathbf{v}_{\iota}-\mathbf{v}_{is}\right)\cdot\mathbf{n}_{s}\rangle_{\Omega_{\iota},\Omega}\\
&-\sum_{i\in I_{s\iota}}\langle\mathbf{n}_{s}\cdot\left(\frac{2}{j_{s}}\sigma_{s}:(\nabla_{X}\mathbf{x}\nabla_{X}\mathbf{x})\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{is}}\right)\right)\omega^{i\overline{s}}\rangle_{\Omega_{ss},\Omega}\\
&+\sum_{i\in I_{s\iota}}\langle\left[\nabla\cdot\left(\frac{2}{j_{s}}\sigma_{s}:(\nabla_{X}\mathbf{x}\nabla_{X}\mathbf{x})\right)-\nabla\sigma_{s}:\frac{\mathbf{C}_{s}}{j_{s}}\right]\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{is}}\right)\omega^{i\overline{s}}\rangle_{\Omega_{ss},\Omega}\\
&+\sum_{i\in I_{s\iota}}\left(\varepsilon^{s}\sigma^{\overline{\overline{s}}}:\frac{\mathbf{C}^{s}}{j^{s}}\mathbf{I}-\langle\frac{2}{j_{s}}\sigma_{s}:(\nabla_{X}\mathbf{x}\nabla_{X}\mathbf{x})\rangle_{\Omega_{s},\Omega}\right):\left(\omega^{i\overline{s}}\mathbf{d}^{\overline{\overline{is}}}+\mathbf{v}^{\overline{is}}\nabla\omega^{i\overline{s}}\right)\\
&-\sum_{i\in I_{s\iota}}\nabla\cdot\langle\left(\frac{2}{j_{s}}\sigma_{s}:(\nabla_{X}\mathbf{x}\nabla_{X}\mathbf{x})-\sigma_{s}:\frac{\mathbf{C}_{s}}{j_{s}}\mathbf{I}\right)\cdot\left(\mathbf{v}_{s}-\mathbf{v}^{\overline{is}}\right)\omega^{i\overline{s}}\rangle_{\Omega_{s},\Omega}=0
\end{aligned}\tag{118}$$

Following the general ACIT species formulation detailed above for phase volumes and restricting to an interface as detailed in Gray [15] yields the general material derivative thermodynamic equation for an interface

$$\begin{aligned}
\mathrm{T}^{\iota}=&\frac{\mathrm{D}^{\overline{\iota}}E^{\overline{\overline{\iota}}}}{\mathrm{D}t}-\theta^{\overline{\overline{\iota}}}\frac{\mathrm{D}^{\overline{\iota}}\eta^{\overline{\overline{\iota}}}}{\mathrm{D}t}-\sum_{i\in I_{s\iota}}\mu^{\overline{i\iota}}\frac{\mathrm{D}^{\overline{\iota}}(\varepsilon^{\iota}\rho^{\iota}\omega^{i\overline{\iota}})}{\mathrm{D}t}-\gamma^{\iota}\frac{\mathrm{D}^{\overline{\iota}}\varepsilon^{\iota}}{\mathrm{D}t}\\
&+\langle\eta_{\iota}\frac{\mathrm{D}^{\prime\overline{\iota}}\left(\theta_{\iota}-\theta^{\overline{\overline{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in I_{s\iota}}\rho_{\iota}\omega_{i\iota}\frac{\mathrm{D}^{\prime\overline{\iota}}(\mu_{i\iota}-\mu^{\overline{i\iota}})}{\mathrm{D}t}\rangle_{\Omega_{\iota},\Omega}\\
&+\nabla\cdot\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)(\gamma_{\iota}-\gamma^{\iota})\rangle_{\Omega_{\iota},\Omega}+\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot(\gamma_{\iota}-\gamma^{\iota})\rangle_{\Omega_{\iota},\Omega}:\mathbf{d}^{\overline{\overline{\iota}}}\\
&+\nabla\theta^{\overline{\overline{\iota}}}\cdot\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)\eta_{\iota}\rangle_{\Omega_{\iota},\Omega}+\nabla\gamma^{\iota}\cdot\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)\rangle_{\Omega_{\iota},\Omega}\\
&+\sum_{i\in I_{s\iota}}\nabla\mu^{\overline{i\iota}}\cdot\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)\rho_{\iota}\omega_{i\iota}\rangle_{\Omega_{\iota},\Omega}\\
&-\langle(\gamma_{\iota}-\gamma^{\iota})(\nabla'\cdot\mathbf{n}_{\alpha})\,\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)\rangle_{\Omega_{\iota},\Omega}\\
&-\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{C}}}\langle(\gamma_{\iota}-\gamma^{\iota})\,\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{\iota}}\right)\rangle_{\Omega_{\kappa},\Omega}=0\quad\text{for}\quad\iota\in I_{\mathrm{I}}
\end{aligned}\tag{119}$$

for

$$\frac{\mathrm{D}^{\prime\overline{\iota}}}{\mathrm{D}t}=\frac{\partial'}{\partial t}+\mathbf{v}^{\overline{\iota}}\cdot\nabla'\tag{120}$$

and

$$\frac{\mathrm{D}^{\prime\overline{\iota}}}{\mathrm{D}t}=\frac{\mathrm{D}^{\overline{\iota}}}{\mathrm{D}t}+\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{\iota}}\right)\cdot\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\nabla\tag{121}$$

where $\iota\in I_{\mathrm{I}},\Omega_{\iota}=\overline{\Omega}_{\alpha}\cap\overline{\Omega}_{\beta},\mathbf{n}_{\alpha}$ is the outward unit normal vector from phase volume Ω_{α}, and γ is the interfacial tension.

The thermodynamics of interfaces at the macroscale requires restriction of microscale quantities to the interface and averaging of these quantities to the macroscale. Because of this, the material derivatives within the averaging operators are restricted to the interface at the microscale.

For utility with a set of momentum equations for the momentum of each species in the interface rather than for the velocity of the interface as a whole, Eq. (119) is re-expressed in the form

$$\begin{aligned}
\mathrm{T}^{\iota}=&\sum_{i\in I_{s\iota}}\omega^{i\bar{\iota}}\left(\frac{\mathrm{D}^{\overline{i\iota}}E^{\bar{\bar{\iota}}}}{\mathrm{D}t}-\theta^{\bar{\bar{\iota}}}\frac{\mathrm{D}^{\overline{i\iota}}\eta^{\bar{\bar{\iota}}}}{\mathrm{D}t}-\sum_{k\in I_{s\iota}}\mu^{\overline{k\iota}}\frac{\mathrm{D}^{\overline{i\iota}}\left(\varepsilon^{\iota}\rho^{\iota}\omega^{k\bar{\iota}}\right)}{\mathrm{D}t}-\gamma^{\iota}\frac{\mathrm{D}^{\overline{i\iota}}\varepsilon^{\iota}}{\mathrm{D}t}\right)\\
&+\sum_{i\in I_{s\iota}}\omega^{i\bar{\iota}}\left\langle\eta_{\iota}\frac{\mathrm{D}'^{\overline{i\iota}}\left(\theta_{\iota}-\theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}+\sum_{k\in I_{s\iota}}\rho_{\iota}\omega^{k\bar{\iota}}\frac{\mathrm{D}'^{\overline{i\iota}}\left(\mu_{k\iota}-\mu^{\overline{k\iota}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\\
&+\sum_{i\in I_{s\iota}}\omega^{i\bar{\iota}}\nabla\cdot\left\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{i\iota}}\right)\left(\gamma_{\iota}-\gamma^{\iota}\right)\right\rangle_{\Omega_{\iota},\Omega}\\
&+\sum_{i\in I_{s\iota}}\left\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\gamma_{\iota}-\gamma^{\iota}\right)\right\rangle_{\Omega_{\iota},\Omega}:\left(\omega^{i\bar{\iota}}\mathrm{d}^{\bar{\bar{\overline{i\iota}}}}+\mathbf{v}^{\overline{i\iota}}\nabla\omega^{i\bar{\iota}}\right)\\
&+\sum_{i\in I_{s\iota}}\omega^{i\bar{\iota}}\nabla\theta^{\bar{\bar{\iota}}}\cdot\left\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{i\iota}}\right)\eta_{\iota}\right\rangle_{\Omega_{\iota},\Omega}\\
&+\sum_{i\in I_{s\iota}}\omega^{i\bar{\iota}}\nabla\gamma^{\iota}\cdot\left\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_{\iota},\Omega}\\
&+\sum_{i\in I_{s\iota}}\sum_{k\in I_{s\iota}}\omega^{i\bar{\iota}}\nabla\mu^{\overline{k\iota}}\cdot\left\langle\mathbf{n}_{\alpha}\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{i\iota}}\right)\rho_{\iota}\omega_{k\iota}\right\rangle_{\Omega_{\iota},\Omega}\\
&-\sum_{i\in I_{s\iota}}\omega^{i\bar{\iota}}\left\langle\left(\gamma_{\iota}-\gamma^{\iota}\right)\left(\nabla'\cdot\mathbf{n}_{\alpha}\right)\mathbf{n}_{\alpha}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_{\iota},\Omega}\\
&-\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{C}}}\sum_{i\in I_{s\iota}}\omega^{i\bar{\iota}}\left\langle\left(\gamma_{\iota}-\gamma^{\iota}\right)\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{i\iota}}\right)\right\rangle_{\Omega_{\kappa},\Omega}=0\quad\text{for}\quad\iota\in I_{\mathrm{I}}
\end{aligned}\tag{122}$$

Following the general ACIT species formulation detailed above for phase volumes and restricting to a common curve as detailed in Gray [15] yields the general material derivative thermodynamic equation for a common curve

$$\begin{aligned}
\mathrm{T}^{\iota}=&\frac{\mathrm{D}^{\bar{\iota}}E^{\bar{\bar{\iota}}}}{\mathrm{D}t}-\theta^{\bar{\bar{\iota}}}\frac{\mathrm{D}^{\bar{\iota}}\eta^{\bar{\bar{\iota}}}}{\mathrm{D}t}-\sum_{i\in I_{s\iota}}\mu^{\overline{i\iota}}\frac{\mathrm{D}^{\bar{\iota}}\left(\varepsilon^{\iota}\rho^{\iota}\omega^{\overline{i\iota}}\right)}{\mathrm{D}t}-\gamma^{\iota}\frac{\mathrm{D}^{\bar{\iota}}\varepsilon^{\iota}}{\mathrm{D}t}\\
&+\left\langle\eta_{\iota}\frac{\mathrm{D}''^{\bar{\iota}}\left(\theta_{\iota}-\theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}+\sum_{i\in I_{s\iota}}\rho_{\iota}\omega_{i\iota}\frac{\mathrm{D}''^{\bar{\iota}}\left(\mu_{i\iota}-\mu^{\overline{i\iota}}\right)}{\mathrm{D}t}\right\rangle_{\Omega_{\iota},\Omega}\\
&-\nabla\cdot\left\langle\left(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)\left(\gamma_{\iota}-\gamma^{\iota}\right)\right\rangle_{\Omega_{\iota},\Omega}\\
&-\left\langle\left(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota}\right)\left(\gamma_{\iota}-\gamma^{\iota}\right)\right\rangle_{\Omega_{\iota},\Omega}:\mathbf{d}^{\bar{\bar{\iota}}}\\
&+\nabla\theta^{\bar{\bar{\iota}}}\cdot\left\langle\left(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)\eta_{\iota}\right\rangle_{\Omega_{\iota},\Omega}\\
&-\nabla\gamma^{\iota}\cdot\left\langle\left(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)\right\rangle_{\Omega_{\iota},\Omega}\\
&\sum_{i\in I_{s\iota}}\nabla\mu^{\overline{i\iota}}\cdot\left\langle\left(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota}\right)\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)\rho_{\iota}\omega_{i\iota}\right\rangle_{\Omega_{i},\Omega}\\
&-\left\langle\mathbf{n}_{\iota}\cdot\nabla''\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)\left(\gamma_{\iota}-\gamma^{\iota}\right)\right\rangle_{\Omega_{\iota},\Omega}\\
&+\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{Pt}}}\left\langle\mathbf{e}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\bar{\iota}}\right)\left(\gamma_{\iota}-\gamma^{\iota}\right)\right\rangle_{\Omega_{\kappa},\Omega}=0\quad\text{for}\quad\iota\in I_{\mathrm{C}}
\end{aligned}\tag{123}$$

where

$$\frac{\mathrm{D}''^{\bar{\iota}}}{\mathrm{D}t}=\frac{\partial''}{\partial t}+\mathbf{v}^{\bar{\iota}}\cdot\nabla''\tag{124}$$

and

$$\frac{\mathrm{D}''^{\bar{\iota}}}{\mathrm{D}t}=\frac{\mathrm{D}^{\bar{\iota}}}{\mathrm{D}t}+\left(\mathbf{v}_{\iota}-\mathbf{v}^{\bar{\iota}}\right)\cdot\left(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota}\right)\cdot\nabla\tag{125}$$

where γ is the curvilinear tension. The thermodynamics of a common curve at the macroscale requires restriction of microscale quantities to the common curve and averaging of these quantities to the macroscale. Because of this, the material derivatives within the averaging operators are restricted to the interface at the microscale.

For use with the species based momentum equations, the thermodynamic condition may be rearranged to

$$\begin{aligned}
\mathrm{T}^{\iota}=&\sum_{i\in I_{s\iota}}\omega^{\overline{i\iota}}\left(\frac{\mathrm{D}^{\overline{i\iota}}E^{\bar{\iota}}}{\mathrm{D}t}-\theta^{\bar{\bar{\iota}}}\frac{\mathrm{D}^{\overline{i\iota}}\eta^{\bar{\iota}}}{\mathrm{D}t}-\sum_{k\in I_{s\iota}}\mu^{\overline{k\iota}}\frac{\mathrm{D}^{\overline{i\iota}}(\varepsilon^{\iota}\rho^{\iota}\omega^{\overline{i\iota}})}{\mathrm{D}t}-\gamma^{\iota}\frac{\mathrm{D}^{\bar{\iota}}\varepsilon^{\iota}}{\mathrm{D}t}\right)\\
&+\sum_{i\in I_{s\iota}}\omega^{\overline{i\iota}}\langle\eta_{\iota}\frac{\mathrm{D}''^{\overline{i\iota}}\left(\theta_{\iota}-\theta^{\bar{\bar{\iota}}}\right)}{\mathrm{D}t}+\sum_{k\in I_{s\iota}}\rho_{\iota}\omega_{k\iota}\frac{\mathrm{D}''^{\overline{i\iota}}\left(\mu_{k\iota}-\mu^{\overline{k\iota}}\right)}{\mathrm{D}t}\rangle_{\Omega_{\iota},\Omega}\\
&-\sum_{i\in I_{s\iota}}\omega^{\overline{i\iota}}\nabla\cdot\langle(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota})\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{i\iota}}\right)(\gamma_{\iota}-\gamma^{\iota})\rangle_{\Omega_{\iota},\Omega}\\
&-\sum_{i\in I_{s\iota}}\langle(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota})(\gamma_{\iota}-\gamma^{\iota})\rangle_{\Omega_{\iota},\Omega}:\left(\omega^{\overline{i\iota}}\mathbf{d}^{\overline{\overline{i\iota}}}+\mathbf{v}^{\overline{i\iota}}\nabla\omega^{\overline{i\iota}}\right)\\
&+\sum_{i\in I_{s\iota}}\omega^{\overline{i\iota}}\nabla\theta^{\bar{\bar{\iota}}}\cdot\langle(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota})\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{i\iota}}\right)\eta_{\iota}\rangle_{\Omega_{\iota},\Omega}\\
&-\sum_{i\in I_{s\iota}}\omega^{\overline{i\iota}}\nabla\gamma^{\iota}\cdot\langle(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota})\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{i\iota}}\right)\rangle_{\Omega_{\iota},\Omega}\\
&+\sum_{i\in I_{s\iota}}\sum_{k\in I_{s\iota}}\omega^{\overline{i\iota}}\nabla\mu^{\overline{k\iota}}\cdot\langle(\mathbf{I}-\mathbf{n}_{\iota}\mathbf{n}_{\iota})\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{i\iota}}\right)\rho_{\iota}\omega_{k\iota}\rangle_{\Omega_{i},\Omega}\\
&-\sum_{i\in I_{s\iota}}\omega^{\overline{i\iota}}\langle\mathbf{n}_{\iota}\cdot\nabla''\mathbf{n}_{\iota}\cdot\left(\mathbf{v}_{\iota}-\mathbf{v}^{\overline{i\iota}}\right)(\gamma_{\iota}-\gamma^{\iota})\rangle_{\Omega_{\iota},\Omega}\\
&+\sum_{i\in I_{s\iota}}\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{P}\iota}}\langle\omega^{\overline{i\iota}}\mathbf{e}_{\iota}\cdot\left(\mathbf{v}_{\kappa}-\mathbf{v}^{\overline{i\iota}}\right)(\gamma_{\iota}-\gamma^{\iota})\rangle_{\Omega_{\kappa},\Omega}=0\quad\text{for}\quad\iota\in I_{\mathrm{C}}
\end{aligned}\tag{126}$$

4.3 Equilibrium Conditions

The conditions that dictate when the system of interest is at equilibrium are very useful for description of the system away from equilibrium. In fact, to close our system, we will use expansions around the equilibrium state to describe the dynamics. Our approach will be to first obtain the conditions for equilibrium at the microscale. Then, consistent with our averaging of microscale conservation equations and thermodynamic expressions to the macroscale, we will average the microscale equilibrium results to the macroscale.

Boruvka and coworkers [3–5,13] have provided an analysis of microscale equilibrium using a variational approach. By making use of the fact that the energy is a minimum at equilibrium, they established relationships among variables that must hold at equilibrium. They concentrated on systems composed of multiple fluid phases. Here, we will extend those studies by considering a multiphase system in which one of the phases is a solid. We will also obtain the macroscale equilibrium conditions as averages of their microscale precursors.

Within an averaging volume, there are phase volumes, interfaces, common curves, and common points. We will be making use of the variations of all of these quantities within the volume. The variational expression for a phase volume property f_ι is [14]

$$\bar{\delta}\left(\varepsilon^{\iota}f^{\iota}\right)=\langle\bar{\bar{\delta}}f_{\iota}\rangle_{\Omega_{\iota},\Omega}+\sum_{\kappa\in I_{c\iota}}\langle f_{\iota}\delta\xi\cdot\mathbf{n}_{\iota}\rangle_{\Omega_{\kappa},\Omega}\quad\text{for}\quad\iota\in I_{\mathrm{P}}\tag{127}$$

where δ is a spatial variation involving both a quantity of interest and its microscale coordinates, $\bar{\delta}$ is the variation of the quantity at the macroscale, $\bar{\bar{\delta}}$ is a fixed-point microscale variation, and ξ is a microscale position vector. Eq. (127) may be used with insight when f_ι is a thermodynamic property that does not depend on position. However, the strain tensor $\mathbf{C}_s$ depends on the deformation of the solid. Thus, it will prove convenient to make use of the relation between the general microscale variation and the fixed-point variation as given by

$$\bar{\bar{\delta}}=\delta-\delta\xi\cdot\nabla \tag{128}$$

For an interfacial property, the variational expression is

$$\bar{\delta}\,(\varepsilon^\iota f^\iota)=\langle\bar{\bar{\delta}}'\,f_\iota\rangle_{\Omega_\iota,\Omega}+\langle f_\iota\nabla'\cdot\mathbf{n}_\alpha\delta\xi\cdot\mathbf{n}_\alpha\rangle_{\Omega_\iota,\Omega}+\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{C}}}\langle f_\iota\delta\xi\cdot\mathbf{n}_\iota\rangle_{\Omega_\kappa,\Omega}\quad\text{for}\quad\iota\in I_{\mathrm{I}} \tag{129}$$

where $\mathbf{n}_\alpha$ is a unit vector normal to the surface ι positive outward from the surface $\Omega_\iota=\overline{\Omega}_\alpha\quad\cap\quad\overline{\Omega}_\beta$. The variation $\bar{\bar{\delta}}'$ is a fixed-point variation with respect to surface coordinates and $\nabla'\cdot$ is a surface divergence. Because we are working with properties within an averaging volume, f^ι has dimensions of quantity per averaging volume while f_ι has dimensions of quantity per unit area.

For a common curve, the variational equation is

$$\bar{\delta}\,(\varepsilon^\iota f^\iota)=\langle\bar{\bar{\delta}}''\,f_\iota\rangle_{\Omega_\iota,\Omega}-\langle f_\iota\mathbf{n}_\iota\cdot\nabla''\cdot\mathbf{n}_\iota\cdot\delta\xi\rangle_{\Omega_\iota,\Omega}+\sum_{\kappa\in I_{c\iota}\cap I_{\mathrm{Pt}}}\langle f_\iota\delta\xi\cdot\mathbf{e}_\iota\rangle_{\Omega_\kappa,\Omega}\quad\text{for}\quad\iota\in I_{\mathrm{C}} \tag{130}$$

and $\mathbf{n}_\iota$ is a unit vector tangent to the common curve, $\mathbf{e}_\iota$ is a unit vector tangent to the common curve at the common point oriented outward from the common curve. The divergence along the curve is denoted as $\nabla''\cdot$, and the variation at the fixed point on the curve is $\bar{\bar{\delta}}''$.

To obtain information about the equilibrium state, we minimize the functional

$$F=\sum_{\iota\in I}\left(E^{\bar{\bar{\iota}}}+\sum_{i\in I_{s\iota}}\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\psi^{\overline{i\iota}}\right)-T\sum_{\iota\in I}\eta^{\bar{\bar{\iota}}}-\sum_{\iota\in I}\sum_{i\in I_{s\iota}}M_{i\iota}\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}} \tag{131}$$

The first sum is over the internal plus potential energy. This total energy should be a minimum at equilibrium. We know, however, that this minimum is obtained when the entropy is a maximum and with mass being conserved.

The other sums in the expression for F impose these conditions. The coefficient T is a constant used in constraining the energy variation to occur at maximum entropy. The coefficients $M_{i\iota}$ are constants that multiply amounts of mass to ensure that the total mass of each species is unchanged during a variation around equilibrium. These coefficients are chosen subject to the mass conservation constraint that if a species i can be transferred between two entities α and β then $M_{i\alpha}=M_{i\beta}$. The variation of F around equilibrium is zero so the variation of Eq. (131) is

$$0=\sum_{\iota\in I}\left[\bar{\delta}E^{\bar{\bar{\iota}}}+\sum_{i\in I_{s\iota}}\bar{\delta}\,\left(\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\psi^{\overline{i\iota}}\right)\right]-T\sum_{\iota\in I}\bar{\delta}\eta^{\bar{\bar{\iota}}}-\sum_{\iota\in I}\sum_{i\in I_{s\iota}}M_{i\iota}\bar{\delta}\,\left(\varepsilon^\iota\rho^\iota\omega^{\overline{i\iota}}\right) \tag{132}$$

The expressions for the energy of the fluid phase per unit volume of the phase are

$$E_\iota=\eta_\iota\theta_\iota+\sum_{i\in I_{s\iota}}\rho_\iota\omega_{i\iota}\mu_{i\iota}-p_\iota\quad\text{for}\quad\iota\in I_{\mathrm{f}} \tag{133}$$

where I_{f} is the index set of fluid phase volumes.

The solid phase energy per volume of solid is given by

$$E_s=\eta_s\theta_s+\sum_{i\in I_{ss}}\rho_s\omega_{is}\mu_{is}+\frac{1}{j_s}\sigma_s:\mathbf{C}_s \tag{134}$$

The interfacial energy per unit area is

$$E_\iota=\eta_\iota\theta_\iota+\sum_{i\in I_{s\iota}}\rho_\iota\omega_{i\iota}\mu_{i\iota}+\gamma_\iota \quad \text{for} \quad \iota\in I_{\mathrm{I}} \tag{135}$$

where γ_ι is the interfacial tension. In selecting this form, we are not considering highly curved interfaces. The common curve energy per unit length is

$$E_\iota=\eta_\iota\theta_\iota+\sum_{i\in I_{s\iota}}\rho_\iota\omega_{i\iota}\mu_{i\iota}-\gamma_\iota \quad \text{for} \quad \iota\in I_{\mathrm{C}} \tag{136}$$

where γ_ι is the curvilinear tension.

Substitution of the definitions of the variations into Eq. (132) followed by algebraic combinations of corresponding terms yields conditions of equilibrium based on the fact that all coefficients of independent variations must be zero. Manipulations are similar to those in Gray and Schrefler [20] and Gray and Miller [19], so the details are not presented here. The microscale thermodynamic equilibrium conditions obtained are

$$T=\theta_\iota \quad \iota\in I \tag{137}$$

$$M_{i\iota}=\mu_{i\iota}+\psi_{i\iota} \quad \iota\in I_{\mathrm{f}},i\in I_{s\iota} \tag{138}$$

$$M_{is}=\mu_{is}+\psi_{is}+\frac{\sigma_s}{\rho_s j_s}:\mathbf{C}_s-\frac{\mathbf{t}_s:\mathbf{I}}{3\rho_s} \quad i\in I_{ss} \tag{139}$$

where the solid phase Cauchy stress tensor is

$$\mathbf{t}_s=\frac{2}{j_s}\sigma_s:(\nabla_X\mathbf{x}\nabla_X\mathbf{x}) \tag{140}$$

It is worth reiterating that if species *i* can be transferred between any two entities ι and κ then $M_{i\iota}=M_{i\kappa}$ at equilibrium. Additional equilibrium constraints relate to the mechanical balances at the boundaries between and among entities. We constrain the solid phase surface to be smooth such that tangents to the surface do not undergo any discontinuous changes in direction. Thus, an interface or common curve that involves the solid phase is mechanically different from one that involves only fluid phases. On the interfaces that involve the solid phase, we have the following conditions

$$p_\alpha+\gamma_\iota\nabla'\cdot\mathbf{n}_s-\rho_\iota\mathbf{n}_s\cdot\mathrm{g}_\iota+\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s=0 \quad \text{on} \quad \Omega_\iota \tag{141}$$

$$\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'=0 \quad \text{on} \quad \Omega_\iota \tag{142}$$

where $\iota\in I_{\mathrm{I}s}$, $I_{\mathrm{I}s}$ is the index set of interfaces that include an intersection with the solid phase volume, $\Omega_\iota=\overline{\Omega}_s \quad \cap \quad \overline{\Omega}_\alpha$, and Ω_α is a fluid phase volume that contacts the solid phase.

On fluid-fluid interfaces, we have the condition

$$p_\beta-p_\alpha+\gamma_\iota\nabla'\cdot\mathbf{n}_\alpha-\rho_\iota\mathbf{n}_\alpha\cdot\mathbf{g}_\iota=0 \quad \text{on} \quad \Omega_\iota \tag{143}$$

where $\iota\in I_{\mathrm{I}/s}$, $\iota\in I_{\mathrm{I}/s},\Omega_\iota=\overline{\Omega}_\alpha \quad \cap \quad \overline{\Omega}_\beta$, and $I_{\mathrm{I}/s}$ is the index set of all interfaces that do not include an intersection with the solid phase volume, which is the set of fluid-fluid interfaces.

For common curves involving an intersection of the solid phase volume and two fluid phase volumes, the equilibrium conditions are

$$\delta_{\mathrm{C}}\left(\xi_\iota\right)\left(\gamma_\iota\kappa_{N_\iota}-\gamma_\kappa\sin\phi_\kappa-\rho_\iota\mathbf{g}_\iota\cdot\mathbf{n}_s\right)+\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s=0\quad\text{on }\Omega_\iota \tag{144}$$

and

$$\delta_{\mathrm{C}}\left(\xi_\iota\right)\left(\gamma_\lambda-\gamma_\mu+\gamma_\kappa\cos\phi_\kappa+\gamma_\iota\kappa_{G_\iota}-\rho_\iota\mathbf{g}_\iota\cdot\mathbf{n}_\lambda\right)+\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_\lambda=0\quad\text{on }\Omega_\iota \tag{145}$$

where

$\iota\in I_{\mathrm{C}s};\Omega_\iota=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta\cap\overline{\Omega}_s;\alpha,\beta\in I_{\mathrm{f}};\Omega_\kappa=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta;\Omega_\lambda=\overline{\Omega}_\alpha\cap\overline{\Omega}_s;\Omega_\mu=\overline{\Omega}_\beta\cap\overline{\Omega}_s;\kappa,\lambda,\mu\in I_{\mathrm{I}};I_{\mathrm{C}s}$ is the index set of common curves that include an intersection with the solid phase volume, δ_{C} is a Dirac delta function corresponding to the common curve, ϕ_κ is the contact angle from the boundary of the solid phase volume to the Ω_κ interface, κ_{N_ι} is the normal curvature of the common curve, κ_{G_ι} is the Gaussian curvature of the common curve, and following our usual convention $\mathbf{n}_\lambda$ is the unit vector that is tangent to the Ω_λ interface and oriented outward from the common curve Ω_ι.

For common curves involving the intersection of three fluid phase volumes, the equilibrium condition is

$$\gamma_\kappa\mathbf{n}_\kappa+\gamma_\lambda\mathbf{n}_\lambda+\gamma_\mu\mathbf{n}_\mu+\gamma_\iota\mathbf{n}_\iota\cdot\nabla''\mathbf{n}_\iota-\rho_\iota\left(\mathbf{I}-\mathbf{n}_\iota\mathbf{n}_\iota\right)\cdot\mathbf{g}_\iota=0\quad\text{on }\Omega_\iota \tag{146}$$

where $\iota\in I_{\mathrm{C}/s}$, $I_{\mathrm{C}/s}$ is the index set of common curves that do not include an intersection with the solid phase volume; the common curve $\Omega_\iota=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta\cap\overline{\Omega}_\gamma$; the three fluid-fluid interfaces are defined as $\Omega_\kappa=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta,\Omega_\lambda=\overline{\Omega}_\alpha\cap\overline{\Omega}_\gamma$, and $\Omega_\mu=\overline{\Omega}_\beta\cap\overline{\Omega}_\gamma$; and $\mathbf{n}_\iota$ is the unit vector tangent to the common curve.

For common points involving an intersection of the solid phase volume and three fluid phase volumes, the equilibrium conditions are

$$\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{n}_s-\delta_{\mathrm{Pt}}\left(\xi_\iota\right)\gamma_\kappa\mathbf{e}_\kappa\cdot\mathbf{n}_s=0\quad\text{on }\Omega_\iota \tag{147}$$

and

$$\mathbf{n}_s\cdot\mathbf{t}_s\cdot\mathbf{I}'-\delta_{\mathrm{Pt}}\left(\xi_\iota\right)\left(\gamma_\kappa\mathbf{e}_\kappa+\gamma_\lambda\mathbf{e}_\lambda+\gamma_\mu\mathbf{e}_\mu+\gamma_\nu\mathbf{e}_\nu\right)\cdot\mathbf{I}'=0\quad\text{on }\Omega_\iota \tag{148}$$

where $\iota\in I_{\mathrm{Pt}s}$; $I_{\mathrm{Pt}s}$ is the index set of common points that include an intersection with the solid phase volume; the common point $\Omega_\iota=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta\cap\overline{\Omega}_\gamma\cap\overline{\Omega}_s$; the corresponding common curves are $\Omega_\kappa=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta\cap\overline{\Omega}_\gamma,\Omega_\lambda=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta\cap\overline{\Omega}_s,\Omega_\mu=\overline{\Omega}_\alpha\cap\overline{\Omega}_\gamma\cap\overline{\Omega}_s$, and $\Omega_\nu=\overline{\Omega}_\beta\cap\overline{\Omega}_\gamma$; and δ_{Pt} is a Dirac delta function corresponding to the common point.

For common points involving an intersection of four fluid phase volumes, the equilibrium condition is

$$\gamma_\kappa\mathbf{e}_\kappa+\gamma_\lambda\mathbf{e}_\lambda+\gamma_\mu\mathbf{e}_\mu+\gamma_\nu\mathbf{e}_\nu=0\quad\text{on }\Omega_\iota \tag{149}$$

where $\iota\in I_{\mathrm{Pt}/s}$; $I_{\mathrm{Pt}/s}$ is the index set of common points that do not involve an intersection with a solid phase volume; the common point $\Omega_\iota=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta\cap\overline{\Omega}_\gamma\cap\overline{\Omega}_\delta$; and the corresponding common curves are $\Omega_\kappa=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta\cap\overline{\Omega}_\gamma,\Omega_\lambda=\overline{\Omega}_\alpha\cap\overline{\Omega}_\beta\cap\overline{\Omega}_\delta,\Omega_\mu=\overline{\Omega}_\alpha\cap\overline{\Omega}_\gamma\cap\overline{\Omega}_\delta$, and $\Omega_\nu=\overline{\Omega}_\beta\cap\overline{\Omega}_\gamma$.

Averaging of these equilibrium constraints to the macroscale is straightforward, perhaps with the exception of the constraints on the solid surface. Because this surface is constrained to be smooth, the macroscale normal equilibrium condition is obtained as an integral of the various terms over the entire surface. We obtain

$$\begin{aligned}&\langle \mathbf{n}_s \cdot \mathbf{t}_s \cdot \mathbf{n}_s \rangle_{\Omega_{ss},\Omega_{ss}} + \sum_{\iota \in I_{\mathrm{I}s}} \langle p_\alpha + \gamma_\iota \nabla\prime \cdot \mathbf{n}_s - \rho_\iota \mathbf{n}_s \cdot \mathbf{g}_\iota \rangle_{\Omega_{ss},\Omega_{ss}} \\ &+ \sum_{\iota \in I_{\mathrm{C}s}} \langle \delta_C\left(\xi_\iota\right)\left(\gamma_\iota \kappa_{N\iota} - \gamma_\kappa \sin\varphi_\kappa - \rho_\iota g_\iota \cdot \mathbf{n}_s\right)\rangle_{\Omega_{ss},\Omega_{ss}} \\ &- \sum_{\iota \in I_{\mathrm{Pts}}} \langle \delta_P\left(\xi_\iota\right)\gamma_\lambda \mathbf{e}_\lambda \cdot \mathbf{n}_s \rangle_{\Omega_{ss},\Omega_{ss}} = 0\end{aligned} \tag{150}$$

where interfaces are of the form $\Omega_\iota = \overline{\Omega}_\alpha \cap \overline{\Omega}_s$, common curves are of the form $\Omega_\iota = \overline{\Omega}_\alpha \cap \overline{\Omega}_\beta \cap \overline{\Omega}_s$, common points are of the form $\Omega_\iota = \overline{\Omega}_\alpha \cap \overline{\Omega}_\beta \cap \overline{\Omega}_\gamma \cap \overline{\Omega}_s$; the type of entity being summed over is determined by the respective index set of interfaces, common curves and common points all of which involve an intersection with the solid phase volume; the fluid-fluid interface is $\Omega_\kappa = \overline{\Omega}_\alpha \cap \overline{\Omega}_\beta$, and the common curve consisting of the intersection of the three fluid phases is $\Omega_\lambda = \overline{\Omega}_\alpha \cap \overline{\Omega}_\beta \cap \overline{\Omega}_\gamma$.

5 Constraint Approaches

The TCAT approach relies upon a system EI to guide the development of closure relations. To be of use for this purpose, it is necessary to incorporate the conservation equations for which closure relations are sought. This incorporation is accomplished by arranging conservation equations such that they are equal to zero, multiplying them by a Lagrange multiplier, and summing them with the system EI. The resultant expression lacks a connection between material derivatives of entropy and material derivatives of the conserved quantities. To make this connection, thermodynamic expressions relating the material derivative of internal energy, entropy, mass, and volume and related intensive quantities are arranged to equate to zero, multiplied by a Lagrange multiplier, and summed to the system EI as well, yielding an augmented EI (AEI). For the general case of multispecies flow in a multiphase system, the AEI is

$$\sum_{\iota \in I} \sum_{i \in I_{s\iota}} \left(S^{i\iota} + \lambda_{\mathscr{M}}^{i\iota} \mathscr{M}^{i\iota} + \lambda_P^{i\iota} \cdot P^{i\iota} + \lambda_\varepsilon^{i\iota} \varepsilon^{i\iota} + \lambda_{\mathrm{T}}^{i\iota} \mathrm{T}^{i\iota} \right) = \Lambda \geq 0 \tag{151}$$

Eq. (151) is a general AEI and simpler versions may be used in many cases. For example under most circumstances, it will be allowable to consider an entity-based, rather than species-based, entropy balance and conservation of energy. If this decision is made, then the thermodynamic expressions relating the material derivatives of energy, entropy, and other quantities would typically assume a corresponding form. For such a case, a resultant formulation would be

$$\lambda_T^{i\iota} = \lambda_T^\iota, \quad \forall i \tag{152}$$

$$\lambda_\varepsilon^{i\iota} = \lambda_\varepsilon^\iota, \quad \forall i \tag{153}$$

$$\sum_{i \in I_{s\iota}} S^{i\iota} = S^\iota \tag{154}$$

$$\sum_{i \in I_{s\iota}} \varepsilon^{i\iota} = \varepsilon^\iota \tag{155}$$

$$\sum_{i \in I_{s\iota}} T^{i\iota} = T^\iota \tag{156}$$

resulting in an AEI of the form

$$\sum_{\iota \in I} \left[S^{\iota} + \lambda_{\varepsilon}^{\iota} \varepsilon^{\iota} + \lambda_{T}^{\iota} T^{\iota} + \sum_{i \in I_{s\iota}} \left(\lambda_{\mathscr{M}}^{i\iota} \mathscr{M}^{i\iota} + \lambda_{P}^{i\iota} \cdot P^{i\iota} \right) \right] = \Lambda \geq 0 \tag{157}$$

The AEI given by Eq. (157) retains the species forms of the mass and momentum equations for all entities. However, other choices are possible. For example, a species summed version of the momentum equation could be used following a similar approach that was used to combine the energy and entropy equations. The consequence of such an action would be that the difference in the mass-averaged species and entity velocities would require a closure approximation in the species summed momentum equation, while the species stress tensors would be combined such that a closure relation would be needed only for the entity based stress tensors. It is also possible to consider cases in which species are not of concern in certain entities. For example, an inert solid phase could be considered in which composition effects are relatively unimportant and could thus be ignored. The point of these examples is that a variety of models can be derived from the TCAT approach through the selection of different forms of the AEI as obtained by judicious selection of conditions relating the Lagrange multipliers. Additional work will be needed to compare such models and determine the appropriate level of detail for any given case.

6 Discussion

The preceding work details the formulation of important components needed to advance more sophisticated TCAT models than those formulated to date. In particular, the multiphase species conservation and the entropy balance equations for phase volumes, interfaces, and common curves are now complete. The averaged forms of CIT for these entities has been formulated as well, and the conditions that must hold at equilibrium have further been detailed.

These components can be used to formulate a range of models, such as species transport in single-fluid-phase systems, multiphase flow, and multiphase flow and species transport. Because these fundamental components will not change as a function of the application of concern, these results can be used for any of these applications without modification. The TCAT framework that has been developed and the components detailed herein thus form the basis upon which hierarchies of models of various levels of sophistication can be built. This leaves the important future work to focus on model closure methods and detailed validation by comparison to microscale experimental observations and highly resolved simulations.

Further theoretical work is certainly possible, which would require the derivation of additional modeling components. We would advocate such approaches if models built upon the existing theoretical components proved to be inadequate. Advances that might warrant consideration would include the following:

- species internal energy form of ACIT—the averaged thermodynamics in this work is based upon the internal energy for an entity; an extension to this approach would be to develop the averaged thermodynamics for a species-entity combination; such an approach might prove to have utility in the future for more sophisticated models than those considered to date;
- alternative averaged thermodynamic basis—TCAT requires a thermodynamic representation at the microscale be averaged to the macroscale; to date we have relied upon classical irreversible thermodynamics; other approaches are possible and may be required to describe certain systems; such work would lead to alternative forms for the relationship between the material derivatives of internal energy, entropy, densities, entity measures, and other quantities that are intensive quantities at the microscale;

- consideration of systems that containmore than two separated length scales—the work accomplished to date has considered a microscale and a macroscale, with the intent being to develop macroscale models that are connected to the microscale; systems of concern may include additional scales of interest, which will require modifications to the basic TCAT methodology developed to date; and
- even more fundamentally, the lack of existence of an REV for certain systems of interest would require a detailed theoretical investigation of the underlying conservation equations; we acknowledge that many natural systems of concern have such characteristics and ultimately this issue should be considered, but doing so is beyond the scope of our current endeavors.

7 Summary and Conclusions

The development of TCAT models for complex multispecies, multiphase systems requires a significant amount of machinery: conservation and entropy balance equations for phase volumes, interfaces, common curves, and common points; thermodynamic expressions for material derivatives; knowledge of equilibrium conditions; and theorems needed to change scales for differential and integral operators and restrict operators to surfaces and curves. Understanding of the details of this mathematical machinery and model building blocks is necessary for those wishing to develop models using the TCAT approach.

This work builds upon previous work in this series by deriving conservation and balance equations needed to consider species transport in complex multiphase systems, formulating ACIT in species forms for the entities of concern, and detailing the derivation and final form of equilibrium conditions for the entities of concern in species form.

The building blocks established in this work will be essential ingredients in the derivation of a wide range of more sophisticated TCAT models, which will include species transport and multiphase systems. With the details of how these components were derived established in this work, it will be possible to simply borrow the final results when deriving new TCAT models, which will streamline future work, while still providing a means to examine the details of any part of the work for those wishing to develop their own models.

The fundamentals outlined in this work are not the final word. TCAT models can be extended in a variety of ways. Some of these extensions include consideration of alternative thermodynamic forms both in terms of the thermodynamic basis and the averaged forms derived; multiple length scale systems; non-local systems; and other higher order effects, such as an alternative treatment of common points.

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Notation

Roman letters

$\boldsymbol{b}$

	entropy source density
$\mathbf{C}$	Greens' deformation tensor
$\mathbf{d}$	rate of strain tensor
$\boldsymbol{E}$	internal energy density
$\boldsymbol{E_T}$	total energy density
$\boldsymbol{\varepsilon}$	the set of entities
$\boldsymbol{\varepsilon}_{\mathbf{C}}$	the set of common curve entities
$\boldsymbol{\varepsilon}_{\mathbf{I}}$	the set of interface entities
$\boldsymbol{\varepsilon}_{\mathbf{P}}$	the set of phase volume entities
$\boldsymbol{\varepsilon}_{\mathbf{Pt}}$	the set of common point entities
$\boldsymbol{\varepsilon}$	conservation of energy equation
	internal energy
$\boldsymbol{\varepsilon}_{\mathbf{c}}$	connected set of entities
$\mathbf{e}$	unit vector tangent to a common curve and oriented positive outward
$\boldsymbol{e_{i\iota}}$	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
$\boldsymbol{e_{Ti\iota}}$	total macroscale energy transfered intra-entity from all other species in entity ι to the *i* species per unit measure of the ι entity
$e_T^{i\iota}$	total macroscale energy transfered intra-entity from all other species in entity ι to the *i* species per unit measure of the ι entity
$\boldsymbol{F}$	thermodynamic functional to be minimized
$\boldsymbol{f}$	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
$\boldsymbol{h}$	heat source density
$\mathbf{I}$	identity tensor
$\mathbf{I}'$	surface identity tensor
$\boldsymbol{I}$	index set of entities
$\boldsymbol{I}_{\mathbf{C}}$	index set of common curve entities
$\boldsymbol{I}_{\mathbf{C}\boldsymbol{s}}$	index set of common curve entities that include an intersection with the solid phase volume
$\boldsymbol{I}_{\mathbf{C}/\boldsymbol{s}}$	index set of common curve entities that do not include an intersection with the solid phase volume
$\boldsymbol{I}_{\mathbf{c}}$	index set of connected entities
$\boldsymbol{I}_{\mathbf{f}}$	index set of fluid phase volumes
$\boldsymbol{I}_{\mathbf{I}}$	index set of interface entities
$\boldsymbol{I}_{\mathbf{I}\boldsymbol{s}}$	index set of interface entities that include an intersection with the solid phase volume
$\boldsymbol{I}_{\mathbf{I}/\boldsymbol{s}}$	index set of interface entities that do not include an intersection with the solid phase volume
$\boldsymbol{I}_{\mathbf{P}}$	index set of phase volume entities
$\boldsymbol{I}_{\mathbf{Pt}}$	index set of common point entities
$\boldsymbol{I}_{\mathbf{Pt}\iota}$	

	index set of all microscale points in the REV that describes Ω_ι
$\boldsymbol{I}_{\mathbf{Pt}\boldsymbol{s}}$	index set of common point entities that include an intersection with the solid phase volume entity
$\boldsymbol{I}_{\mathbf{Pt}/\boldsymbol{s}}$	index set of common pont entities that do not include and intersection the solid phase volume entity
$\boldsymbol{I}_{\boldsymbol{s}}$	index set of species
$\boldsymbol{I}_{\boldsymbol{s\iota}}$	index set of species in entity ι
$\boldsymbol{j}_{\boldsymbol{s}}$	solid-phase Jacobian
$\boldsymbol{K}_{\boldsymbol{E}}$	macroscale kinetic energy per unit mass due to microscale velocity fluctuations
	mass
$\boldsymbol{M}$	variational constant subject to mass conservation constraint
$\mathfrak{M}$	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
$\overset{i\kappa\to i\iota}{M}_{\upsilon_i}$	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
$\boldsymbol{P}$	conservation of momentum equation
i	general microscale property
$\boldsymbol{p}$	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
	entropy
S	set of all species
$\mathcal{T}$	constant used to constrain a variation to occur at maximum entropy
T	CIT-based thermodynamic equation for material derivative of internal energy
$\overset{j\kappa\to i\iota}{\mathbf{T}}$	transfer of momentum from species in the κ entity to the *i* species in the ι entity due to stress and deviation from mean processes per unit volume per unit time
$\overset{j\kappa\to i\iota}{T}_{v_i}$	transfer of energy from species in the κ entity to the *i* species in the ι entity due to work and deviation from mean processes per unit volume per unit time
$\mathbf{t}$	stress tensor
t	time
V	volume
$\mathbf{V}$	constant reference velocity

$\mathbf{v}$	velocity
W	weighting function in averaging operator
$\mathbf{X}$	material coordinate position vector
$\mathbf{x}$	position vector in the solid phase
$\underset{j\kappa\to i\iota}{z_Q}$	fraction of heat energy transferred from species in the κ entity to the ι entity that impacts the *i* species in the ι entity
$\underset{j\kappa\to i\iota}{z_T}$	fraction of stress transferred from species in the κ entity to the ι entity that impacts the *i* species in the ι entity
$\underset{j\kappa\to i\iota}{z_\Phi}$	fraction of entropy transferred from species in the κ entity to the ι entity that impacts the *i* species in the ι entity

Greek letters

$\boldsymbol{\Gamma}$	boundary of domain of interest
$\boldsymbol{\gamma}$	interfacial tension
$\boldsymbol{\delta}$	spatial variation involving a quantity and its microscale coordinates
$\bar{\boldsymbol{\delta}}$	variation of a quantity at the macroscale
$\bar{\bar{\boldsymbol{\delta}}}$	fixed-point spatial variation
$\bar{\bar{\boldsymbol{\delta}}}'$	fixed-point spatial variation with respect to surface coordinates
$\bar{\bar{\boldsymbol{\delta}}}''$	fixed-point spatial variation with respect to curvilinear coordinates
$\boldsymbol{\delta}_{ij}$	Kronecker delta function
$\boldsymbol{\varepsilon}^{\iota}$	measure of quantity of entity ι per macroscale volume
$\boldsymbol{\eta}$	entropy density
$\boldsymbol{\theta}$	temperature

$\boldsymbol{\kappa}_{G\iota}$	Gaussian curvature of the ι common curve entity
$\boldsymbol{\kappa}_{N\iota}$	normal curvature of the ι common curve entity
$\boldsymbol{\Lambda}$	entropy production rate density
$\boldsymbol{\lambda}$	vector of Lagrange multipliers
$\boldsymbol{\lambda}$	Lagrange multiplier
$\boldsymbol{\mu}$	chemical potential
$\boldsymbol{\xi}$	microscale position vector
$\boldsymbol{\rho}$	mass density
$\boldsymbol{\sigma}$	Lagrangian stress tensor for the solid phase
$\overset{j\kappa\to i\iota}{\Phi}$	transfer of entropy from species in the κ entity to the *i* species in the ι entity per unit volume per unit time
$\boldsymbol{\phi}_{\iota}$	contact angle between the solid phase and the ι interface
$\boldsymbol{\varphi}$	entropy density flux vector
$\boldsymbol{\psi}$	acceleration potential (e.g., gravitational potential)
$\boldsymbol{\Omega}$	spatial domain
$\bar{\boldsymbol{\Omega}}$	closed spatial domain
$\boldsymbol{\Omega}_{ss}$	solid surface spatial domain
$\boldsymbol{\omega}$	mass fraction of a species in an entity

Subscripts and superscripts

ε	energy equation qualifier (subscript)
i	general index denoting a species (subscript and superscript)

$\boldsymbol{j}$	general index (subscript)
$\boldsymbol{k}$	general index denoting a species (subscript and superscript)
$\boldsymbol{l}$	general index (subscript)
$\mathcal{M}$	mass equation qualifier (subscript)
$\boldsymbol{P}$	momentum equation qualifier (subscript)
$\boldsymbol{s}$	index that indicates a solid phase (subscript and superscript)
$\mathbf{T}$	thermodynamic equation qualifier (subscript)
$\boldsymbol{\alpha}$	entity qualifier (subscript)
$\boldsymbol{\beta}$	entity qualifier (subscript)
$\boldsymbol{\gamma}$	entity qualifier (subscript)
$\boldsymbol{\delta}$	entity qualifier (subscript)
$\boldsymbol{\iota}$	entity qualifier (subscript and superscript)
$\boldsymbol{\kappa}$	entity qualifier (subscript and superscript)
$\boldsymbol{\lambda}$	entity qualifier (subscript)
$\boldsymbol{\mu}$	entity qualifier (subscript)
$\boldsymbol{\nu}$	entity qualifier (subscript)

Other mathematical symbols

$\overline{}$	closure of set (overline)
$\langle\ \rangle$	averaging operator
$\mathbf{D}^{\overline{i\iota}}/\mathbf{D}t$	material derivative as defined by Eq. (56)

$\partial'/\partial t$	partial derivative of a point on a potentially moving interface as defined in Eq. (72)
$\partial''/\partial t$	partial derivative of a point on a potentially moving common curve as defined by Eq. (83)
∇'	microscale surficial del operator on an interface as defined in Eq. (71)
∇''	microscale curvilinear del operator on a common curve as defined by Eq. (82)

Abbreviations

ACIT	averaged classical irreversible thermodynamics
AEI	augmented entropy inequality
CIT	classical irreversible thermodynamics
EI	entropy inequality
n	entity index corresponding to the non-wetting phase volume
ns	entity index corresponding to the non-wetting-solid interface
REV	representative elementary volume
s	entity index corresponding to the solid phase volume
TCAT	thermodynamically constrained averaging theory
w	entity index corresponding to the wetting phase volume
wn	entity index corresponding to the wetting-non-wetting interface
wns	entity index corresponding to the wetting-non-wetting-solid common curve
ws	entity index corresponding to the wetting-solid interface