

Chapter 2

Microscale Conservation Principles

2.1 Overview

TCAT models are developed by formally upscaling conservation and balance equations, thermodynamic relations, and equilibrium conditions from the microscale to a macroscale, a megascale, or some combination of the two scales. A prerequisite of a TCAT implementation is thus the full set of microscale equations that are to be upscaled. The purpose of this chapter is to provide the necessary understanding and forms of the microscale conservation and balance equations. Microscale thermodynamics will be presented in Chap. 3 and the microscale equilibrium conditions will be developed in Chap. 4.

Recall that the microscale is sufficiently large to allow the use of a continuum, rather than a molecular, representation of the physical system and sufficiently well resolved that the geometry of each entity is completely represented. This means that phases are viewed as being juxtaposed and a geometric description of the regions occupied by each phase is employed. The interfacial areas between phases, common curves where three phases come together, and common points where four phases come together are all parts of the problem description. Solution for the locations of the boundaries of the phases may be necessary for the microscale problem (i.e., for the case of a moving boundary problem [4]). Certain extensive quantities are known to be conserved or balanced within each of the entity types. Extensive properties of a system, such as mass, momentum, angular momentum, energy, entropy, and electrical charge, are additive.¹ The total amount of an extensive quantity in a system is the sum of the amounts of the extensive quantity associated with each element of the system. Intensive quantities are not additive. For example, temperatures, pressures, and chemical potentials are not additive. A system that is formed as a combination of two identical systems possesses twice the amount of extensive properties of each contributing system, while the intensive properties of the individual and combined

¹ Although conservation of electrical charge is an important principle that has applicability in porous media problems such as fuel cells and capillary electrochromatography [5, 11, 13], this is not covered in this book.

systems are the same. Conservation and balance equations are not derived for intensive quantities, only for extensive quantities. Conservation and balance equations describe the rate of change of the amount of an extensive quantity in a region. They account for flows of the property into and out of the region as well as sources and generation of the quantity. Formulation of these equations in terms of microscale properties is the subject of this chapter.

Traditional treatments of conservation principles are primarily concerned with conservation of properties of a phase. Exchanges between phases at interfaces between phases are accounted for by jump conditions [e.g., 6]. Our study adopts a more comprehensive approach. For porous medium problems, the dynamics of processes occurring at microscale discontinuities, including interfaces, common curves, and common points, are important to the system behavior. By their nature, porous media are highly heterogeneous from a microscale perspective due to these discontinuities. Thus, it is imperative that all important features of conservation and balance principles involving these entities be accounted for in larger scale equations, as well as at the microscale. Therefore, we will make use of general conservation and balance equations not only for phases but also for interfaces, common curves, and common points. Conservation principles will be developed for material in an entity as a whole and also based on each species that may be present in an entity. Summation of the species-based forms of conservation relations will provide the entity-based forms; for an entity consisting of a single chemical species, the entity- and species-based forms are identical.

The ability to account for processes occurring in regions of discontinuity between phases in porous media is conceptually appealing. However, in practice this ability comes only with significant overhead due to the expansion in the number of conservation equations that must be employed. A brief count will reinforce this notion. There are four different types of entities: phases, interfaces, common curves, and common points. For each entity, we can consider three types of conservation and balance equations by formulating them for each chemical species, for an entity composed of a single chemical species, and by considering the entity equations as accounting for the behavior of all species collectively. This suggests that 12 different classes of equations exist. For each of these 12 classes there are nine conservation or balance equations, excluding conservation of charge. These are the scalar mass conservation, energy conservation, and entropy balance equations plus the vector momentum and angular momentum equations, each of which consists of three components. Thus, we can potentially form 108 different conservation or balance equations. For common points, the radius of possible rotation is zero so that we need not consider the nine possible equation types of angular momentum counted above. Thus, there are 99 equations that may potentially be employed in modeling a system. All of these equations are not needed to describe a given system (e.g., for a single-fluid-phase porous media system, no common curves or common points exist; if one employs conservation equations for all species in an entity, the entity-based equation is not needed). For some systems, more than 99 equations will be employed since species-based equations can be employed for each chemical species present in each entity. By considering the differences in the full set of equations, however, we

will have a basis for selection of equations to be used to model a system of interest. The focus of this chapter is on providing examples of the derivation of the equations and on listing the equations of importance.

Several approaches exist for deriving the microscale conservation and balance equations. One approach is to derive a general conservation equation for each type of entity and to specify the appropriate mapping between the general conservation equation and the physical phenomena of interest for a particular conservation equation. We will follow this approach because it provides the opportunity to minimize the calculations that must be performed in comparison to ignoring similarities and developing equations for each conserved quantity by independent calculations.

2.2 General Conservation and Balance Principles

This section proceeds by first presenting a conceptual conservation or balance equation that describe the physical processes that must be considered in the formulation of an appropriate equation. Then, in the subsequent subsections, the conceptual physical description provided is translated into a mathematical form that is appropriate for each of the four types of entities.

2.2.1 General Qualitative Formulation

Because we are interested in changes with time of extensive properties, we will develop equations that describe the rate of change of a property in a domain of interest. A change in the amount of a property in a region must be due to advective transport of the property across the boundary, the rate at which the property is added within the domain due to body sources, non-advective boundary fluxes of the property, and generation of the property within the domain. These mechanisms can be combined in a conceptual balance equation that accounts for the rate of change of the extensive property within a domain as

$$\begin{aligned} & \left[\begin{array}{c} \text{Rate of} \\ \text{Accumulation} \end{array} \right] + \left[\begin{array}{c} \text{Net Outward} \\ \text{Advective Flux} \end{array} \right] - \left[\begin{array}{c} \text{Body} \\ \text{Sources} \end{array} \right] \\ & - \left[\begin{array}{c} \text{Non-advective} \\ \text{Boundary Sources} \end{array} \right] - \left[\begin{array}{c} \text{Rate of} \\ \text{Generation} \end{array} \right] = 0 . \end{aligned} \quad (2.1)$$

The dimensions, or units, of Eq. (2.1) are the dimensions of the extensive property being considered per time. The challenge is to convert this verbal equation into an appropriate and useful mathematical form. The ease with which this can be done depends on the extensive property that is being conserved and physical insight about the forms of the source and generation terms. Insight exists based on the shared

human experience over centuries that has resulted in detailed studies of physical systems including highly resolved experimental results and computational analyses across many scales.

Equation (2.1) can be used to formulate microscale conservation equations by first considering a megascale region whose boundary is resolved at the microscale. There are several aspects of this region that should be noted. The extent and location of the region are not necessarily fixed. Note, however, that for the extensive property of interest to enter (or exit) the region, it must be transported in a direction normal to the boundary of the region. Thus, the normal velocity of advective transport at the boundary relative to the velocity of the boundary is important, not just the velocity alone. Advection tangent to the surface, or normal to the surface but at the same velocity as the normal velocity of the boundary, will not result in a flux of a property of interest into or out of the system. The boundaries of a region need not be coincident with any physical boundary, but can be located as is convenient or desirable to identify a particular study region. For example, a portion of an interface between phases may be considered rather than the entire interface; or a volume can be considered that moves through a larger system at some selected velocity to model the rate of change of the extensive property in that volume. For convenience here, though not generally required, the domains will be selected such that microscale properties are continuous within the region and are first-order differentiable with respect to space. If a fluid is in a porous medium, the microscale domain chosen is such that it consists exclusively of that fluid. An interface between fluids, for example, will be studied in a surficial domain that contains only that interface type. Additionally, the requirement of first order differentiability is employed so that the normal to an interface domain is unique and the tangent to a common curve is unique. This condition does not preclude the ability to consider piecewise continuous or disconnected regions in identifying a domain. For the continuum mechanical approach taken here, small changes in the size of a region should in turn lead to small changes in respective extensive quantities.

2.2.2 General Quantitative Formulation

Suppose it is desired to develop a conservation equation for an extensive property in a region Ω with boundary Γ . When considering a phase, Ω is a volumetric region with surface Γ ; for an interface property, Ω is a surface region with bounding curve Γ ; for a curve, Ω is a one-dimensional region with end points at Γ . Note that while a volume always has a boundary, a closed surface or a closed common curve will not have a boundary. Common points have no boundaries. Now designate the extensive property of interest as \mathbb{F} . Furthermore, let the point value per unit region (i.e., the density of \mathbb{F}) be indicated as F . Thus for a spatial domain, F has units of the extensive property per unit volume; while for a surficial domain, F has units of the extensive property per unit area; and so forth. In formulating a balance equation, it is important to take into account the fact that although \mathbb{F} is an extensive quantity,

it may vary at the microscale throughout the region such that \mathbb{F} is not necessarily equal to the product of F at any given point in Ω and the extent of the integration region, which could be a volume, area, length, or number of points depending upon the type of entity represented by Ω . Additionally, the material within the region might not have a uniform microscale velocity; and the fluxes at the boundary are not necessarily uniform across the boundary. Thus, the successful development of a conservation equation with units of the extensive quantity per unit time must depend upon integral expressions over the domains and their boundaries. For example, the extensive property, \mathbb{F} , is related to its density distribution within a domain, F , according to

$$\mathbb{F} = \int_{\Omega} F \, d\tau . \quad (2.2)$$

The rate of accumulation term in Eq. (2.1) for extensive property \mathbb{F} is expressed as

$$\left[\begin{array}{c} \text{Rate of} \\ \text{Accumulation} \end{array} \right] = \frac{d\mathbb{F}}{dt} = \frac{d}{dt} \int_{\Omega} F \, d\tau . \quad (2.3)$$

The net rate of advective transport out of Ω is related to the advective flux across the boundary, Γ . Denote the advective velocity as \mathbf{v} , the velocity of the boundary of the domain as \mathbf{w} and the unit normal vector to the boundary oriented to be positive outward as \mathbf{n} . The amount of \mathbb{F} that will cross the boundary depends upon the density distribution F at the boundary and the normal advective velocity, $\mathbf{v} \cdot \mathbf{n}$, relative to the normal velocity of the boundary, $\mathbf{w} \cdot \mathbf{n}$. The rate of depletion of \mathbb{F} in the region of interest due to advective flux across the boundary, the second term in Eq. (2.1), is

$$\left[\begin{array}{c} \text{Net Outward} \\ \text{Advective Flux} \end{array} \right] = \int_{\Gamma} F (\mathbf{v} - \mathbf{w}) \cdot \mathbf{n} \, d\tau . \quad (2.4)$$

It is helpful to realize that the sign of $(\mathbf{v} - \mathbf{w}) \cdot \mathbf{n}$ determines whether the flux is into (negative) or out of (positive) the region.

The body source rate of supply of \mathbb{F} per unit of domain is denoted $S_{\Omega T}$, where the subscript T indicates that we are considering the total body source which can be broken into components as will be seen subsequently. The rate of generation within the body per unit of domain is denoted G_{Ω} . These two quantities may be integrated over the domain so that the third and fifth terms in Eq. (2.1) are expressed as

$$\left[\begin{array}{c} \text{Body} \\ \text{Sources} \end{array} \right] + \left[\begin{array}{c} \text{Rate of} \\ \text{Generation} \end{array} \right] = \int_{\Omega} S_{\Omega T} \, d\tau + \int_{\Omega} G_{\Omega} \, d\tau . \quad (2.5)$$

The supply of \mathbb{F} at the boundary due to processes other than advection still involves transfer across the boundary and therefore is in the direction normal to the boundary. Because non-advective transport may also occur in directions tangent to the boundary, it is important to isolate the component of this transport that is normal

to the boundary. The non-advective transfer of \mathbb{F} per unit of boundary in the normal direction is denoted as $\mathbf{S}_\Gamma \cdot \mathbf{n}$ so that the fourth term in Eq. (2.1) is accounted for as

$$\left[\begin{array}{c} \text{Non-advective} \\ \text{Boundary Sources} \end{array} \right] = \int_\Gamma \mathbf{S}_\Gamma \cdot \mathbf{n} \, d\tau . \quad (2.6)$$

Substitution of Eqs. (2.3)–(2.6) into Eq. (2.1) yields the general conservation equation,

$$\frac{d}{dt} \int_\Omega F \, d\tau + \int_\Gamma F (\mathbf{v} - \mathbf{w}) \cdot \mathbf{n} \, d\tau - \int_\Omega S_{\Omega T} \, d\tau - \int_\Gamma \mathbf{S}_\Gamma \cdot \mathbf{n} \, d\tau - \int_\Omega G_\Omega \, d\tau = 0 . \quad (2.7)$$

The particular forms that the integrands take in this equation depend upon the extensive quantity being conserved or balanced and the geometric dimensionality of the region being considered.

Equation (2.7) provides a good beginning point to develop conservation and balance equations for properties of entities as a whole, whether those entities be volumes, surfaces, curves, or common points. A small twist has to be accommodated in considering common curves and points due to their geometric character. For instance, the boundary of a curve is the points at the end of the curve. Thus the integral over the boundary of a common curve has to be simplified to be explicitly represented as a sum over the end points of the curve. This issue will be treated in detail when developing the equations for the common curve explicitly.

2.2.3 Species-based Quantitative Formulation

In most porous medium systems of interest, a phase will consist of multiple species. For example, a water phase may contain not only hydrogen and oxygen, but also a wide range of other inorganic and organic species—hundreds of different species in some cases. Species-based models are important under two conditions. First, the composition of a phase may be of interest intrinsically. This would be the case if a species in the phase were a contaminant of interest and it were important to model the spatial and temporal distribution of the species. Second, the composition of a phase can influence its physical or chemical properties and hence its behavior. For example, changes in the mass fraction of an inorganic salt can affect the density or viscosity of a water phase. Similar comments apply for other entities as well. Therefore, species-based, or compositional, porous medium models can be important.

In the interest of generality, we will be developing conservation and balance equations for the properties of individual species in an entity. The species-based equations can be obtained by identification of the chemical species processes corresponding to terms in Eq. (2.7). The equations obtained apply directly for the single-species and multiple-species situations. Summation of a species conservation equa-

tion over all species impacting the entity yields a conservation or balance equation for the entity as a whole. Here we provide the general species-based form. The “derivation” involves little more than the introduction of some subscript notation into Eq. (2.7).

Because we are studying species in phase, interface, common curve, and common point entities, it is helpful to make use of notation that identifies both the species and the entity of interest. We will make use of subscripts to designate quantities of interest as being microscale properties.² The subscript i is used to designate an individual chemical species from among the full set of chemical species in the system. The subscript α is used to indicate the entity that is being considered. For example, in the general equation, $F_{i\alpha}$ would be the density of the microscale property of interest for chemical species i in entity α . The domain of all species in entity α is Ω_α and the boundary of that domain is Γ_α . Neither the domain nor the boundary depends on the chemical species being considered in the entity. The outwardly directed normal from the boundary of Ω_α is the unit vector \mathbf{n}_α . Each chemical species may have a different advective velocity so that the velocity of species i in entity α is designated as $\mathbf{v}_{i\alpha}$. Although each species may have a different velocity, thereby requiring the use of subscript i to differentiate among the species present, the velocity of the boundary of the domain is species independent. Therefore, the boundary velocity is denoted as \mathbf{w}_α . The body source, non-advective surface source, and the generation terms in Eq. (2.7) all may depend on the species being considered and the entity. Therefore, the subscript $i\alpha$ will be appended to each of these. Thus, the general conservation equation for an extensive property of a chemical species in an entity α can be written in terms of microscale variables as:

$$\begin{aligned} \frac{d}{dt} \int_{\Omega_\alpha} F_{i\alpha} d\tau + \int_{\Gamma_\alpha} F_{i\alpha} (\mathbf{v}_{i\alpha} - \mathbf{w}_\alpha) \cdot \mathbf{n}_\alpha d\tau - \int_{\Omega_\alpha} S_{\Omega T i \alpha} d\tau \\ - \int_{\Gamma_\alpha} \mathbf{S}_{\Gamma i \alpha} \cdot \mathbf{n}_\alpha d\tau - \int_{\Omega_\alpha} G_{\Omega i \alpha} d\tau = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}, \end{aligned} \quad (2.8)$$

where \mathcal{J}_s is the set of species indices and \mathcal{J} is the set of entity indices, which includes the indices of phases (\mathcal{J}_P), interfaces (\mathcal{J}_I), common curves (\mathcal{J}_C), and common points (\mathcal{J}_{Pt}) such that $\mathcal{J} = \mathcal{J}_P \cup \mathcal{J}_I \cup \mathcal{J}_C \cup \mathcal{J}_{Pt}$. We will refer to all of the sets of indices as index sets.

With Eq. (2.8) as a starting point, we will make use of theorems that allow equations for an entire entity to be localized so that they apply at any point in the entity. The theorems depend on the dimensionality of the entity. The entity types will be considered in turn, starting with phases and proceeding in order to entities of lower dimensionality. We will then identify the quantities that appear in the general equations based on the processes of interest so that they are particularized to the members of the set of conservation and balance equations.

² It is perhaps premature, but may be helpful, to note that while subscripts are used for microscale quantities, superscripts will be used to designate larger scale quantities in subsequent chapters.

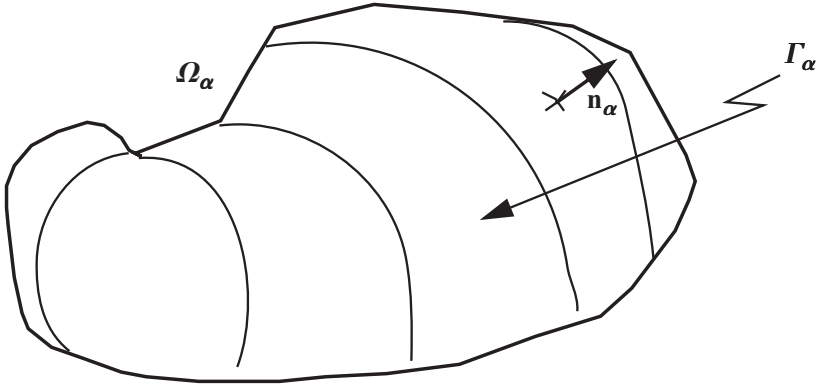


Fig. 2.1 Arbitrary closed volume $\Omega_\alpha \subset \mathbb{R}^3$ containing phase $\alpha \in \mathcal{J}_P$ with boundary $\Gamma_\alpha \subset \mathbb{R}^2$. Unit vector \mathbf{n}_α is normal to Γ_α and oriented to be positive outward from Ω_α

2.3 Conservation and Balance Principles for a Phase

The objectives of this section, which focuses on conservation and balance equations for phases, are twofold. First, the general conservation equation for a species-based extensive property given in Eq. (2.8) will be changed from the given form appropriate for a phase as a whole to a form that is appropriate at any microscale point in the phase. Second, particular forms of the conservation and balance equations will be developed for mass, momentum, energy, and entropy.

2.3.1 General Microscale Point Forms

The study of conservation of a property of an α phase, where $\alpha \in \mathcal{J}_P$, requires that the region of study, Ω_α with boundary Γ_α be a closed volume, as depicted in Fig. 2.1. The fact that this phase occupies volume can be expressed as $\Omega_\alpha \subset \mathbb{R}^3$, which states that the domain is in three-dimensional real space. The extent of α is the volume it occupies, \mathbb{V}_α . The boundary is a two-dimensional surface, implying that $\Gamma_\alpha \subset \mathbb{R}^2$, and the extent of Γ_α is measured by the area $\mathbb{A}_{\alpha\alpha}$. The double subscript on \mathbb{A} is used to indicate the total boundary area of Ω_α , regardless of any other phase or phases also contacting Γ_α .

Equation (2.8) can be focused further for the specific case of species-based conservation of a phase property and then reduced to a point form. With just the minor tweak of restricting \mathcal{J} to be \mathcal{J}_P , and with proper identification of the integrand terms, Eq. (2.8) becomes a statement of mass, momentum, or energy conservation, or an entropy balance, for a species in a phase. Each of these equations will be formulated after first reducing the equation to point form.

The conversion of Eq. (2.8), with \mathcal{J} restricted to \mathcal{J}_p , to the form that applies at a point within a phase requires that the surface integral terms be converted to volume integrals. This task can be accomplished making use of mathematical theorems. Because a variety of theorems will be relied upon in this work, we adopt a previously established convention to name these theorems [8, 12] of the form $\langle \text{letter} \rangle [i, (j, k), l]$. For a transport theorem $\langle \text{letter} \rangle$ is T while $\langle \text{letter} \rangle$ is replaced by D for a divergence theorem. Gradient theorems, which are similar to divergence theorems, replace $\langle \text{letter} \rangle$ with G. Theorems involving material derivatives and averages of deviations between quantities at different scales are designated as M theorems. The index i indicates the dimensionality of the microscale domain, j refers to the number of macroscale dimensions that make use of differential operators, k is the number of macroscale dimensions over which integration occurs, and l is the number of megascale dimensions. For the theorems of this chapter, conversion is from the megascale, with integrals over the entire domain, to integrals over the microscale. Thus both j and k are zero.

Two theorems are employed to eliminate the surface integrals in Eq. (2.8). The transport theorem is as follows [3, 8, 10, 15]:

Theorem 2.1 (T[3,(0,0),3]) *For a smooth continuous and differentiable function f defined over a domain $\Omega_\alpha \subset \mathbb{R}^3$ that may deform with time t due to velocity \mathbf{w}_α of closed boundary Γ_α with outward normal from the boundary \mathbf{n}_α ,*

$$\frac{d}{dt} \int_{\Omega_\alpha(t)} f \, d\mathbf{r} = \int_{\Omega_\alpha(t)} \frac{\partial f}{\partial t} \, d\mathbf{r} + \int_{\Gamma_\alpha(t)} f \mathbf{w}_\alpha \cdot \mathbf{n}_\alpha \, d\mathbf{r}. \quad (2.9)$$

Physically, when f is the density of some conserved quantity, the left side of Eq. (2.9) represent the change in the total amount of the conserved quantity with time over the entire domain. This change is accounted for on the right side by changes of the property density within Ω_α and movement of the domain boundary Γ_α that could affect both the location of Ω_α where changes in f are being studied and the size of \mathbb{V}_α .

Also of use for manipulations with integrals over the boundary of the domain is the divergence theorem [3, 8, 10, 15]:

Theorem 2.2 (D[3,(0,0),3]) *For a smooth continuous and differentiable tensor function \mathbf{f} defined over a domain $\Omega_\alpha \subset \mathbb{R}^3$ that may deform with time t due to velocity \mathbf{w}_α of closed boundary Γ_α with outward normal from the boundary \mathbf{n}_α ,*

$$\int_{\Omega_\alpha(t)} \text{div} \mathbf{f} \, d\mathbf{r} = \int_{\Gamma_\alpha(t)} \mathbf{f} \cdot \mathbf{n}_\alpha \, d\mathbf{r}, \quad (2.10)$$

where div is a divergence operator that contracts the last index of \mathbf{f} .

If \mathbf{f} is a vector or a symmetric second order tensor, then $\text{div} \mathbf{f}$ may be written equivalently as $\nabla \cdot \mathbf{f}$. In general, if \mathbf{f} is a second order tensor, $\text{div} \mathbf{f}$ is equal to $\nabla \cdot \mathbf{f}^T$, where the superscript T indicates the transpose. Physically, Eq. (2.10) equates the sum of

the net outward fluxes from all points within the spatial domain on the left side to the flux across the domain boundary on the right side.

With f replaced by $F_{i\alpha}$, and \mathbf{f} replaced by $F_{i\alpha}\mathbf{v}_{i\alpha}$ in one instance and by $\mathbf{S}_{\Gamma i\alpha}$ in another, Eqs. (2.9) and (2.10) can be used to eliminate the surface integrals from Eq. (2.8) giving

$$\int_{\Omega_\alpha} \left[\frac{\partial F_{i\alpha}}{\partial t} + \nabla \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega T i\alpha} - \text{div} \mathbf{S}_{\Gamma i\alpha} - G_{\Omega i\alpha} \right] d\mathbf{r} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_p. \quad (2.11)$$

For a phase, the body source does not include fluxes from adjacent entities that act as body sources because a point within a phase is not in contact with any other entities; other entities are encountered only at the boundary of the phase. The portion of the total body source that is independent of adjacent entities is designated as $S_{\Omega i\alpha}$, such that, for a phase,

$$S_{\Omega T i\alpha} = S_{\Omega i\alpha} \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_p. \quad (2.12)$$

Because the integration volume is arbitrary, Eq. (2.11) must hold for any volume that is sufficiently large to meet the previously noted continuum hypothesis requirements. This fact implies that the integrand itself must be zero at each microscale point within the volume. Recall that a value of a microscale quantity at a point implies an average about a volume with a length scale that is long compared to the mean distance between molecules. Thus the general point conservation equation for an extensive property of a species per unit microscale volume in a phase is

$$\frac{\partial F_{i\alpha}}{\partial t} + \nabla \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega i\alpha} - \text{div} \mathbf{S}_{\Gamma i\alpha} - G_{\Omega i\alpha} = 0, \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_p. \quad (2.13)$$

This equation may also be written equivalently using the material derivative as

$$\frac{D_{i\alpha} F_{i\alpha}}{Dt} + F_{i\alpha} \mathbf{l} : \mathbf{d}_{i\alpha} - S_{\Omega i\alpha} - \text{div} \mathbf{S}_{\Gamma i\alpha} - G_{\Omega i\alpha} = 0, \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_p, \quad (2.14)$$

where the material derivative is defined as

$$\frac{D_{i\alpha}}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}_{i\alpha} \cdot \nabla; \quad (2.15)$$

the symmetric rate of strain tensor for species i in phase α is defined as

$$\mathbf{d}_{i\alpha} = \frac{1}{2} \left[\nabla \mathbf{v}_{i\alpha} + (\nabla \mathbf{v}_{i\alpha})^T \right]; \quad (2.16)$$

and \mathbf{l} is the unit tensor. Because our interest in the microscale is primarily to provide equations for transformation to the larger scale, we will work mostly with microscale equations in the form of Eq. (2.13) because mathematical theorems for change in scale are more directly available for the partial time derivative than the material

derivative. We emphasize, however, that Eqs. (2.13) and (2.14) are exactly equivalent.

When a phase consists of only one chemical species, the subscript i may be deleted from Eqs. (2.13)–(2.16) to obtain the general equation for a phase. When a phase is composed of multiple species, a conservation equation for a property of the phase as a whole may be obtained by summing all the conservation equations for that property based on the species present. Then judicious choice of the variables deemed to be characteristic of the phase as a whole, rather than of species-based properties, results in the phase-based conservation equation. This procedure is best accomplished based on the particular property being conserved or balanced to ensure that the phase-based variables are properly defined in terms of the species-based variables.

2.3.2 *Specific Conservation and Balance Principles*

Specific conservation and balance equations can be derived directly from general Eq. (2.13), or the equivalent form given by Eq. (2.14), by selecting a property to be conserved or balanced and then specifying the mapping between the general variables in the equations and specific applicable physical quantities. These quantities must be specified such that all of the operative processes that affect the conservation or balance principle are included in the equation. The discussion here will focus on the physical basis for the respective mapping assignments, and the resulting equation forms will be listed.

The mappings for conservation of species mass, momentum, and energy and for the balance of species entropy are given in Table 2.1. A notation that will prove to be convenient is introduced such that \mathcal{M} , \mathcal{P} , \mathcal{E} , \mathcal{S} , and \mathcal{G} represent equations for conservation of mass, momentum, and energy, and balance of entropy and gravitational potential, respectively, written in partial time derivative form. Additionally, we make use of the notation \mathcal{M}_* , \mathcal{P}_* , \mathcal{E}_* , \mathcal{S}_* , and \mathcal{G}_* to denote the corresponding, and equivalent, equations written using material derivatives. In the table each of the conservation equation types is subscripted with the species qualifier, $i \in \mathcal{I}_s$, and the entity qualifier, $\alpha \in \mathcal{I}_p$ to indicate that the equations apply to that species and phase.

Conservation and balance equations for phase entities accounting for the species collectively rather than individually are given in Table 2.2. Each of the properties appropriate for the conservation equation of interest is given. Note that the sum of a set of species-based equations for a property over all species present is equal to the corresponding phase-based equation. Based on this fact, it is tempting to think that an entry in Table 2.2 is equal to the sum over all species of the corresponding entry in Table 2.1. However this is not so for all terms! Rather the relations between the phase-based and species-based terms must be determined carefully such that multiple definitions for a designated quantity do not arise.

Table 2.1 can be used along with Eq. (2.13) or Eq. (2.14), which are repeated for convenience at the top of the table, to write a full set of species-based conservation

Table 2.1 Physical variables for species-based phase equations in partial derivative or material derivative form. $\mathcal{M}_{i\alpha}$, $\mathcal{P}_{i\alpha}$, $\mathcal{E}_{i\alpha}$, $\mathcal{S}_{i\alpha}$, and $\mathcal{G}_{i\alpha}$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential for species i in phase α

$\mathcal{F}_{i\alpha} = \frac{\partial F_{i\alpha}}{\partial t} + \nabla \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega i\alpha} - \text{div} \mathbf{S}_{\Gamma i\alpha} - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_p$ <p style="text-align: center;">or</p> $\mathcal{F}_{*i\alpha} = \frac{D_{i\alpha} F_{i\alpha}}{Dt} + F_{i\alpha} \mathbf{l} : \mathbf{d}_{i\alpha} - S_{\Omega i\alpha} - \text{div} \mathbf{S}_{\Gamma i\alpha} - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_p$				
$\mathcal{F}_{i\alpha}$	$F_{i\alpha}$	$S_{\Omega i\alpha}$	$\mathbf{S}_{\Gamma i\alpha}$	$G_{\Omega i\alpha}$
$\mathcal{M}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha}$	—	—	$r_{i\alpha}$
$\mathcal{P}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha}$	$\mathbf{t}_{i\alpha}$	$\mathbf{p}_{i\alpha} + r_{i\alpha} \mathbf{v}_{i\alpha}$
$\mathcal{E}_{i\alpha}$	$E_{i\alpha} + \rho_\alpha \omega_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2}$	$\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha} + h_{i\alpha}$	$\mathbf{t}_{i\alpha}^T \cdot \mathbf{v}_{i\alpha} + \mathbf{q}_{i\alpha}$	$e_{i\alpha} + \mathbf{p}_{i\alpha} \cdot \mathbf{v}_{i\alpha} + r_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2}$
$\mathcal{S}_{i\alpha} - \Lambda_{i\alpha}$	$\eta_{i\alpha}$	$b_{i\alpha}$	$\boldsymbol{\varphi}_{i\alpha}$	$\Lambda_{i\alpha}$
$\mathcal{G}_{i\alpha}$	$\Psi_{i\alpha}$	$-\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha}$	—	$\rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} + r_{i\alpha} \psi_{i\alpha}$

and balance equations for a phase. For example, making use of the table, one obtains the equation of conservation of mass of a chemical species in partial time derivative form as:

$$\mathcal{M}_{i\alpha} = \frac{\partial(\rho_\alpha \omega_{i\alpha})}{\partial t} + \nabla \cdot (\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}) - r_{i\alpha} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_p, \quad (2.17)$$

where ρ_α is the mass density equal to mass of α phase per volume of α phase; $\omega_{i\alpha}$ is the mass fraction of species i in phase α (i.e., the fraction of the mass of the phase that is due to the presence of species i); and the generation term, $r_{i\alpha}$, accounts for the set of reactions that produce species i in phase α by conversion from other species. Many simultaneous reactions that either produce or consume species i may be operative. Therefore, $r_{i\alpha}$ is a variable that represents the net result of some set of intraphase biogeochemical reactions. The precise form of these reactions will be system dependent, and the mathematical representation of $r_{i\alpha}$ may be mechanistically rigorous or an approximation that tries to account for the important elements of the reaction. One example of an approximate relation for $r_{i\alpha}$ would be the representation of a complex reaction pathway by only accounting for the rate-limiting step. Another case is the approximation of a higher order reaction by a lower order expression when the mass fraction of one of the reactants is approximately constant. Simplifications of these types are commonplace. Finally, note that in Eq. (2.17) there are no non-advective sources of the species because the only mechanisms for modification of the amount of a chemical constituent at a point are advection and reaction.

The species mass conservation equation in material derivative form, $\mathcal{M}_{*i\alpha}$, may also be obtained directly from Table 2.1 as

Table 2.2 Physical variables for entity-based phase equations in partial derivative or material form. \mathcal{M}_α , \mathcal{P}_α , \mathcal{E}_α , \mathcal{S}_α , and \mathcal{G}_α correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential in phase α

$\mathcal{F}_\alpha = \frac{\partial F_\alpha}{\partial t} + \nabla \cdot (\mathbf{v}_\alpha F_\alpha) - S_{\Omega\alpha} - \nabla \cdot \mathbf{S}_{F\alpha} - \sum_{i \in \mathcal{I}_s} G_{\Omega i\alpha} = 0 \quad \text{for } \alpha \in \mathcal{I}_p$ <p style="text-align: center;">or</p> $\mathcal{F}_{*\alpha} = \frac{D_\alpha F_\alpha}{Dt} + F_\alpha \mathbf{l} : \mathbf{d}_\alpha - S_{\Omega\alpha} - \nabla \cdot \mathbf{S}_{F\alpha} - \sum_{i \in \mathcal{I}_s} G_{\Omega i\alpha} = 0 \quad \text{for } \alpha \in \mathcal{I}_p$				
\mathcal{F}_α	F_α	$S_{\Omega\alpha}$	$\mathbf{S}_{F\alpha}$	$G_{\Omega i\alpha}$
\mathcal{M}_α	ρ_α	—	—	—
\mathcal{P}_α	$\rho_\alpha \mathbf{v}_\alpha$	$\rho_\alpha \mathbf{g}_\alpha$	\mathbf{t}_α	—
\mathcal{E}_α	$E_\alpha + \rho_\alpha \left(\frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} + K_{E\alpha} \right)$	$\rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha + h_\alpha$ $+ \sum_{i \in \mathcal{I}_s} \rho_\alpha \omega_{i\alpha} \mathbf{u}_{i\alpha} \cdot \mathbf{g}_{i\alpha}$	$\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha$	—
$\mathcal{S}_\alpha - \Lambda_\alpha$	η_α	b_α	$\boldsymbol{\phi}_\alpha$	$\Lambda_{i\alpha}$
\mathcal{G}_α	Ψ_α	$-\rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha - \sum_{i \in \mathcal{I}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{u}_{i\alpha}$	$-\sum_{i \in \mathcal{I}_s} \rho_\alpha \omega_{i\alpha} \Psi_{i\alpha} \mathbf{u}_{i\alpha}$	$\rho_\alpha \omega_\alpha \frac{\partial \Psi_{i\alpha}}{\partial t}$ $+ r_{i\alpha} \Psi_{i\alpha}$

$$\mathcal{M}_{*i\alpha} = \frac{D_{i\alpha}(\rho_\alpha \omega_{i\alpha})}{Dt} + \rho_\alpha \omega_{i\alpha} \mathbf{l} : \mathbf{d}_{i\alpha} - r_{i\alpha} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_p. \quad (2.18)$$

Mathematically, this equation is equivalent to Eq. (2.17), and the two equations are interchangeable. Throughout the text, however, we will be careful to make use of the notation $\mathcal{M}_{i\alpha}$ vs. $\mathcal{M}_{*i\alpha}$ to distinguish between the forms of the species conservation equation being employed. In many cases, one form as opposed to the other is more appropriate for a particular analysis.

There are a couple of ways to obtain an equation of mass conservation for the α entity as a whole as in the \mathcal{M}_α row in Table 2.2. For example, the material derivative form for mass conservation is

$$\mathcal{M}_{*\alpha} = \frac{D_\alpha \rho_\alpha}{Dt} + \rho_\alpha \mathbf{l} : \mathbf{d}_\alpha = 0 \quad \text{for } \alpha \in \mathcal{I}_p. \quad (2.19)$$

Note that there are no terms specific to any species or any chemical reaction term in this equation. Unlike the species mass, which can be generated by transformation from a different chemical species, the total mass of all species combined in an entity is not impacted by reactions such that

$$\sum_{i \in \mathcal{I}_s} r_{i\alpha} = 0. \quad (2.20)$$

Although Eq. (2.19) applies whether or not a phase is composed of multiple species, it cannot distinguish among the conservation behaviors of different species. If there is only one species present, then the species-based and phase-based equations are equivalent since $\omega_{i\alpha} = 1$, $\mathbf{v}_{i\alpha} = \mathbf{v}_\alpha$, and $r_{i\alpha} = 0$ in the species-based equation.

Even though the conservation equation for a phase can be obtained as a sum over all the species, this process is not as direct using the material derivative forms as with the partial derivative forms. This is because the velocity in the material derivative can be different for each species. Thus, it is easiest to obtain the phase-based mass conservation equation from the species-based form as

$$\mathcal{M}_\alpha = \frac{\partial \rho_\alpha}{\partial t} + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha) = 0 \quad \text{for } \alpha \in \mathcal{J}_P \quad (2.21)$$

by summing Eq. (2.17) over all species. By making use of the fact that, by definition, the sum of the mass fractions of all species is 1 such that

$$\sum_{i \in \mathcal{J}_s} \omega_{i\alpha} = 1, \quad (2.22)$$

and by choosing \mathbf{v}_α to be the velocity of the center of mass of the material, the barycentric velocity, defined as

$$\mathbf{v}_\alpha = \sum_{i \in \mathcal{J}_s} \omega_{i\alpha} \mathbf{v}_{i\alpha}, \quad (2.23)$$

one obtains Eq. (2.21). Then Eq. (2.19) is obtained directly from Eq. (2.21) by making use of the definition of the material derivative. We can also define the diffusion velocity of a chemical species, $\mathbf{u}_{i\alpha}$, as the species velocity relative to the barycentric velocity such that

$$\mathbf{u}_{i\alpha} = \mathbf{v}_{i\alpha} - \mathbf{v}_\alpha. \quad (2.24)$$

Therefore Eqs. (2.23) and (2.24) can be combined to show that the diffusion velocity must satisfy the constraint that

$$\sum_{i \in \mathcal{J}_s} \omega_{i\alpha} \mathbf{u}_{i\alpha} = \mathbf{0}. \quad (2.25)$$

These last two equations dictate that for a system composed of N chemical constituents, only $N - 1$ of the mass fractions and diffusion velocities are independent; the remaining value of each can be calculated, respectively, from Eqs. (2.22) and (2.25).

Tables 2.1 and 2.2, respectively, can be used to obtain the conservation of momentum vector equation for a species in a phase

$$\begin{aligned} \mathcal{P}_{i\alpha} = & \frac{\partial(\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha})}{\partial t} + \nabla \cdot (\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} \mathbf{v}_{i\alpha}) - \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} - \nabla \cdot \mathbf{t}_{i\alpha}^T \\ & - \mathbf{p}_{i\alpha} - r_{i\alpha} \mathbf{v}_{i\alpha} = \mathbf{0} \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_P, \end{aligned} \quad (2.26)$$

and for the phase as a whole³

³ Because it is somewhat tangential to our objectives here, we will not prove that the stress tensor for an entity is symmetric while the species-based stress tensor is not necessarily symmetric. In the

$$\mathcal{P}_\alpha = \frac{\partial(\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \nabla \cdot (\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha) - \rho_\alpha \mathbf{g}_\alpha - \nabla \cdot \mathbf{t}_\alpha = \mathbf{0} \quad \text{for } \alpha \in \mathcal{J}_P, \quad (2.27)$$

where \mathbf{t} is the stress tensor, \mathbf{g} is the body force per unit mass, and $\mathbf{p}_{i\alpha}$ represents the interspecies transfer of momentum from all other species within phase α to species i .

The conservation of momentum equation relates the change in momentum per volume to the advective transport of momentum, surface forces, body forces, and, for the species-based equation, to inter-species momentum transfer processes. The stress tensor accounts for the effects of material behavior in response to surface forces that act on the entity, such as pressure and frictional effects. The mathematical form of the stress tensor depends upon material properties and is approximated by what is called a constitutive or closure relation. The body force per unit mass accounts for the effects of gravity, Coriolis effects, and electromagnetic forces that act at all points within the entire domain of the phase, Ω_α . While the conservation equation formulated can include all of these body forces, we are primarily concerned with gravitational effects.

Just as $r_{i\alpha}$ represents the net effect of all reactions on the mass production rate of species i per volume, $\mathbf{p}_{i\alpha} + r_{i\alpha} \mathbf{v}_{i\alpha}$ includes two terms that account for the net transfer of momentum from all other species to species i due to interspecies collisions and reactions, respectively.⁴ The net transfer to all species must be zero such that

$$\sum_{i \in \mathcal{J}_s} (\mathbf{p}_{i\alpha} + r_{i\alpha} \mathbf{v}_{i\alpha}) = \mathbf{0}. \quad (2.28)$$

The body force per unit mass for the phase, \mathbf{g}_α is the barycentric sum of the forces acting on each species with

$$\mathbf{g}_\alpha = \sum_{i \in \mathcal{J}_s} \omega_{i\alpha} \mathbf{g}_{i\alpha}. \quad (2.29)$$

Because momentum transferred between species does not impact the total momentum of the system, the sum of the transfer term over all species must be zero. It is a useful exercise to show that obtaining Eq. (2.27) from Eq. (2.26) by summing over all species requires that the entity-based stress tensor be related to the species-based stress tensor according to:

$$\mathbf{t}_\alpha = \sum_{i \in \mathcal{J}_s} (\mathbf{t}_{i\alpha} - \rho_\alpha \omega_{i\alpha} \mathbf{u}_{i\alpha} \mathbf{u}_{i\alpha}). \quad (2.30)$$

Tables 2.1 and 2.2 can also be used directly to state the conservation of energy equations for a species in a phase and for a phase, respectively, as

entity-based equations, either the stress tensor or its transpose may be used equivalently because of symmetry [1, 7, 9].

⁴ A different perspective on the velocity that should multiply $r_{i\alpha}$ in the generation term of Eq. (2.26) has been provided in [16]. However, this issue is not important if one notes that a complementary definition of $\mathbf{p}_{i\alpha}$ can account for any choice of velocity.

$$\begin{aligned}
\mathcal{E}_{i\alpha} = & \frac{\partial}{\partial t} \left(E_{i\alpha} + \rho_{\alpha} \omega_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2} \right) + \nabla \cdot \left[\left(E_{i\alpha} + \rho_{\alpha} \omega_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2} \right) \mathbf{v}_{i\alpha} \right] \\
& - \rho_{\alpha} \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha} - h_{i\alpha} - \nabla \cdot (\mathbf{t}_{i\alpha}^T \cdot \mathbf{v}_{i\alpha} + \mathbf{q}_{i\alpha}) \\
& - e_{i\alpha} - \mathbf{p}_{i\alpha} \cdot \mathbf{v}_{i\alpha} - r_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_p
\end{aligned} \tag{2.31}$$

and

$$\begin{aligned}
\mathcal{E}_{\alpha} = & \frac{\partial}{\partial t} \left[E_{\alpha} + \rho_{\alpha} \left(\frac{\mathbf{v}_{\alpha} \cdot \mathbf{v}_{\alpha}}{2} + K_{E\alpha} \right) \right] + \nabla \cdot \left\{ \left[E_{\alpha} + \rho_{\alpha} \left(\frac{\mathbf{v}_{\alpha} \cdot \mathbf{v}_{\alpha}}{2} + K_{E\alpha} \right) \right] \mathbf{v}_{\alpha} \right\} \\
& - \rho_{\alpha} \mathbf{g}_{\alpha} \cdot \mathbf{v}_{\alpha} - \sum_{i \in \mathcal{I}_s} \rho_{\alpha} \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{u}_{i\alpha} - h_{\alpha} - \nabla \cdot (\mathbf{t}_{\alpha} \cdot \mathbf{v}_{\alpha} + \mathbf{q}_{\alpha}) = 0 \quad \text{for } \alpha \in \mathcal{I}_p.
\end{aligned} \tag{2.32}$$

In these equations, E is the internal energy per volume, which is due to random molecular motion and the chemical bonds present; $K_{E\alpha}$ is a kinetic energy term due to velocity fluctuations of the species relative to the barycentric velocity of the phase; \mathbf{q} is the non-advective heat flux; h is an energy body source term (e.g. radiation); and $e_{i\alpha}$ accounts for the internal energy transferred to species i from all other species. We note that the net transfer of internal and kinetic energy (due to collisions and reaction) among all the species present must be zero such that

$$\sum_{i \in \mathcal{I}_s} \left(e_{i\alpha} + \mathbf{p}_{i\alpha} \cdot \mathbf{v}_{i\alpha} + r_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2} \right) = 0. \tag{2.33}$$

The energy equation warrants careful consideration to ensure that it is well understood on a physical basis. Consider Eq. (2.32), the microscale conservation of energy equation for a phase. The quantity being conserved is the sum of internal and kinetic energy. Internal energy of a phase is obtained as the sum of the species internal energies with

$$E_{\alpha} = \sum_{i \in \mathcal{I}_s} E_{i\alpha}. \tag{2.34}$$

Kinetic energy for the phase equation has two components. The leading order component, $\rho_{\alpha} \mathbf{v}_{\alpha} \cdot \mathbf{v}_{\alpha} / 2$, is based on the barycentric velocity of the phase and the density of the phase. The second component, $\rho_{\alpha} K_{E\alpha}$, provides an addition to this term due to the deviations of the individual species velocities from the barycentric velocity of the phase. To gain insight into this situation, consider a microscale point where the barycentric velocity as defined in Eq. (2.23) is zero. The case that $\mathbf{v}_{\alpha} = 0$ does not imply that all species velocities are zero but merely that the sum of these velocities weighted by their respective mass fractions is zero. Kinetic energy does not depend on the direction of the velocities as it only involves velocity squared. Thus the deviations of species velocities from the barycentric velocity make a contribution to kinetic energy beyond that of the barycentric velocity. By summing Eq. (2.31) over all species and requiring that the result provides the conservation of phase energy equation, one can show that

$$K_{E\alpha} = \sum_{i \in \mathcal{J}_s} \omega_{i\alpha} \frac{\mathbf{u}_{i\alpha} \cdot \mathbf{u}_{i\alpha}}{2} . \quad (2.35)$$

The first divergence term in Eq. (2.32) accounts for the net outward flux of internal plus kinetic energy resulting from advective transport. The non-advective surface sources of energy are included in the next divergence term. The first of these terms is $\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha$, where \mathbf{t}_α is the same quantity defined in Eq. (2.30). This is the rate of work done on the system per volume due to surface forces resulting from stress. This interpretation follows because stress is a force per area and the product with velocity yields the rate of work per area. The second non-advective flux is \mathbf{q}_α , and it is the heat flux into the system that contributes to a change in the system energy. The heat flux vector is another quantity for which a closure relation is needed.

The product $\rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha$ is a body source of energy. The product $\rho_\alpha \mathbf{g}_\alpha$ is a force per volume and the dot product of this product with velocity yields a rate of work per volume. If the force per volume is different for each species in the system, the summation term in Eq. (2.32) will contribute an additional body source due to a non-uniform distribution of chemical species in the system. The energy of a system can also be influenced by an additional type of body source, which is indicated as h_α . This source accounts for non-mechanical physical processes such as radiative transport. The dimensions of this term are energy contributed to the system per volume per time. By using the fact that the sum of the body source terms based on the species over all species must equal the body source terms for the phase, one obtains

$$h_\alpha = \sum_{i \in \mathcal{J}_s} h_{i\alpha} . \quad (2.36)$$

Terms similar to those described above for the phase-based energy equation appear also in the species-based form of Eq. (2.31). The physical descriptions of the terms are similar, although they pertain to species rather than to the entity as a whole. One important difference is the presence of the last three terms on the left side of Eq. (2.31) that account for inter-species transfer of energy. The quantity $r_{i\alpha} \mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha} / 2$ accounts for the rate of change in kinetic energy of the species per volume that accompanies a chemical reaction. The term $\mathbf{p}_{i\alpha} \cdot \mathbf{v}_{i\alpha}$ is the rate of work done on species i due to collisions with other species. Finally, $e_{i\alpha}$ accounts for any other contributions of energy to species i due to interactions with other species. Because these terms all involve inter-species exchanges of energy, their collective sum over all species must be zero, as stated in Eq. (2.33).

Finally, with \mathbf{t}_α defined as in Eq. (2.30), one can show that in terms of species-based quantities,

$$\mathbf{q}_\alpha = \sum_{i \in \mathcal{J}_s} \left\{ \mathbf{q}_{i\alpha} + \left[\mathbf{t}_{i\alpha}^T - \left(E_{i\alpha} + \rho_\alpha \omega_{i\alpha} \frac{\mathbf{u}_{i\alpha} \cdot \mathbf{u}_{i\alpha}}{2} \right) \mathbf{I} \right] \cdot \mathbf{u}_{i\alpha} \right\} . \quad (2.37)$$

This equation states that some processes associated with species movement relative to the barycentric velocity are accounted for on a phase basis as part of the non-advective surface source. We have stated that \mathbf{q}_α is a “heat” flux vector, and this

is the case if one considers the apparent mechanical processes in brackets to be subscale sources of energy. Alternatively, one can recognize that \mathbf{q}_α is composed of heat conduction effects plus energy transport due to variability in the species velocities.

The species-based and entity-based entropy balances for a phase can be obtained, respectively, from Tables 2.1 and 2.2 as

$$\mathcal{S}_{i\alpha} = \frac{\partial \eta_{i\alpha}}{\partial t} + \nabla \cdot (\eta_{i\alpha} \mathbf{v}_{i\alpha}) - b_{i\alpha} - \nabla \cdot \boldsymbol{\phi}_{i\alpha} = \Lambda_{i\alpha} \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_p \quad (2.38)$$

and

$$\mathcal{S}_\alpha = \frac{\partial \eta_\alpha}{\partial t} + \nabla \cdot (\eta_\alpha \mathbf{v}_\alpha) - b_\alpha - \nabla \cdot \boldsymbol{\phi}_\alpha = \Lambda_\alpha \geq 0 \quad \text{for } \alpha \in \mathcal{I}_p, \quad (2.39)$$

where η is the entropy per volume, $\boldsymbol{\phi}$ is an entropy flux vector, b an entropy source, and Λ is an entropy generation rate.

Entropy is postulated to be an extensive thermodynamic variable and thus the balance equation is written for an entropy density, which is consistent in form with the conservation equations. The balance equations account for the rate of change of entropy, the advective flux, the non-advective flux, the body source and, on the right side, a generation term. In Eq. (2.38), $\Lambda_{i\alpha}$ accounts for exchange of entropy of species i with other species in addition to the generation of entropy by irreversible, dissipative processes. Because it is impacted by both these processes, $\Lambda_{i\alpha}$ can be either positive or negative.

Summation of the species entropy equation over all species yields Eq. (2.39). The definitions of the phase-based variables in terms of the species-based quantities are:

$$\eta_\alpha = \sum_{i \in \mathcal{I}_s} \eta_{i\alpha}, \quad (2.40)$$

$$\boldsymbol{\phi}_\alpha = \sum_{i \in \mathcal{I}_s} (\boldsymbol{\phi}_{i\alpha} - \eta_{i\alpha} \mathbf{u}_{i\alpha}), \quad (2.41)$$

$$b_\alpha = \sum_{i \in \mathcal{I}_s} b_{i\alpha}, \quad (2.42)$$

and

$$\Lambda_\alpha = \sum_{i \in \mathcal{I}_s} \Lambda_{i\alpha}. \quad (2.43)$$

In contrast to the situation with the conservation equations where the sum over the species of generation terms equals zero, the sum of the generation terms for the entropy balance is non-zero. The portion of $\Lambda_{i\alpha}$ that is due to entropy exchanges between species will sum to zero, but the portion that is due to irreversible processes will sum such that $\Lambda_\alpha \geq 0$. The non-negative character of the right side of Eq. (2.39) indicates that entropy is not a conserved quantity. The generation rate per volume, Λ_α , will be zero only when all processes in the system are occurring reversibly

(e.g., at equilibrium). In other instances Λ_α will be non-zero and is required to be non-negative by the second law of thermodynamics.

One other equation that will prove useful is the relation between the rate of change of the body force potential energy per unit volume and the body force per unit mass. Because the body force potential, usually specified to be the gravitational potential, does not appear in any of the conservation equations, we have to develop an additional condition based on mathematical identities, conservation of mass, and the definition of the body force per volume in terms of the potential.

The body force potential per unit volume of species i in phase α , $\Psi_{i\alpha}$, is defined as

$$\Psi_{i\alpha} = \rho_\alpha \omega_{i\alpha} \psi_{i\alpha} . \quad (2.44)$$

Application of the product rule to this identity yields the definition of $\mathcal{T}_{\mathcal{G}*i\alpha}$ as

$$\mathcal{T}_{\mathcal{G}*i\alpha} = \frac{D_{i\alpha} \Psi_{i\alpha}}{Dt} - \psi_{i\alpha} \frac{D_{i\alpha} (\rho_\alpha \omega_{i\alpha})}{Dt} - \rho_\alpha \omega_{i\alpha} \frac{D_{i\alpha} \psi_{i\alpha}}{Dt} = 0 . \quad (2.45)$$

We may also define the body force potential per mass, ψ_α , and the body force potential, Ψ_α , on entity bases, respectively, as

$$\psi_\alpha = \sum_{i \in \mathcal{I}_s} \omega_{i\alpha} \psi_{i\alpha} \quad (2.46)$$

and

$$\Psi_\alpha = \sum_{i \in \mathcal{I}_s} \rho_\alpha \omega_{i\alpha} \psi_{i\alpha} = \sum_{i \in \mathcal{I}_s} \Psi_{i\alpha} = \rho_\alpha \psi_\alpha . \quad (2.47)$$

The material derivative of Ψ_α , taken using the α phase velocity, is

$$\mathcal{T}_{\mathcal{G}* \alpha} = \frac{D_\alpha \Psi_\alpha}{Dt} - \sum_{i \in \mathcal{I}_s} \psi_{i\alpha} \frac{D_\alpha (\rho_\alpha \omega_{i\alpha})}{Dt} - \sum_{i \in \mathcal{I}_s} \rho_\alpha \omega_{i\alpha} \frac{D_\alpha \psi_{i\alpha}}{Dt} = 0 . \quad (2.48)$$

Another useful expression relates the change in potential to gravity and mass conservation. This will be obtained next. The species mass conservation equation in terms of a material derivative, $\mathcal{M}_{*i\alpha}$ as given in Eq. (2.18), may be used to eliminate $D_{i\alpha} (\rho_\alpha \omega_{i\alpha}) / Dt$ from Eq. (2.45). Also the definition of the material derivative in Eq. (2.15) may be used to expand $D_{i\alpha} \psi_{i\alpha} / Dt$ so that we convert Eq. (2.45) to

$$\frac{D_{i\alpha} \Psi_{i\alpha}}{Dt} + \psi_{i\alpha} (\rho_\alpha \omega_{i\alpha} \mathbf{l} : \mathbf{d}_{i\alpha} - r_{i\alpha}) - \rho_\alpha \omega_{i\alpha} \frac{\partial \psi_{i\alpha}}{\partial t} - \rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} \cdot \nabla \psi_{i\alpha} = 0 . \quad (2.49)$$

The body force potential per unit mass of species i in phase α , $\psi_{i\alpha}$, is related to the body force per mass, $\mathbf{g}_{i\alpha}$, according to

$$\nabla \psi_{i\alpha} + \mathbf{g}_{i\alpha} = \mathbf{0} . \quad (2.50)$$

Substitution of this identity into Eq. (2.49) and use of the definition provided in Eq. (2.44) provides the microscale balance equation for the body force potential of

chemical species i in phase α ,

$$\mathcal{G}_{*i\alpha} = \frac{D_{i\alpha}\Psi_{i\alpha}}{Dt} + \Psi_{i\alpha}\mathbf{l}:\mathbf{d}_{i\alpha} + \rho_{\alpha}\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{v}_{i\alpha} - \rho_{\alpha}\omega_{i\alpha}\frac{\partial\Psi_{i\alpha}}{\partial t} - r_{i\alpha}\Psi_{i\alpha} = 0$$

for $i \in \mathcal{I}_s, \alpha \in \mathcal{I}_p$. (2.51)

This equation has attributes that make it similar in form to the conservation and balance equations. Thus its elements have been collected as appropriate, and the equation appears in Table 2.1.

For the phase entity, summation of $\mathcal{G}_{i\alpha}$ over all species and rearrangement into material derivative form yields

$$\begin{aligned} \mathcal{G}_{*\alpha} = & \frac{D_{\alpha}\Psi_{\alpha}}{Dt} + \Psi_{\alpha}\mathbf{l}:\mathbf{d}_{\alpha} + \nabla \cdot \left(\sum_{i \in \mathcal{I}_s} \rho_{\alpha}\omega_{i\alpha}\Psi_{i\alpha}\mathbf{u}_{i\alpha} \right) + \rho_{\alpha}\mathbf{g}_{\alpha}\cdot\mathbf{v}_{\alpha} \\ & + \sum_{i \in \mathcal{I}_s} \rho_{\alpha}\omega_{i\alpha}\mathbf{g}_{i\alpha}\cdot\mathbf{u}_{i\alpha} - \sum_{i \in \mathcal{I}_s} \rho_{\alpha}\omega_{i\alpha}\frac{\partial\Psi_{i\alpha}}{\partial t} - \sum_{i \in \mathcal{I}_s} r_{i\alpha}\Psi_{i\alpha} = 0 \end{aligned}$$

for $\alpha \in \mathcal{I}_p$. (2.52)

2.4 Conservation and Balance Principles for an Interface

Interfaces are the second type of entity of interest in the development of conservation and balance equations. Interfaces are the regions in a multiphase system that exist at the boundary between two phases. Because interfaces are boundaries of three-dimensional entities, they are two-dimensional objects. As a result of their dimensionality, interfaces do not occupy any volume in a system. This makes the notion of conservation principles within an interface seem, perhaps, a bit elusive.

Different phases contain matter in different states and typically of different chemical composition. As a result of these differences, a heterogeneity in composition and resulting chemical forces can exist at the interface between two phases. Correspondingly, physical quantities such as density, mass fractions, and others can change significantly as one moves from the interior of one phase to the interior of an adjoining phase. This transition region is treated conceptually as an interface. Quantities that are assigned to an interface account mechanistically for underlying heterogeneous molecular structure and forces. Some species, such as surfactants, accumulate at interfaces so the molecular structure may be very different at the boundary between two phases from that in the bulk phase; there is always a transition from the composition in one bulk phase to the composition in another bulk phase.

Furthermore, in multiphase systems, interfaces play a crucial role as the location where mass, momentum, energy, and entropy can be exchanged between adjoining phases. The extent of the interfacial area thus affects the degree and rate at which exchanges occur and can easily be seen to be a crucial quantity in the description of

system behavior. Conventional multiphase models do not explicitly model the full dynamics of interfaces and interface properties, although jump conditions between phases are commonly formulated. By formulating conservation and balance equations for interfaces, we will produce the fundamental relations needed to properly account for the impacts of interfaces between phases.

In this section, conservation and balance laws for interfaces will be developed. As with the study of phases, general conservation equations will first be presented. Then particular forms of these equations will be tabulated and discussed for both species-based and entity-based equations of mass, momentum, and energy conservation along with the entropy and body force potential balances.

2.4.1 General Microscale Point Form

The study of conservation of an interfacial property is developed for a surface domain, Ω_α , with boundary curve Γ_α , where $\alpha \in \mathcal{I}_I$ as depicted in Fig. 2.2. This notation specifies that α is in the index set of interfaces, such that $\Omega_\alpha \subset \mathbb{R}^2$. This means that the interface is a surface in two-dimensional space. The extent of Ω_α is designated as the area \mathbb{A}_α . The boundary curve is a one-dimensional entity such that $\Gamma_\alpha \subset \mathbb{R}^1$. Its extent is measured by the length $\mathbb{L}_{\alpha\alpha}$. Interfaces exist as the boundary between two phases. If the phases on each side of the interface α are designated as $\beta \in \mathcal{I}_P$ and $\gamma \in \mathcal{I}_P$ then $\Omega_\alpha = \bar{\Omega}_\beta \cap \bar{\Omega}_\gamma$ where the overbar on Ω indicates a union of a domain with its boundary, for example, $\bar{\Omega}_\beta = \Omega_\beta \cup \Gamma_\beta$. At points on the interface, outward normal vectors from each adjacent phase can be denoted as \mathbf{n}_β and \mathbf{n}_γ where $\mathbf{n}_\beta = -\mathbf{n}_\gamma$. On Γ_α , outwardly directed unit vectors from Ω_α that are normal to Γ_α and tangent to Ω_α are denoted as \mathbf{n}_α . The interface moves with velocity \mathbf{w}_α . However, $\mathbf{w}_\alpha \cdot \mathbf{n}_\beta = \mathbf{v}_\alpha \cdot \mathbf{n}_\beta$ on Ω_α because a microscale particle on the interface whose normal velocity is different from the normal velocity of the interface will no longer be on the interface and thus does not contribute to the measure of the velocity of the interface. The tangential velocity of material in the interface need not be equal to the tangential velocity of the interface. The velocity of the boundary of the interface in the direction tangent to the interface and normal to Γ_α , $\mathbf{w}_\alpha \cdot \mathbf{n}_\alpha$, relates to the stretching or contracting of the interface at its edges. Flow can occur across this boundary, in the same way that flow crosses the boundary of a volume, so that this velocity is not necessarily equal to the velocity of flow. Conservation and balance equations associated with an interface must necessarily take into account the translation and deformation of the interface.

With the preceding definitions and considerations, a species-based general conservation or balance equation follows directly from Eq. (2.8) as

$$\frac{d}{dt} \int_{\Omega_\alpha} F_{i\alpha} d\tau + \int_{\Gamma_\alpha} F_{i\alpha} (\mathbf{v}_{i\alpha} - \mathbf{w}_\alpha) \cdot \mathbf{n}_\alpha d\tau - \int_{\Omega_\alpha} S_{\Omega T i \alpha} d\tau$$

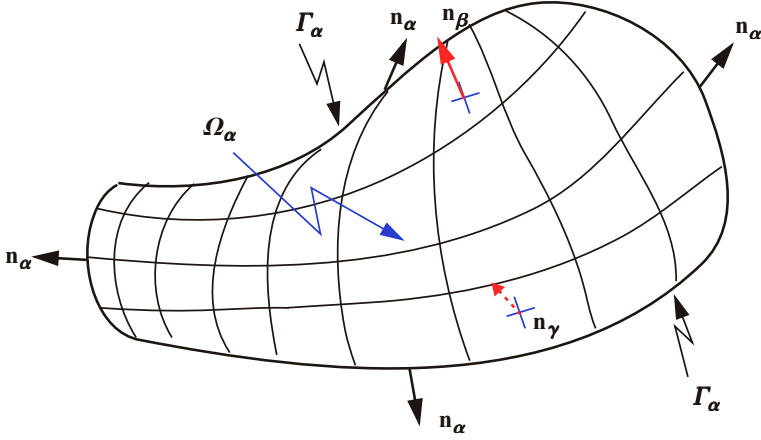


Fig. 2.2 Arbitrary finite, non-closed surface in the region $\Omega_\alpha \subset \mathbb{R}^2$ containing interface $\alpha \in \mathcal{I}_1$ with boundary $\Gamma_\alpha \subset \mathbb{R}^1$. Unit vector \mathbf{n}_α is normal to Γ_α and oriented to be outward positive from and tangent to Ω_α . Unit vector \mathbf{n}_β is normal to Ω_α and positive outward from phase β on one side of the interface while unit vector \mathbf{n}_γ is also normal to Ω_α but is positive outward from phase γ on the other side of the interface such that at any point on the surface, $\mathbf{n}_\beta \cdot \mathbf{n}_\gamma = -1$

$$-\int_{\Gamma_\alpha} \mathbf{S}_{\Gamma\alpha} \cdot \mathbf{n}_\alpha \, d\mathbf{r} - \int_{\Omega_\alpha} G_{\Omega i \alpha} \, d\mathbf{r} = 0, \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_1. \quad (2.53)$$

This equation is notationally identical and conceptually similar to the corresponding equation for a phase, Eq. (2.8), with the differences being that the surface domain is two-dimensional, the boundary is one-dimensional, and all densities are per unit area rather than per unit volume.

The conversion of Eq. (2.53) for an interface to the form that applies at a point within the interface requires that the integrals over Γ_α be transformed to integrals over Ω_α . Part of this task can be accomplished making use of the surface transport theorem [8]:

Theorem 2.3 (**T[2,(0,0),2]**) *For a smooth continuous and differentiable function f defined over a domain $\Omega_\alpha \subset \mathbb{R}^2$ that may deform with time t due to velocity \mathbf{w}_α of the domain and of its closed boundary, Γ_α , designate the normal to Ω_α as \mathbf{n}_β , the normal to Γ_α that is tangent to Ω_α as \mathbf{n}_α , and define the unit tensor $\mathbf{l}'_\alpha = \mathbf{l} - \mathbf{n}_\beta \mathbf{n}_\beta$. Then,*

$$\frac{d}{dt} \int_{\Omega_\alpha(t)} f \, d\mathbf{r} = \int_{\Omega_\alpha(t)} \frac{\partial' f}{\partial t} \, d\mathbf{r} - \int_{\Omega_\alpha(t)} f \mathbf{w}_\alpha \cdot (\nabla' \cdot \mathbf{l}'_\alpha) \, d\mathbf{r} + \int_{\Gamma_\alpha(t)} f \mathbf{w}_\alpha \cdot \mathbf{n}_\alpha \, d\mathbf{r}, \quad (2.54)$$

where the partial derivative with respect to time for a point fixed to Ω_α is defined as

$$\frac{\partial'}{\partial t} = \frac{d}{dt} - \mathbf{w}_\alpha \cdot \nabla'; \quad (2.55)$$

and $\nabla' \cdot$ and ∇' are the surface divergence and surface gradient operators, respectively, defined as

$$\nabla' \cdot = (\mathbf{l}'_\alpha \cdot \nabla) \cdot \quad (2.56)$$

and

$$\nabla' = \mathbf{l}'_\alpha \cdot \nabla. \quad (2.57)$$

Note that \mathbf{l}'_α is the unit tensor in the surface α (i.e., in diagonal form, the entries on the diagonal associated with tangential directions in the surface are both 1, while the component associated with the normal direction is zero). When f is the density of a conserved quantity and Ω_α is an interface between phases, the left side of Eq. (2.54) is the change in the total amount of the conserved quantity with time over the interfacial area. The three terms on the right side of Eq. (2.54) contribute to this change, respectively, due to the change in f at a point fixed on the surface, due to expansion of the size of the surface because of deformation of its shape, and due to changes in the size of the surface due to movement of the boundary curve.

Also of use in transforming the general conservation equation is the surface divergence theorem [8]:

Theorem 2.4 (D[2,(0,0),2]) *For a smooth continuous and differentiable tensor function \mathbf{f} defined over a domain $\Omega_\alpha \subset \mathbb{R}^2$ that may deform with time t due to velocity \mathbf{w}_α of the domain and of its closed boundary, Γ_α , designate the normal to Ω_α as \mathbf{n}_β , the normal to Γ_α that is tangent to Ω_α as \mathbf{n}_α , and define the unit tensor $\mathbf{l}'_\alpha = \mathbf{l} - \mathbf{n}_\beta \mathbf{n}_\beta$. Then,*

$$\int_{\Omega_\alpha(t)} \text{div}' \mathbf{f} d\tau = - \int_{\Omega_\alpha(t)} \mathbf{f} \cdot (\nabla' \cdot \mathbf{l}'_\alpha) d\tau + \int_{\Gamma_\alpha(t)} \mathbf{f} \cdot \mathbf{n}_\alpha d\tau, \quad (2.58)$$

where div' is the surface divergence operator that contracts the last index of \mathbf{f} and $\nabla' \cdot$ is the surface divergence operator defined as

$$\nabla' \cdot = (\mathbf{l}'_\alpha \cdot \nabla) \cdot. \quad (2.59)$$

Because

$$\nabla' \cdot \mathbf{l}'_\alpha = - (\nabla' \cdot \mathbf{n}_\beta) \mathbf{n}_\beta, \quad (2.60)$$

Equation (2.58) can be written as

$$\int_{\Omega_\alpha(t)} [\text{div}' \mathbf{f} - (\nabla' \cdot \mathbf{n}_\beta) \mathbf{f} \cdot \mathbf{n}_\beta] d\tau = \int_{\Gamma_\alpha(t)} \mathbf{f} \cdot \mathbf{n}_\alpha d\tau. \quad (2.61)$$

Application of the product rule to the second term gives

$$\int_{\Omega_\alpha(t)} \text{div}' (\mathbf{f} - \mathbf{f} \cdot \mathbf{n}_\beta \mathbf{n}_\beta) d\tau = \int_{\Gamma_\alpha(t)} \mathbf{f} \cdot \mathbf{n}_\alpha d\tau. \quad (2.62)$$

However,

$$\mathbf{f} - \mathbf{f} \cdot \mathbf{n}_\beta \mathbf{n}_\beta = \mathbf{f} \cdot (\mathbf{I} - \mathbf{n}_\beta \mathbf{n}_\beta) = \mathbf{f} \cdot \mathbf{l}'_\alpha . \quad (2.63)$$

Substitution of Eq. (2.63) into Eq. (2.62), provides an alternative, but equivalent, form of $D[2,(0,0),2]$ as:

$$\int_{\Omega_\alpha(t)} \text{div}' (\mathbf{f} \cdot \mathbf{l}'_\alpha) \, d\tau = \int_{\Gamma_\alpha(t)} \mathbf{f} \cdot \mathbf{n}_\alpha \, d\tau . \quad (2.64)$$

With f replaced by $F_{i\alpha}$ in transport theorem Eq. (2.54), \mathbf{f} replaced by $F_{i\alpha} \mathbf{v}_{i\alpha}$ in divergence theorem Eq. (2.58), and \mathbf{f} replaced by $\mathbf{S}_{\Gamma i\alpha}$ in alternative divergence theorem Eq. (2.64), relations are obtained that allow the boundary integrals to be eliminated from Eq. (2.53). The result is the following:

$$\begin{aligned} \int_{\Omega_\alpha} \left[\frac{\partial' F_{i\alpha}}{\partial t} + \nabla' \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) + F_{i\alpha} (\mathbf{v}_{i\alpha} - \mathbf{w}_\alpha) \cdot (\nabla' \cdot \mathbf{l}'_\alpha) \right] d\tau \\ - \int_{\Omega_\alpha} [S_{\Omega T i\alpha} + \text{div}' (\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}'_\alpha) + G_{\Omega i\alpha}] \, d\tau = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_1 . \end{aligned} \quad (2.65)$$

In this equation, $(\mathbf{v}_{i\alpha} - \mathbf{w}_\alpha) \cdot (\nabla' \cdot \mathbf{l}'_\alpha) = 0$ because this quantity is the difference between the species velocity and the interface velocity in the direction normal to the surface multiplied by the surface curvature. As discussed previously, this velocity difference is zero. Also the total body source is composed of two components. The first is due to external sources acting on the entity. The second is due to the fact that at every point within the surface, an adjacent phase can impact the properties of the surface. Thus, fluxes from a phase to an interface at a point are treated as part of the body source. To make this explicit, we break the body source into these two components according to

$$S_{\Omega T i\alpha} = S_{\Omega i\alpha} + \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} X_{j\kappa \rightarrow i\alpha} , \quad (2.66)$$

where $\mathcal{J}_{c\alpha}^+$ is the connected set for interface α that is of higher dimensionality (i.e., phases in the connected set), and $X_{j\kappa \rightarrow i\alpha}$ is the body source component due to transfer of the property being conserved from species j in entity κ to species i in entity α . Because the extent of the surface domain, Ω_α , is arbitrary, the integrand in Eq. (2.65) must be zero at every microscale point, not just when integrated over the domain. Application of these conditions provides the general microscale point form of the surface conservation equation,

$$\begin{aligned} \frac{\partial' F_{i\alpha}}{\partial t} + \nabla' \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} X_{j\kappa \rightarrow i\alpha} - \text{div}' (\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}'_\alpha) - G_{\Omega i\alpha} = 0 \\ \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_1 . \end{aligned} \quad (2.67)$$

This equation may also be written in terms of the material derivative as

$$\frac{D_{i\alpha} F_{i\alpha}}{Dt} + F_{i\alpha} \mathbf{l}'_{\alpha} \cdot \mathbf{d}'_{i\alpha} - S_{\Omega i\alpha} - \sum_{\kappa \in \mathcal{I}_{\alpha}^{+}} \sum_{j \in \mathcal{I}_s} X_{j\kappa \rightarrow i\alpha} - \text{div}' (\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}'_{\alpha}) - G_{\Omega i\alpha} = 0$$

for $i \in \mathcal{I}_s, \alpha \in \mathcal{I}_I$, (2.68)

where

$$\frac{D_{i\alpha}}{Dt} = \frac{\partial'}{\partial t} + \mathbf{v}_{i\alpha} \cdot \nabla' \quad (2.69)$$

and

$$\mathbf{d}'_{i\alpha} = \left[\nabla' \mathbf{v}_{i\alpha} + (\nabla' \mathbf{v}_{i\alpha})^T \right]. \quad (2.70)$$

The general microscale conservation equation given as Eq. (2.67) is a more convenient form to work with than Eq. (2.68) for deriving larger scale equations because of the forms of the theorems used to affect the change. Considerations for changing the species equations indicated to forms that apply for a surface entity as a whole are the same as those discussed in the first full paragraph following Eq. (2.16). In the following section, we will provide the specific conservation and balance equations for interfaces. Note that, although the appearance of the general forms for the surface and phase equations as given by Eqs. (2.67) and (2.13) are quite similar, the contributions to specific body source terms will be seen to be very different because of the transfer from adjacent phases to the interface.

2.4.2 Specific Conservation and Balance Principles

Specific conservation and balance equations can be stated by proper identification of the variables that appear in Eq. (2.67) or its equivalent version, Eq. (2.68). Here a full set of microscale conservation and balance equations for an interface is provided. This is accomplished in a manner similar to that employed with phases in Sect. 2.3.2.

The prime conceptual extension required for interfaces in comparison to phases is related to the fact that transfer of a property at the boundary of a phase is with the domain of an interface. Therefore, processes that are accounted for as boundary conditions for phase equations are parts of the body source terms for interface equations. These additional terms are related to advective and non-advective boundary sources for the phases that are body sources for the interface. The domain of an α interface, Ω_{α} , is the boundary of two phases on each side of the interface. Note that an interface is defined such that it is the boundary between a particular pair of phases; a different pair of phases is separated by a different interface. Also, if a third phase is present, the interface may have an edge boundary that is a common curve. At the microscale, we will only be interested in members of the connected set that are of higher order dimensionality than the entity of interest. Thus if the two phases that bound interface α are designated as β and γ , we can define the set of phase

Table 2.3 Physical variables for species-based interface equations in partial derivative or material form. $\mathcal{M}_{i\alpha}$, $\mathcal{P}_{i\alpha}$, $\mathcal{E}_{i\alpha}$, $\mathcal{S}_{i\alpha}$, and $\mathcal{G}_{i\alpha}$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential for species i in interface α

$\mathcal{F}_{i\alpha} = \frac{\partial' F_{i\alpha}}{\partial t} + \nabla' \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} X_{j\kappa \rightarrow i\alpha} - \text{div}' (S_{\Gamma i\alpha} \mathbf{l}'_{i\alpha}) - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_1$ $\mathcal{F}_{*i\alpha} = \frac{D_{i\alpha} F_{i\alpha}}{Dt} + F_{i\alpha} \mathbf{l}'_{i\alpha} : \mathbf{d}'_{i\alpha} - S_{\Omega i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} X_{j\kappa \rightarrow i\alpha} - \text{div}' (S_{\Gamma i\alpha} \mathbf{l}'_{i\alpha}) - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_1$					
$\mathcal{F}_{i\alpha}$	$F_{i\alpha}$	$S_{\Omega i\alpha}$	$X_{j\kappa \rightarrow i\alpha}$	$S_{\Gamma i\alpha}$	$G_{\Omega i\alpha}$
$\mathcal{M}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha}$	—	$\delta_{ij} \frac{M}{i\kappa \rightarrow i\alpha}$	—	$r_{i\alpha}$
$\mathcal{P}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}$	$\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha}$	$\delta_{ij} \mathbf{v}_{i\kappa} \frac{M}{j\kappa \rightarrow i\alpha} + \frac{\mathbf{T}}{j\kappa \rightarrow i\alpha}$	$\mathbf{t}_{i\alpha}$	$\mathbf{p}_{i\alpha} + r_{i\alpha} \mathbf{v}_{i\alpha}$
$\mathcal{E}_{i\alpha}$	$E_{i\alpha} + \rho_\alpha \omega_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2}$	$\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha} + h_{i\alpha}$	$\delta_{ij} \left(\frac{E_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} + \frac{\mathbf{v}_{i\kappa} \cdot \mathbf{v}_{i\kappa}}{2} \right) \frac{M}{i\kappa \rightarrow i\alpha} + \mathbf{v}_{j\kappa} \cdot \frac{\mathbf{T}}{j\kappa \rightarrow i\alpha} + \frac{Q}{j\kappa \rightarrow i\alpha}$	$\mathbf{t}_{i\alpha}^T \cdot \mathbf{v}_{i\alpha} + \mathbf{q}_{i\alpha}$	$e_{i\alpha} + \mathbf{p}_{i\alpha} \cdot \mathbf{v}_{i\alpha} + r_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2}$
$\mathcal{S}_{i\alpha} - \Lambda_{i\alpha}$	$\eta_{i\alpha}$	$b_{i\alpha}$	$\delta_{ij} \frac{\eta_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} \frac{M}{i\kappa \rightarrow i\alpha} + \frac{\Phi}{j\kappa \rightarrow i\alpha}$	$\boldsymbol{\varphi}_{i\alpha}$	$\Lambda_{i\alpha}$
$\mathcal{G}_{i\alpha}$	$\Psi_{i\alpha}$	$-\rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha}$	$\delta_{ij} \frac{M}{i\kappa \rightarrow i\alpha} \Psi_{i\alpha}$	—	$\rho_\alpha \omega_{i\alpha} \left[\frac{\partial' \Psi_{i\alpha}}{\partial t} + \mathbf{g}_{i\alpha} \cdot (\mathbf{I} - \mathbf{l}'_{i\alpha}) \cdot \mathbf{v}_{i\alpha} \right] + r_{i\alpha} \Psi_{i\alpha}$
Inter-entity Exchange Terms					
$\frac{M}{i\kappa \rightarrow i\alpha} = \mathbf{n}_\kappa \cdot [\rho_\kappa \omega_{i\kappa} (\mathbf{v}_{i\kappa} - \mathbf{v}_\alpha)] \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$					
$\frac{\mathbf{T}}{j\kappa \rightarrow i\alpha} = -z_T \frac{\mathbf{t}_{j\kappa} \cdot \mathbf{n}_\kappa}{j\kappa \rightarrow i\alpha} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$					
$\frac{Q}{j\kappa \rightarrow i\alpha} = -z_Q \frac{\mathbf{q}_{j\kappa} \cdot \mathbf{n}_\kappa}{j\kappa \rightarrow i\alpha} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$					
$\frac{\Phi}{j\kappa \rightarrow i\alpha} = -z_\Phi \frac{\boldsymbol{\varphi}_{j\kappa} \cdot \mathbf{n}_\kappa}{j\kappa \rightarrow i\alpha} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$					

entities bounded by interface α as the connected set $\mathcal{J}_{c\alpha} \cap \mathcal{J}_P = \{\beta, \gamma\}$, where $\mathcal{J}_{c\alpha}$ is the connected set of phases and common curves to interface α and \mathcal{J}_P is the index set of phases in the system. A simpler notation can be employed by denoting the connected set of higher order that bounds an entity as $\mathcal{J}_{c\alpha}^+$ and one of lower order as $\mathcal{J}_{c\alpha}^-$. Thus, if α refers to an interface, $\mathcal{J}_{c\alpha} \cap \mathcal{J}_P = \mathcal{J}_{c\alpha}^+$ is the set of phases connected to the interface and $\mathcal{J}_{c\alpha} \cap \mathcal{J}_C = \mathcal{J}_{c\alpha}^-$ is the set of common curves bounding the interface. We note also that $\mathcal{J}_{c\alpha}^+ \cup \mathcal{J}_{c\alpha}^- = \mathcal{J}_{c\alpha}$.

Specific forms of conservation and balance equations for properties of a chemical species in an interface are given in Table 2.3. Summation of a particular conservation or balance equation over all species in the interface results in the equations provided in Table 2.4. We will examine these equations in some detail and also indicate the relation between interface-based variables and species-based variables.

The point form of the microscale mass conservation equation for a chemical species i in an interface α is obtained from Table 2.3 based on the variables included in row $\mathcal{M}_{i\alpha}$. Substitution of these variables into Eq. (2.67), which is also the

Table 2.4 Physical variables for entity-based interface equations in partial derivative or material form. \mathcal{M}_α , \mathcal{P}_α , \mathcal{E}_α , S_α , and \mathcal{G}_α correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential in interface α

$\mathcal{F}_\alpha = \frac{\partial' F_\alpha}{\partial t} + \nabla' \cdot (\mathbf{v}_\alpha F_\alpha) - S_{\Omega\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \frac{X}{\kappa \rightarrow \alpha} - \text{div}' (S_{\Gamma\alpha} \mathbf{l}'_\alpha) - G_{\Omega\alpha} = 0 \quad \text{for } \alpha \in \mathcal{J}_I$					
$\mathcal{F}_{* \alpha} = \frac{D_\alpha F_\alpha}{Dt} + F_\alpha \mathbf{l}'_\alpha \cdot \mathbf{d}'_\alpha - S_{\Omega\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \frac{X}{\kappa \rightarrow \alpha} - \text{div}' (S_{\Gamma\alpha} \mathbf{l}'_\alpha) - G_{\Omega\alpha} = 0 \quad \text{for } \alpha \in \mathcal{J}_I$					
\mathcal{F}_α	F_α	$S_{\Omega\alpha}$	$\frac{X}{\kappa \rightarrow \alpha}$	$S_{\Gamma\alpha}$	$G_{\Omega\alpha}$
\mathcal{M}_α	ρ_α	—	$\frac{M}{\kappa \rightarrow \alpha}$	—	—
\mathcal{P}_α	$\rho_\alpha \mathbf{v}_\alpha$	$\rho_\alpha \mathbf{g}_\alpha$	$\mathbf{v}_\kappa \frac{M}{\kappa \rightarrow \alpha} + \frac{\mathbf{T}}{\kappa \rightarrow \alpha}$	\mathbf{t}_α	—
\mathcal{E}_α	E_α $+ \rho_\alpha \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2}$ $+ \rho_\alpha K_{E\alpha}$	$\rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha$ $+ h_\alpha$ $+ \sum_{i \in \mathcal{J}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{l}'_{i\alpha} \mathbf{u}_{i\alpha}$	$\left(\frac{E_\kappa}{\rho_\kappa} + \frac{\mathbf{v}_\kappa \cdot \mathbf{v}_\kappa}{2} + K_{E\kappa} \right) \frac{M}{\kappa \rightarrow \alpha}$ $+ \mathbf{v}_\kappa \cdot \frac{\mathbf{T}}{\kappa \rightarrow \alpha} + \frac{Q}{\kappa \rightarrow \alpha}$	$\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha$	—
$S_\alpha - \Lambda_\alpha$	η_α	b_α	$\frac{\eta_\kappa}{\rho_\kappa} \frac{M}{\kappa \rightarrow \alpha} + \frac{\Phi}{\kappa \rightarrow \alpha}$	$\boldsymbol{\varphi}_\alpha$	Λ_α
\mathcal{G}_α	Ψ_α	$-\rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha$ $-\sum_{i \in \mathcal{J}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{l}'_{i\alpha} \mathbf{u}_{i\alpha}$	$+\sum_{i \in \mathcal{J}_s} \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \frac{M}{i\kappa \rightarrow i\alpha} \psi_{i\alpha}$	$-\sum_{i \in \mathcal{J}_s} \rho_\alpha \omega_{i\alpha} \psi_{i\alpha} \mathbf{u}_{i\alpha}$ $+\sum_{i \in \mathcal{J}_s} \rho_\alpha \omega_{i\alpha} \left[\frac{\partial' \psi_{i\alpha}}{\partial t} + \mathbf{g}_{i\alpha} \cdot (\mathbf{I} - \mathbf{l}'_\alpha) \cdot \mathbf{v}_{i\alpha} \right]$ $+ \sum_{i \in \mathcal{J}_s} r_{i\alpha} \psi_{i\alpha}$	
Inter-entity Exchange Terms					
$\frac{M}{\kappa \rightarrow \alpha} = \sum_{i \in \mathcal{J}_s} \frac{M}{i\kappa \rightarrow i\alpha} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$					
$\frac{\mathbf{T}}{\kappa \rightarrow \alpha} = \sum_{j \in \mathcal{J}_s} \sum_{i \in \mathcal{J}_s} \left[\frac{\mathbf{T}}{j\kappa \rightarrow i\alpha} + \delta_{ij} (\mathbf{v}_{i\kappa} - \mathbf{v}_\kappa) \frac{M}{i\kappa \rightarrow i\alpha} \right] \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$					
$\frac{Q}{\kappa \rightarrow \alpha} = \sum_{j \in \mathcal{J}_s} \sum_{i \in \mathcal{J}_s} \left\{ \frac{Q}{j\kappa \rightarrow i\alpha} + (\mathbf{v}_{j\kappa} - \mathbf{v}_\kappa) \cdot \frac{\mathbf{T}}{j\kappa \rightarrow i\alpha} + \delta_{ij} \left[\frac{E_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} + \frac{\mathbf{u}_{i\kappa} \cdot \mathbf{u}_{i\kappa}}{2} - \left(\frac{E_\kappa}{\rho_\kappa} + K_{E\kappa} \right) \right] \frac{M}{i\kappa \rightarrow i\alpha} \right\} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$					
$\frac{\Phi}{\kappa \rightarrow \alpha} = \sum_{j \in \mathcal{J}_s} \sum_{i \in \mathcal{J}_s} \left\{ \frac{\Phi}{j\kappa \rightarrow i\alpha} + \delta_{ij} \left[\frac{\eta_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} - \frac{\eta_\kappa}{\rho_\kappa} \right] \frac{M}{i\kappa \rightarrow i\alpha} \right\} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$					

equation at the top of the table, yields

$$\mathcal{M}_{i\alpha} = \frac{\partial' (\rho_\alpha \omega_{i\alpha})}{\partial t} + \nabla' \cdot (\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}) - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \frac{M}{i\kappa \rightarrow i\alpha} - r_{i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_I, \quad (2.71)$$

where ρ_α is the mass per area, $\omega_{i\alpha}$ is the mass fraction of species i , $\mathbf{v}_{i\alpha}$ is the velocity of species i (which, in the normal direction to the interface, is equal to the interface velocity), $\frac{M}{i\kappa \rightarrow i\alpha}$ is an effective body source for the species i in the interface due to transfer of i from the phases within $\mathcal{J}_{c\alpha}^+$ to interface α , and $r_{i\alpha}$ is the rate of generation of species i in interface α due to any and all chemical reactions within the interface. This equation is very similar to the mass conservation equation for a

species in a phase given as Eq. (2.17). The differences are: the time derivative is at a fixed point in a surface rather than in a phase; the divergence term models outward flux in the surface rather than in three-dimensions; and there is a new term, $M_{i\kappa \rightarrow i\alpha}$. In the bottom portion of Table 2.3, the explicit form of $M_{i\kappa \rightarrow i\alpha}$ is given in terms of the properties of the phases at the interface. Note that κ takes on the index values of the two phases adjacent to the α interface.

The point form of the total mass conservation equation is most directly obtained by substituting the variables in the \mathcal{M}_α row of Table 2.4 into the equation at the top of the table. The result is

$$\mathcal{M}_\alpha = \frac{\partial' \rho_\alpha}{\partial t} + \nabla' \cdot (\rho_\alpha \mathbf{v}_\alpha) - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} M_{\kappa \rightarrow \alpha} = 0 \quad \text{for } \alpha \in \mathcal{J}_1. \quad (2.72)$$

Equation (2.72) can be obtained directly by summing Eq. (2.71) over all chemical species if one makes use of the definition of the barycentric velocity as given by Eq. (2.23) for the interface as well as for the adjacent phases. Also, the traditional jump conditions for mass exchange between phases can be obtained when the interface is considered massless such that ρ_α and $r_{i\alpha}$ are both zero. The species-based jump condition is the statement that the summation in Eq. (2.71) is equal to zero. For the interface entity as a whole, the condition is that the summation in Eq. (2.72) is zero. On a physical basis, both of these jump conditions state that at a point at the boundary of a phase where material leaves that phase, it immediately enters the adjacent phase. The more general mass conservation equations for the interface additionally allow for material to stay in the interface, move in the interfacial surface, and participate in chemical reactions.

The microscale conservation of momentum equations for a species in an interface and for all species in the interface entity as a whole can be obtained, respectively, from Tables 2.3 and 2.4 as

$$\begin{aligned} \mathcal{P}_{i\alpha} = & \frac{\partial'(\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha})}{\partial t} + \nabla' \cdot (\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} \mathbf{v}_{i\alpha}) - \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \\ & - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} \left(\delta_{ij} \mathbf{v}_{i\kappa} M_{i\kappa \rightarrow i\alpha} + \mathbf{T}_{j\kappa \rightarrow i\alpha} \right) \\ & - \nabla' \cdot (\mathbf{l}'_\alpha \cdot \mathbf{t}_{i\alpha}^T) - \mathbf{p}_{i\alpha} - r_{i\alpha} \mathbf{v}_{i\alpha} = \mathbf{0} \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_1 \end{aligned} \quad (2.73)$$

and

$$\begin{aligned} \mathcal{P}_\alpha = & \frac{\partial'(\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \nabla' \cdot (\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha) - \rho_\alpha \mathbf{g}_\alpha \\ & - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \left(\mathbf{v}_\kappa M_{\kappa \rightarrow \alpha} + \mathbf{T}_{\kappa \rightarrow \alpha} \right) - \nabla' \cdot (\mathbf{l}'_\alpha \cdot \mathbf{t}_\alpha) = \mathbf{0} \quad \text{for } \alpha \in \mathcal{J}_1. \end{aligned} \quad (2.74)$$

The notation employed should be clear based on discussions of the phase equations, although there are two additional elements. The quantity δ_{ij} in Eq. (2.73) is

the Kronecker delta, equal to 1 when $i = j$ and zero otherwise. This is necessary because the term it multiplies is momentum transfer between a bounding phase and the interface that accompanies mass exchange between these entities. Thus, only when species i in the phase $\kappa \in \mathcal{J}_{c\alpha}^+$ is involved in inter-entity mass transfer will that impact the momentum of species i in the interface. On the other hand, stress effects can be exerted by a species in a phase on a different species in the interface. The quantity z_T introduced in the definition of \mathbf{T} at the bottom of Table 2.3 is the fraction of stress tensor $\mathbf{t}_{j\kappa}$ (i.e., the stress associated with species j in phase κ) that is exerted on species i in interface α . Thus, z_T will satisfy the condition

$$\sum_{i \in \mathcal{J}_s} z_T = 1 \quad \text{for } j \in \mathcal{J}_s, \kappa \in \mathcal{J}_{c\alpha}^+, \alpha \in \mathcal{J}_I. \quad (2.75)$$

We note also that the surface entity-based stress tensor, \mathbf{t}_α , is defined in terms of the surface species-based stress tensor exactly as in Eq. (2.30) for a phase.

For the situation where the interface is massless, full momentum equations for a species and for an entity simplify to jump conditions for the momentum of the species and of the phase entity, respectively, as

$$- \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} \mathbf{n}_\kappa \cdot \left[\delta_{ij} \rho_\kappa \omega_{i\kappa} (\mathbf{v}_{i\kappa} - \mathbf{v}_\alpha) \mathbf{v}_{i\kappa} - z_T \mathbf{t}_{j\kappa}^T \right] - \nabla' \cdot (\mathbf{l}'_\alpha \cdot \mathbf{t}_{i\alpha}^T) = \mathbf{0} \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_I \quad (2.76)$$

and

$$- \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \mathbf{n}_\kappa \cdot [\rho_\kappa (\mathbf{v}_\kappa - \mathbf{v}_\alpha) \mathbf{v}_\kappa - \mathbf{t}_\kappa] - \nabla' \cdot (\mathbf{l}'_\alpha \cdot \mathbf{t}_\alpha) = \mathbf{0} \quad \text{for } \alpha \in \mathcal{J}_I, \quad (2.77)$$

where the expression for the exchange of momentum between the interface and the adjacent phases has been substituted into the momentum equation; and terms containing ρ_α for $\alpha \in \mathcal{J}_I$ have been dropped because the interface is massless. In practice, the most commonly employed form of the microscale momentum jump condition is Eq. (2.77) with the divergence term dropped when interfacial tension effects are unimportant. In subsequent chapters, the full dynamic equations will be employed.

The species-based conservation of energy equation for an interface can be written, based on the entries in Table 2.3, as

$$\begin{aligned} \mathcal{E}_{i\alpha} = & \frac{\partial'}{\partial t} \left(E_{i\alpha} + \rho_\alpha \omega_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2} \right) + \nabla' \cdot \left[\left(E_{i\alpha} + \rho_\alpha \omega_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2} \right) \mathbf{v}_{i\alpha} \right] \\ & - \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha} - h_{i\alpha} \\ & - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} \left[\delta_{ij} \left(\frac{E_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} + \frac{\mathbf{v}_{i\kappa} \cdot \mathbf{v}_{i\kappa}}{2} \right) \frac{M}{i\kappa \rightarrow i\alpha} + \mathbf{v}_{j\kappa} \cdot \mathbf{T}_{j\kappa \rightarrow i\alpha} + \frac{Q}{j\kappa \rightarrow i\alpha} \right] \end{aligned}$$

$$\begin{aligned}
& -\nabla' \cdot [\mathbf{l}'_\alpha \cdot (\mathbf{t}_{i\alpha}^T \cdot \mathbf{v}_{i\alpha} + \mathbf{q}_{i\alpha})] \\
& -e_{i\alpha} - \mathbf{p}_{i\alpha} \cdot \mathbf{v}_{i\alpha} - r_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_I.
\end{aligned} \tag{2.78}$$

The conservation of energy equation for an interface as a whole is

$$\begin{aligned}
\mathcal{E}_\alpha &= \frac{\partial'}{\partial t} \left[E_\alpha + \rho_\alpha \left(\frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} + K_{E\alpha} \right) \right] + \nabla' \cdot \left\{ \left[E_\alpha + \rho_\alpha \left(\frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} + K_{E\alpha} \right) \right] \mathbf{v}_\alpha \right\} \\
& - \rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha - \sum_{i \in \mathcal{J}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{l}'_\alpha \cdot \mathbf{u}_{i\alpha} - h_\alpha \\
& - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \left[\left(\frac{E_\kappa}{\rho_\kappa} + \frac{\mathbf{v}_\kappa \cdot \mathbf{v}_\kappa}{2} + K_{E\kappa} \right) \frac{M}{\kappa \rightarrow \alpha} + \mathbf{v}_\kappa \cdot \frac{\mathbf{T}}{\kappa \rightarrow \alpha} + \frac{Q}{\kappa \rightarrow \alpha} \right] \\
& - \nabla' \cdot [\mathbf{l}'_\alpha \cdot (\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha)] = 0 \quad \text{for } \alpha \in \mathcal{J}_I.
\end{aligned} \tag{2.79}$$

The definition of $\frac{Q}{\kappa \rightarrow \alpha}$ in Eq. (2.78) provided at the end of Table 2.3 makes use of the parameter $\frac{z_Q}{\kappa \rightarrow i\alpha}$. The purpose of this parameter is to account for the fact that contributions to heat conduction from phase κ due to species j can be to species i in interface entity α . This parameter, or actually set of parameters with the range of indices, satisfies the condition

$$\sum_{i \in \mathcal{J}_s} \frac{z_Q}{\kappa \rightarrow i\alpha} = 1 \quad \text{for } j \in \mathcal{J}_s, \kappa \in \mathcal{J}_{c\alpha}^+, \alpha \in \mathcal{J}_I. \tag{2.80}$$

Note that Eq. (2.79) may also be obtained directly as the sum of Eq. (2.78) over all species i in interface entity α . This is left as an exercise.

The energy jump condition between phases that is usually employed is obtained by dropping all the terms except for the summations over $\mathcal{J}_{c\alpha}^+$ in Eq. (2.78) or Eq. (2.79). This simplification is appropriate under conditions where the mass density of the interface, ρ_α , is negligible, the rates of change and the surficial fluxes of the internal energy of the interface are small, the body sources of energy due to processes such as radiation are negligible, and the work and heat transfer due to movement in the surface is negligible. The statement that a term is “negligible” or “small” is relative to the advective and non-advective fluxes of energy to the interface from the adjacent phases.

The balance of entropy equation for a species in an interface can be assembled from Table 2.3 as

$$\begin{aligned}
\mathcal{S}_{i\alpha} &= \frac{\partial' \eta_{i\alpha}}{\partial t} + \nabla' \cdot (\eta_{i\alpha} \mathbf{v}_{i\alpha}) - b_{i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} \left(\delta_{ij} \frac{\eta_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} \frac{M}{i\kappa \rightarrow i\alpha} + \frac{\Phi}{j\kappa \rightarrow i\alpha} \right) \\
& - \nabla' \cdot (\mathbf{l}'_\alpha \cdot \boldsymbol{\phi}_{i\alpha}) = \Lambda_{i\alpha} \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_I.
\end{aligned} \tag{2.81}$$

The overall balance of entropy equation for an interface from the entries in Table 2.4 is

$$\begin{aligned} \mathcal{S}_\alpha &= \frac{\partial' \eta_\alpha}{\partial t} + \nabla' \cdot (\eta_\alpha \mathbf{v}_\alpha) - b_\alpha - \sum_{\kappa \in \mathcal{J}_{\alpha}^+} \left(\frac{\eta_\kappa}{\rho_\kappa} M_{\kappa \rightarrow \alpha} + \Phi_{\kappa \rightarrow \alpha} \right) \\ &\quad - \nabla' \cdot (\mathbf{l}'_\alpha \cdot \boldsymbol{\phi}_\alpha) = \Lambda_\alpha \quad \text{for } \alpha \in \mathcal{J}_I. \end{aligned} \quad (2.82)$$

The discussion following Eq. (2.43) regarding $\Lambda_{i\alpha}$ and Λ_α for $\alpha \in \mathcal{J}_P$ applies to the preceding equations as well for $\alpha \in \mathcal{J}_I$ such that $\Lambda_\alpha \geq 0$.

The body force potential per unit area acting on species i in interface α is written analogously to Eq. (2.44) for a volume as

$$\Psi_{i\alpha} = \rho_\alpha \omega_{i\alpha} \psi_{i\alpha}, \quad (2.83)$$

with the corresponding expression for the material derivative,

$$\mathcal{T}_{\mathcal{G}*i\alpha} = \frac{D_{i\alpha} \Psi_{i\alpha}}{Dt} - \psi_{i\alpha} \frac{D_{i\alpha}(\rho_\alpha \omega_{i\alpha})}{Dt} - \rho_\alpha \omega_{i\alpha} \frac{D_{i\alpha} \psi_{i\alpha}}{Dt} = 0. \quad (2.84)$$

The potential for the surface entity as a unit, Ψ_α , is defined as in Eq. (2.47); its material derivative is as in Eq. (2.48). Recall that for the surface expressions ρ_α is mass per area while for the phases, ρ_α is mass per volume.

The rate of change of the body force potential acting on an interface is conveniently written in terms of surface differential operators. Use of mass conservation $\mathcal{M}_{*i\alpha}$ based on Table 2.3 to eliminate $D_{i\alpha}(\rho_\alpha \omega_{i\alpha})/Dt$ from Eq. (2.84) and expansion of $D_{i\alpha} \psi_{i\alpha}/Dt$ according to Eq. (2.69) yields

$$\begin{aligned} \frac{D_{i\alpha} \Psi_{i\alpha}}{Dt} + \psi_{i\alpha} \left(\rho_\alpha \omega_{i\alpha} \mathbf{l}'_\alpha : \mathbf{d}'_{i\alpha} - r_{i\alpha} - \sum_{\kappa \in \mathcal{J}_{\alpha}^+} M_{i\kappa \rightarrow i\alpha} \right) \\ - \rho_\alpha \omega_{i\alpha} \frac{\partial' \psi_{i\alpha}}{\partial t} - \rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} \cdot \nabla' \psi_{i\alpha} = 0. \end{aligned} \quad (2.85)$$

Only the surface components of the gradient of the body force potential appear in this equation. Thus, we make use of the identity

$$\nabla' \psi_{i\alpha} + \mathbf{l}'_\alpha \cdot \mathbf{g}_{i\alpha} = \mathbf{0}'. \quad (2.86)$$

With this relation and Eq. (2.83) employed, Eq. (2.85) becomes the microscale balance equation for the body force potential per unit area of chemical species i in interface α

$$\begin{aligned} \mathcal{G}_{*i\alpha} &= \frac{D_{i\alpha} \Psi_{i\alpha}}{Dt} + \Psi_{i\alpha} \mathbf{l}'_\alpha : \mathbf{d}'_{i\alpha} + \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha} - \sum_{\kappa \in \mathcal{J}_{\alpha}^+} M_{i\kappa \rightarrow i\alpha} \psi_{i\alpha} \\ &\quad - \rho_\alpha \omega_{i\alpha} \frac{\partial' \psi_{i\alpha}}{\partial t} - \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot (\mathbf{l} - \mathbf{l}'_\alpha) \cdot \mathbf{v}_{i\alpha} - r_{i\alpha} \psi_{i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_I. \end{aligned} \quad (2.87)$$

The elements of this equation are distributed in the appropriate columns of Table 2.3.

For the interface entity, summation of $\mathcal{G}_{i\alpha}$ over all species and rearrangement to obtain $\mathcal{G}_{*\alpha}$ results in

$$\begin{aligned} \mathcal{G}_{*\alpha} = & \frac{D_\alpha \Psi_\alpha}{Dt} + \Psi_\alpha \mathbf{l}'_\alpha : \mathbf{d}'_\alpha + \nabla' \cdot \left(\sum_{i \in \mathcal{I}_s} \rho_\alpha \omega_{i\alpha} \psi_{i\alpha} \mathbf{l}'_\alpha \cdot \mathbf{u}_{i\alpha} \right) \\ & + \rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha + \sum_{i \in \mathcal{I}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{l}'_\alpha \cdot \mathbf{u}_{i\alpha} - \sum_{i \in \mathcal{I}_s} \sum_{\kappa \in \mathcal{I}_{c\alpha}^+} \frac{M}{i\kappa \rightarrow i\alpha} \psi_{i\alpha} \\ & - \sum_{i \in \mathcal{I}_s} \rho_\alpha \omega_{i\alpha} \frac{\partial' \psi_{i\alpha}}{\partial t} - \sum_{i \in \mathcal{I}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot (\mathbf{l} - \mathbf{l}'_\alpha) \cdot \mathbf{v}_{i\alpha} - \sum_{i \in \mathcal{I}_s} r_{i\alpha} \psi_{i\alpha} = 0 \end{aligned}$$

for $\alpha \in \mathcal{I}_1$. (2.88)

The contributions to this equation are provided in Table 2.4.

2.5 Conservation and Balance Principles for a Common Curve

Common curves⁵ are the third type of entity of interest in the development of conservation and balance equations. Common curves are the regions in a multiphase system that exist where three phases, and also three interfaces, meet. As boundaries of two-dimensional entities, they are one-dimensional regions. Common curves occupy neither volume nor area in a system. The measure of the extent of a common curve is its length.

Common curves play a role in providing the location where mass, momentum, energy, and entropy can be exchanged among the interfaces that meet at a curve. The common curve length thus affects the amount of the exchanges and is of interest. Conventional multiphase dynamic models do not explicitly deal with common curves nor do they evolve the extent of common curve lengths with time. By formulating full conservation and balance equations for common curves, we will provide the opportunity to include common curve phase dynamics, exchanges of properties at the curve, and the length of curves present in the model. We will present the general and then particular forms of microscale species-based and entity-based conservation and balance equations for common curves.

⁵ Although these features of a system are usually referred to as common “lines”, we use the designation common “curves” in recognition of the fact that these one-dimensional regions usually have non-zero curvature.

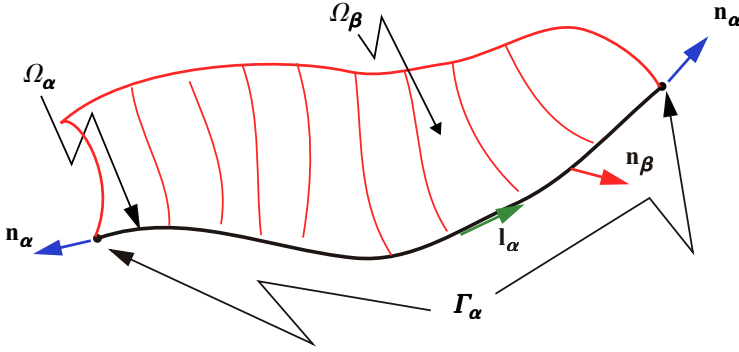


Fig. 2.3 Arbitrary curve in the region $\Omega_\alpha \subset \mathbb{R}^1$ containing common curve $\alpha \in \mathcal{I}_C$ with boundary $\Gamma_\alpha \subset \mathbb{R}^0$ consisting of the two end points of the curve. Unit vector \mathbf{n}_α is outward positive from and tangent to Ω_α at Γ_α . Unit vector \mathbf{l}_α is tangent to Ω_α . Also depicted is interface β with domain $\Omega_\beta \subset \mathbb{R}^2$ whose boundary is composed, at least partly, of Ω_α which is the curve where interface β and two other interfaces between phases meet. Unit vector \mathbf{n}_β is normal to Ω_α and tangent to Ω_β

2.5.1 General Microscale Point Form

The procedure for development of conservation and balance equations for a common curve is almost identical to that employed in developing expressions for phases and interfaces. However, particular attention must be given to the geometry of the common curve that requires a little modification to the general conservation equation for entity properties, Eq. (2.7), or appropriate definition of variables in Eq. (2.8) for species properties.

The domain of a common curve, indicated as entity $\alpha \in \mathcal{I}_C$, that exists where three phases, indicated as β, γ , and $\delta \in \mathcal{I}_P$, meet is Ω_α such that $\Omega_\alpha = \bar{\Omega}_\beta \cap \bar{\Omega}_\gamma \cap \bar{\Omega}_\delta$.⁶ A schematic diagram of the common curve is provided in Fig. 2.3. The fact that Ω_α is a curve means that $\Omega_\alpha \subset \mathbb{R}^1$. The extent of the curve is its length, which is denoted as \mathbb{L}_α . The boundary of the curve consists of the two end-points of the curve denoted $\Gamma_{\alpha 1}$ and $\Gamma_{\alpha 2}$ where $\Gamma_{\alpha m} \subset \mathbb{R}^0$ for $m \in \mathcal{I}_{\Gamma_\alpha}$ and $\mathcal{I}_{\Gamma_\alpha} = \{1, 2\}$. In contrast to the phase and interface boundaries, for which the boundary is continuous, the boundary of a common curve is formed by two disconnected points. The outward unit vectors that are tangent to Ω_α at the two end points are denoted \mathbf{n}_α . The unit vector tangent to the curve is \mathbf{l}_α . Therefore at one end of Ω_α , $\mathbf{n}_\alpha \cdot \mathbf{l}_\alpha = 1$ and at the other end, $\mathbf{n}_\alpha \cdot \mathbf{l}_\alpha = -1$. The velocity of the common curve is denoted as \mathbf{w}_α . In directions normal to the common curve, the velocity of material in the common curve must be equal to the velocity of the common curve such that $(\mathbf{v}_\alpha - \mathbf{w}_\alpha) \cdot (\mathbf{l} - \mathbf{l}_\alpha \mathbf{l}_\alpha) = \mathbf{0}$. We

⁶ A common curve is also the location where three interfaces meet. If the indexes of the interfaces that exist between pairs of the three phases β, γ , and δ are denoted as $\beta\gamma, \beta\delta$, and $\gamma\delta$, the domain of the common curve can alternatively be defined as $\Omega_\alpha = \bar{\Omega}_{\beta\gamma} \cap \bar{\Omega}_{\beta\delta} \cap \bar{\Omega}_{\gamma\delta}$.

will denote the unit tensor for the curve as the 3×3 tensor \mathbf{l}''_α for the curve such that $\mathbf{l}''_\alpha = \mathbf{l}_\alpha \mathbf{l}_\alpha$.

A general conservation equation based on species i in common curve entity α can be developed with reference to Eq. (2.8). A notational change must be introduced to account for the fact that the integral over the boundary reduces to a sum over two end points for a common curve. Thus the general balance equation is

$$\begin{aligned} \frac{d}{dt} \int_{\Omega_\alpha} F_{i\alpha} d\mathbf{r} + \sum_{m \in \mathcal{J}_{\Gamma_\alpha}} F_{i\alpha} (\mathbf{v}_{i\alpha} - \mathbf{w}_\alpha) \cdot \mathbf{n}_\alpha|_{\Gamma_{am}} - \int_{\Omega_\alpha} S_{\Omega T i \alpha} d\mathbf{r} \\ - \sum_{m \in \mathcal{J}_{\Gamma_\alpha}} \mathbf{S}_{\Gamma i \alpha} \cdot \mathbf{n}_\alpha|_{\Gamma_{am}} - \int_{\Omega_\alpha} G_{\Omega i \alpha} d\mathbf{r} = 0, \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C. \end{aligned} \quad (2.89)$$

In this equation, all densities are per unit length, the domain of integration is a one-dimensional curve, and the summations are over the two end points that form the boundary of the curve. In the case when the common curve is closed, the summation terms do not appear. However, reduction of this equation for an entire curve to the part appropriate for a microscale segment inherently changes the equation to apply to a microscale segment that is not closed.

The conversion of this conservation equation for a common curve to the form that applies at a point along a curve requires that the boundary summation terms be converted to integrals over the common curve. Part of this task can be accomplished making use of the transport theorem [8]:

Theorem 2.5 (T[1,(0,0),1]) *For a smooth continuous and differentiable function f defined over a domain $\Omega_\alpha \subset \mathbb{R}^1$ that may deform with time t due to velocity \mathbf{w}_α of the domain and with boundary end points Γ_{am} where $m \in \mathcal{J}_{\Gamma_\alpha}$, designate the unit tangent to the domain as \mathbf{l}_α , the outward vector tangent to the domain at the end point boundaries as \mathbf{n}_α , and the unit tensor $\mathbf{l}''_\alpha = \mathbf{l}_\alpha \mathbf{l}_\alpha$. Then,*

$$\frac{d}{dt} \int_{\Omega_\alpha(t)} f d\mathbf{r} = \int_{\Omega_\alpha(t)} \frac{\partial'' f}{\partial t} d\mathbf{r} - \int_{\Omega_\alpha(t)} f \mathbf{w}_\alpha \cdot (\nabla'' \cdot \mathbf{l}''_\alpha) d\mathbf{r} + \sum_{m \in \mathcal{J}_{\Gamma_\alpha}} f \mathbf{w}_\alpha \cdot \mathbf{n}_\alpha|_{\Gamma_{am}(t)}, \quad (2.90)$$

where the partial derivative with respect to time for a point fixed to Ω_α is defined as

$$\frac{\partial''}{\partial t} = \frac{d}{dt} - \mathbf{w}_\alpha \cdot \nabla''; \quad (2.91)$$

and $\nabla'' \cdot$ and ∇'' are the curve divergence and curve gradient operators, respectively, defined as

$$\nabla'' \cdot = (\mathbf{l}''_\alpha \cdot \nabla) \cdot \quad (2.92)$$

and

$$\nabla'' = \mathbf{l}''_\alpha \cdot \nabla. \quad (2.93)$$

When in diagonal form, the tensor, \mathbf{l}''_{α} has an entry of 1 on the diagonal element aligned with the curve tangent and zeroes elsewhere. When f is the density of a conserved quantity with units of the property per unit length, the left side of Eq. (2.90) is the change in the total amount of the conserved quantity with time over the curve. This is equated to the three terms on the right that account, respectively, for the changes in the quantity per time due to changes in the density of the property at points on the curve, changes in the quantity due to movement of the curve that causes its curvature to change (i.e., the curve can change its length without movement of its end points), and movement of the end points of the curve that cause it to increase or decrease in length.

Also of use in transforming the general conservation equation is the curve divergence theorem [8]:

Theorem 2.6 (D[1,(0,0),1]) *For a smooth continuous and differentiable tensor function \mathbf{f} defined over a domain $\Omega_{\alpha} \subset \mathbb{R}^1$ that may deform with time t due to velocity \mathbf{w}_{α} of the domain and with boundary end points $\Gamma_{\alpha m}$ where $m \in \mathcal{J}_{\Gamma_{\alpha}}$, designate the unit vector tangent to the domain as \mathbf{l}_{α} , the outward vector tangent to the domain at the end boundaries as \mathbf{n}_{α} , and the unit tensor $\mathbf{l}''_{\alpha} = \mathbf{l}_{\alpha}\mathbf{l}_{\alpha}$. Then,*

$$\int_{\Omega_{\alpha}(t)} \text{div}'' \mathbf{f} d\tau = - \int_{\Omega_{\alpha}(t)} \mathbf{f} \cdot (\nabla'' \cdot \mathbf{l}''_{\alpha}) d\tau + \sum_{m \in \mathcal{J}_{\Gamma_{\alpha}}} \mathbf{f} \cdot \mathbf{n}_{\alpha} |_{\Gamma_{\alpha m}(t)}, \quad (2.94)$$

where $\nabla'' \cdot$ is the curve divergence operator defined as

$$\nabla'' \cdot = (\mathbf{l}''_{\alpha} \cdot \nabla) \cdot ; \quad (2.95)$$

and div'' is the divergence operator along the curve that contracts the last index of \mathbf{f} .

It is left as an exercise to show that

$$\text{div}'' \mathbf{f} + \mathbf{f} \cdot (\nabla'' \cdot \mathbf{l}''_{\alpha}) = \text{div}'' (\mathbf{f} \cdot \mathbf{l}''_{\alpha}). \quad (2.96)$$

Making use of this relation, we can write an alternative, but equivalent, form of Eq. (2.94) as

$$\int_{\Omega_{\alpha}(t)} \text{div}'' (\mathbf{f} \cdot \mathbf{l}''_{\alpha}) d\tau = \sum_{m \in \mathcal{J}_{\Gamma_{\alpha}}} \mathbf{f} \cdot \mathbf{n}_{\alpha} |_{\Gamma_{\alpha m}(t)}. \quad (2.97)$$

With f replaced by $F_{i\alpha}$ in transport theorem Eq. (2.90), with \mathbf{f} replaced by $F_{i\alpha}\mathbf{v}_{i\alpha}$ in divergence theorem Eq. (2.94), and \mathbf{f} replaced by $\mathbf{S}_{\Gamma\alpha}$ in alternative divergence theorem Eq. (2.97), equations are obtained that allow the boundary terms in Eq. (2.89) to be eliminated. The result is

$$\int_{\Omega_{\alpha}} \left[\frac{\partial'' F_{i\alpha}}{\partial t} + \nabla'' \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) + F_{i\alpha} (\mathbf{v}_{i\alpha} - \mathbf{w}_{\alpha}) \cdot (\nabla'' \cdot \mathbf{l}''_{\alpha}) \right] d\tau$$

$$- \int_{\Omega_\alpha} [S_{\Omega T i \alpha} + \text{div}'' (\mathbf{S}_{\Gamma i \alpha} \cdot \mathbf{l}''_\alpha) + \mathbf{G}_{\Omega i \alpha}] \, d\mathbf{r} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C. \quad (2.98)$$

In this equation, $\nabla'' \cdot \mathbf{l}''_\alpha$ is a vector accounting for the curvature of the domain and is normal to the curve. The vector product of this term with $\mathbf{v}_{i\alpha} - \mathbf{w}_\alpha$ is zero because mass in the curve moving in a direction normal to the curve moves at the velocity of the curve. The total body source for the curve is composed of three components. External sources acting on the entity are the first component. The common curve is located where three interfaces meet. These interfaces interact with the common curve and can exchange properties with the curve. Thus, at every point on the curve, the exchanges with the interfaces can be considered a second element of a body source. The third component arises from interaction of the common curve with a phase at locations where the surface has a unique normal. At these locations, interactions between the common curve and the phase is modeled as a concentrated force. This singularity, in general, can be composed of advective and non-advective components. Its mathematical form is the same as an interaction term from an interface to a common curve. In subsequent analysis of particular cases, although it is possible that an advective flow could occur directly from a common curve to a phase, this will not be considered. The non-advective component will be incorporated as it impacts common curve dynamics.⁷ The concentrated interaction term will thus be a non-advective flux, such as stress or heat conduction. With these considerations in mind, we express the body source explicitly in terms of these three components as

$$S_{\Omega T i \alpha} = S_{\Omega i \alpha} + \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} X_{j\kappa \rightarrow i\alpha} + \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \sum_{j \in \mathcal{J}_s} X_{j\kappa \rightarrow i\alpha}^*, \quad (2.99)$$

where $\mathcal{J}_{c\alpha}^+$ is the connected set for common curve α that is of higher dimensionality (i.e., interfaces in the connected set), $\mathcal{J}_{c\beta}^+$ is the higher order connected set to these interfaces (i.e., phases), and $X_{j\kappa \rightarrow i\alpha}$ and $X_{j\kappa \rightarrow i\alpha}^*$ are the body source components due to transfer of the property being conserved from species j in entity κ to species i in entity α . For emphasis, a superscript $*$ is used to indicate a transfer term between a phase and a common curve is only non-zero if a concentrated force is operative where the normal direction to the solid is unique. The factor of 1/2 appears with the last term because the double sum over entities will encounter each phase twice.

Because the domain of integration is arbitrary, the integrand itself—not just the integral—must be zero. With the considerations of the last paragraph, the general microscale conservation or balance equation at a point on a common curve is then obtained from Eq. (2.98) as

⁷ This interaction can be conceptualized crudely as transport from a phase to a common curve through zero area. For such a transfer to occur, the quantity being transported would have some magnitude highly concentrated at the curve. The non-advective concentrated component of stress can be thought of as a normal force exerted by the solid that balances the forces of interfaces at the surface.

$$\begin{aligned} \frac{\partial'' F_{i\alpha}}{\partial t} + \nabla'' \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} X_{j\kappa \rightarrow i\alpha} - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \sum_{j \in \mathcal{J}_s} X_{j\kappa \rightarrow i\alpha}^* \\ - \text{div}'' (\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}_{\alpha}'') - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C. \end{aligned} \quad (2.100)$$

This equation may also be written in terms of the material derivative as

$$\begin{aligned} \frac{D_{i\alpha} F_{i\alpha}}{Dt} + F_{i\alpha} \mathbf{l}_{\alpha}'' : \mathbf{d}_{i\alpha}'' - S_{\Omega i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} X_{j\kappa \rightarrow i\alpha} - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \sum_{j \in \mathcal{J}_s} X_{j\kappa \rightarrow i\alpha}^* \\ - \text{div}'' (\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}_{\alpha}'') - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C, \end{aligned} \quad (2.101)$$

where

$$\frac{D_{i\alpha}}{Dt} = \frac{\partial''}{\partial t} + \mathbf{v}_{i\alpha} \cdot \nabla'' \quad (2.102)$$

and

$$\mathbf{d}_{i\alpha}'' = \left[\nabla'' \mathbf{v}_{i\alpha} + (\nabla'' \mathbf{v}_{i\alpha})^T \right]. \quad (2.103)$$

Although Eqs. (2.100) and (2.101) are equivalent forms, the former is more convenient to work with for averaging to obtain larger scale equations.

2.5.2 Specific Conservation and Balance Principles

A comparison of the general point equation for a common curve, Eq. (2.100), with the corresponding equation for a surface, Eq. (2.67), indicates that the equations appear to be different only in the domain, the number of primes in the differential operator and the unit tensor, and in the exchanges with entities two-dimensions higher. When a single prime is used, the differentiation occurs on a surface, while a double prime indicates differentiation on a curve. Both definitions of the material derivatives given by Eqs. (2.69) and (2.102) are time derivatives following the movement of a particle and are equivalent. An important difference between the surface and curve equations is related to the definition of the source terms, $\mathbf{S}_{\Gamma i\alpha}$. Based on the similarities, Tables 2.3 and 2.4 can be used to motivate the specific forms of equations for common curves with allowances made for the particular features of the common curve equations. The corresponding results for species and entity equations are collected in Tables 2.5 and 2.6, respectively. In these tables, the domain of α has been changed from \mathcal{J}_I to \mathcal{J}_C and the single prime (') is replaced by a double prime (") in all instances. The connected set, $\mathcal{J}_{c\alpha}^+$, refers to the three interfaces that meet to form the common curve. The specific balance equations for a common curve are obtained with minor cosmetic differences in notation and will be listed here in their partial time derivative forms. The forms in terms of material derivatives also follow directly.

The most noticeable change between the interface and common curve equation is the presence of the asterisk terms as body sources. These terms appear in the

Table 2.5 Physical variables for species-based common curve equations in partial derivative or material derivative form. $\mathcal{M}_{i\alpha}$, $\mathcal{P}_{i\alpha}$, $\mathcal{E}_{i\alpha}$, $\mathcal{S}_{i\alpha}$, and $\mathcal{G}_{i\alpha}$ correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential for species i in common curve α . Terms with an asterisk describe exchanges between a common curve and a phase. Exchange terms are written in terms of microscale variables at the end of the table

$\mathcal{F}_{i\alpha} = \frac{\partial'' F_{i\alpha}}{\partial t} + \nabla'' \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} \frac{X}{jk \rightarrow i\alpha} - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \sum_{j \in \mathcal{J}_s} \frac{X^*}{jk \rightarrow i\alpha}$ $-\text{div}'' (\mathbf{S}_{\Gamma i\alpha} \mathbf{l}_{i\alpha}'') - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C$					
$\mathcal{F}_{*i\alpha} = \frac{D_{i\alpha} F_{i\alpha}}{Dt} + F_{i\alpha} \mathbf{l}_{i\alpha}'': \mathbf{d}_{i\alpha}'' - S_{\Omega i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} \frac{X}{jk \rightarrow i\alpha} - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \sum_{j \in \mathcal{J}_s} \frac{X^*}{jk \rightarrow i\alpha}$ $-\text{div}'' (\mathbf{S}_{\Gamma i\alpha} \mathbf{l}_{i\alpha}'') - G_{\Omega i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C$					
$\mathcal{F}_{i\alpha}$	$F_{i\alpha}$	$S_{\Omega i\alpha}$	$\frac{X}{jk \rightarrow i\alpha}$	$\mathbf{S}_{\Gamma i\alpha}$	$G_{\Omega i\alpha}$
$\mathcal{M}_{i\alpha}$	$\rho_\alpha \omega_\alpha$	—	$\delta_{ij} \frac{M}{ik \rightarrow i\alpha}$	—	$r_{i\alpha}$
$\mathcal{P}_{i\alpha}$	$\rho_\alpha \omega_\alpha \mathbf{v}_{i\alpha}$	$\rho_\alpha \omega_\alpha \mathbf{g}_{i\alpha}$	$\delta_{ij} \mathbf{v}_{ik} \frac{M}{ik \rightarrow i\alpha} + \frac{\mathbf{T}}{jk \rightarrow i\alpha}$	$\mathbf{t}_{i\alpha}$	$\mathbf{p}_{i\alpha} + r_{i\alpha} \mathbf{v}_{i\alpha}$
$\mathcal{E}_{i\alpha}$	$E_{i\alpha}$ $+ \rho_\alpha \omega_\alpha \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2}$	$\rho_\alpha \omega_\alpha \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha}$ $+ h_{i\alpha}$	$\delta_{ij} \left(\frac{E_{ik}}{\rho_\kappa \omega_{ik}} + \frac{\mathbf{v}_{ik} \cdot \mathbf{v}_{ik}}{2} \right) \frac{M}{ik \rightarrow i\alpha}$ $+ \mathbf{v}_{jk} \cdot \frac{\mathbf{T}}{jk \rightarrow i\alpha} + \frac{Q}{jk \rightarrow i\alpha}$	$\mathbf{t}_{i\alpha}^T \cdot \mathbf{v}_{i\alpha}$ $+ \mathbf{q}_{i\alpha}$	$e_{i\alpha} + \mathbf{p}_{i\alpha} \cdot \mathbf{v}_{i\alpha}$ $+ r_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2}$
$\mathcal{S}_{i\alpha} - \Lambda_{i\alpha}$	$\eta_{i\alpha}$	$b_{i\alpha}$	$\delta_{ij} \frac{\eta_{ik}}{\rho_\kappa \omega_{ik}} \frac{M}{ik \rightarrow i\alpha} + \frac{\Phi}{jk \rightarrow i\alpha}$	$\Phi_{i\alpha}$	$\Lambda_{i\alpha}$
$\mathcal{G}_{i\alpha}$	$\Psi_{i\alpha}$	$-\rho_\alpha \omega_\alpha \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha}$	$\delta_{ij} \frac{M}{ik \rightarrow i\alpha} \Psi_{i\alpha}$	—	$\rho_\alpha \omega_\alpha \left[\frac{\partial'' \Psi_{i\alpha}}{\partial t} + \mathbf{g}_{i\alpha} \cdot (\mathbf{l}_{i\alpha}'') \cdot \mathbf{v}_{i\alpha} \right]$ $+ r_{i\alpha} \Psi_{i\alpha}$
Inter-entity Exchange Terms					
$\frac{M}{ik \rightarrow i\alpha} = \mathbf{n}_\kappa \cdot [\rho_\kappa \omega_{ik} (\mathbf{v}_{ik} - \mathbf{v}_\alpha)]$ for $\kappa \in \mathcal{J}_{c\alpha}^+$			$M^* = 0$ for $\beta \in \mathcal{J}_{c\alpha}^+, \kappa \in \mathcal{J}_{c\beta}^+$		
$\frac{\mathbf{T}}{jk \rightarrow i\alpha} = -z_T \frac{\mathbf{t}_{jk} \cdot \mathbf{n}_\kappa}{jk \rightarrow i\alpha}$ for $\kappa \in \mathcal{J}_{c\alpha}^+$;			$\frac{\mathbf{T}^*}{jk \rightarrow i\alpha} = -z_T^* \frac{\mathbf{t}_{jk}^* \cdot \mathbf{n}_\kappa}{jk \rightarrow i\alpha}$ for $\beta \in \mathcal{J}_{c\alpha}^+, \kappa \in \mathcal{J}_{c\beta}^+$		
$\frac{Q}{jk \rightarrow i\alpha} = -z_Q \frac{\mathbf{q}_{jk} \cdot \mathbf{n}_\kappa}{jk \rightarrow i\alpha}$ for $\kappa \in \mathcal{J}_{c\alpha}^+$;			$\frac{Q^*}{jk \rightarrow i\alpha} = -z_Q^* \frac{\mathbf{q}_{jk}^* \cdot \mathbf{n}_\kappa}{jk \rightarrow i\alpha}$ for $\beta \in \mathcal{J}_{c\alpha}^+, \kappa \in \mathcal{J}_{c\beta}^+$		
$\frac{\Phi}{jk \rightarrow i\alpha} = -z_\Phi \frac{\Phi_{jk} \cdot \mathbf{n}_\kappa}{jk \rightarrow i\alpha}$ for $\kappa \in \mathcal{J}_{c\alpha}^+$			$\frac{\Phi^*}{jk \rightarrow i\alpha} = -z_\Phi^* \frac{\Phi_{jk}^* \cdot \mathbf{n}_\kappa}{jk \rightarrow i\alpha}$ for $\beta \in \mathcal{J}_{c\alpha}^+, \kappa \in \mathcal{J}_{c\beta}^+$		

body force terms for the momentum, energy, and entropy equations. These terms account solely for exchanges between a phase and a common curve on the boundary of the phase when the normal to the phase is unique at the common curve. If the normal is non-unique, an exchange between the phase and the common curve is accomplished through the interfaces. The quantity exchanged to the common curve must come from a concentrated flux in the phase, which contributes to the common curve dynamics as a body source. This arises through modeling of the small surface region where the concentrated source exists as a common curve with no width. In Tables 2.5 and 2.6, it can be seen that, for the sake of generality, the summation occurs over the three phases that meet at the common curve. However, at most only

one of the phases can have a smooth boundary at the common curve. Thus, for a phase κ , if \mathbf{n}_κ is not unique at a common curve, the concentrated momentum, energy, and entropy fluxes of phase κ must all be zero at the common curve.

For the porous media problems we will be studying, only the solid phase will be allowed to have a unique boundary normal at the common curve. Thus the concentrated fluxes will be zero for fluid phases but may be non-zero for the solid. We have not considered advective fluxes from a phase to a common curve. The concentrated terms could be important, for example, in describing the forces acting in the normal direction to the solid exerted by interfaces that meet at a common curve. Alternatively, a common curve with very high heat conductivity on a smooth surface of a phase could exchange heat directly with the phase. The concentrated flux terms are defined at the bottom of Tables 2.5 and 2.6. The factor 1/2 appears in the definitions because, if one makes use of the prescribed summations, each phase is encountered twice. The counterparts to these terms that account for exchanges between the common curve and the interfaces that meet at the common curve retain the same definitions as provided at the bottom of Tables 2.3 and 2.4.

Based on the $\mathcal{M}_{i\alpha}$ row of Table 2.5, the point microscale conservation of mass equation for species i in common curve α is given by

$$\mathcal{M}_{i\alpha} = \frac{\partial''(\rho_\alpha \omega_{i\alpha})}{\partial t} + \nabla'' \cdot (\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha}) - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} M_{i\kappa \rightarrow i\alpha} - r_{i\alpha} = 0$$

for $i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C$. (2.104)

From row \mathcal{M}_α of Table 2.6 or from summation of Eq. (2.104) over all species in Ω_α , the point microscale conservation of mass equation for a common curve α is

$$\mathcal{M}_\alpha = \frac{\partial'' \rho_\alpha}{\partial t} + \nabla'' \cdot (\rho_\alpha \mathbf{v}_\alpha) - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} M_{\kappa \rightarrow \alpha} = 0 \quad \text{for } \alpha \in \mathcal{J}_C. \quad (2.105)$$

The conservation of momentum equation for a species in a common curve based on Table 2.5 is written as

$$\begin{aligned} \mathcal{P}_{i\alpha} = & \frac{\partial''(\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha})}{\partial t} + \nabla'' \cdot (\rho_\alpha \omega_{i\alpha} \mathbf{v}_{i\alpha} \mathbf{v}_{i\alpha}) - \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \\ & - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} \left(\delta_{ij} \mathbf{v}_{i\kappa} M_{i\kappa \rightarrow i\alpha} + \mathbf{T}_{j\kappa \rightarrow i\alpha} \right) - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \sum_{j \in \mathcal{J}_s} \mathbf{T}_{j\kappa \rightarrow i\alpha}^* \\ & - \nabla'' \cdot (\mathbf{l}_\alpha'' \mathbf{t}_{i\alpha}^T) - \mathbf{p}_{i\alpha} - r_{i\alpha} \mathbf{v}_{i\alpha} = \mathbf{0} \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C. \end{aligned} \quad (2.106)$$

The entity-based conservation of momentum equation for a common curve that makes use of information in Table 2.6 is

$$\mathcal{P}_\alpha = \frac{\partial''(\rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \nabla'' \cdot (\rho_\alpha \mathbf{v}_\alpha \mathbf{v}_\alpha) - \rho_\alpha \mathbf{g}_\alpha - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \left(\mathbf{v}_\kappa M_{\kappa \rightarrow \alpha} + \mathbf{T}_{\kappa \rightarrow \alpha} \right)$$

Table 2.6 Physical variables for entity-based common curve equations in partial derivative or material derivative form. \mathcal{M}_α , \mathcal{P}_α , \mathcal{E}_α , \mathcal{S}_α , and \mathcal{G}_α correspond, respectively, to conservation of mass, momentum, and energy, and balance equations of entropy and body force potential in common curve α . Terms with an asterisk describe possible exchanges between the common curve and a phase with a unique normal at the common curve. Exchange terms are at the end of the table

$\mathcal{F}_\alpha = \frac{\partial'' F_\alpha}{\partial t} + \nabla'' \cdot (\mathbf{v}_\alpha F_\alpha) - S_{\Omega\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \frac{X}{\kappa \rightarrow \alpha} - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \frac{X^*}{\kappa \rightarrow \alpha}$ $-\text{div}'' (\mathbf{S}_{\Gamma\alpha} \cdot \mathbf{l}_\alpha'') - G_{\Omega\alpha} = 0 \quad \text{for } \alpha \in \mathcal{J}_C$ $\mathcal{F}_{*\alpha} = \frac{D_\alpha F_\alpha}{Dt} + F_\alpha \mathbf{l}_\alpha' : \mathbf{d}_\alpha'' - S_{\Omega\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \frac{X}{\kappa \rightarrow \alpha} - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \frac{X^*}{\kappa \rightarrow \alpha}$ $-\text{div}'' (\mathbf{S}_{\Gamma\alpha} \cdot \mathbf{l}_\alpha'') - G_{\Omega\alpha} = 0 \quad \text{for } \alpha \in \mathcal{J}_C$						
\mathcal{F}_α	F_α	$S_{\Omega\alpha}$	$\frac{X}{\kappa \rightarrow \alpha}$	$\frac{X^*}{\kappa \rightarrow \alpha}$	$\mathbf{S}_{\Gamma\alpha}$	$G_{\Omega\alpha}$
\mathcal{M}_α	ρ_α	—	$M_{\kappa \rightarrow \alpha}$	—	—	—
\mathcal{P}_α	$\rho_\alpha \mathbf{v}_\alpha$	$\rho_\alpha \mathbf{g}_\alpha$	$\mathbf{v}_\kappa M_{\kappa \rightarrow \alpha} + \mathbf{T}_{\kappa \rightarrow \alpha}$	$\mathbf{T}_{\kappa \rightarrow \alpha}^*$	\mathbf{t}_α	—
\mathcal{E}_α	E_α $+ \rho_\alpha \frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2}$ $+ \rho_\alpha K_{E\alpha}$	$\rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha$ $+ h_\alpha$ $+ \sum_{i \in \mathcal{J}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{l}_\alpha'' \cdot \mathbf{u}_{i\alpha}$	$\left(\frac{E_\kappa}{\rho_\kappa} + \frac{\mathbf{v}_\kappa \cdot \mathbf{v}_\kappa}{2} + K_{E\kappa} \right) M_{\kappa \rightarrow \alpha} + \mathbf{v}_\kappa \cdot \mathbf{T}_{\kappa \rightarrow \alpha} + Q_{\kappa \rightarrow \alpha}^*$	$\mathbf{v}_\kappa \cdot \mathbf{T}_{\kappa \rightarrow \alpha}^*$	$\mathbf{t}_\alpha^T \cdot \mathbf{v}_\alpha$ $+ \mathbf{q}_\alpha$	—
$\mathcal{S}_\alpha - \Lambda_\alpha$	η_α	b_α	$\frac{\eta_\kappa}{\rho_\kappa} M_{\kappa \rightarrow \alpha} + \Phi_{\kappa \rightarrow \alpha}$	$\Phi_{\kappa \rightarrow \alpha}^*$	$\boldsymbol{\varphi}_\alpha$	Λ_α
\mathcal{G}_α	Ψ_α	$-\rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha$ $- \sum_{i \in \mathcal{J}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{l}_\alpha'' \cdot \mathbf{u}_{i\alpha}$	$\sum_{i \in \mathcal{J}_s} M_{i\kappa \rightarrow i\alpha} \Psi_{i\alpha}$	—	$-\sum_{i \in \mathcal{J}_s} \rho_\alpha \omega_{i\alpha} \Psi_{i\alpha} \mathbf{u}_{i\alpha}$ $+ \sum_{i \in \mathcal{J}_s} \rho_\alpha \omega_{i\alpha} \left[\frac{\partial'' \Psi_{i\alpha}}{\partial t} + \mathbf{g}_{i\alpha} \cdot (\mathbf{l}_\alpha'' - \mathbf{l}_\alpha') \cdot \mathbf{v}_{i\alpha} \right]$ $+ \sum_{i \in \mathcal{J}_s} r_{i\alpha} \Psi_{i\alpha}$	
Inter-entity Exchange Terms						
$M_{\kappa \rightarrow \alpha} = \sum_{i \in \mathcal{J}_s} M_{i\kappa \rightarrow i\alpha} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$						
$\mathbf{T}_{\kappa \rightarrow \alpha} = \sum_{j \in \mathcal{J}_s} \sum_{i \in \mathcal{J}_s} \left[\mathbf{T}_{j\kappa \rightarrow i\alpha} + \delta_{ij} (\mathbf{v}_{i\kappa} - \mathbf{v}_\kappa) M_{i\kappa \rightarrow i\alpha} \right] \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$						
$Q_{\kappa \rightarrow \alpha} = \sum_{j \in \mathcal{J}_s} \sum_{i \in \mathcal{J}_s} \left\{ Q_{j\kappa \rightarrow i\alpha} + (\mathbf{v}_{j\kappa} - \mathbf{v}_\kappa) \cdot \mathbf{T}_{j\kappa \rightarrow i\alpha} + \delta_{ij} \left[\frac{E_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} + \frac{\mathbf{u}_{i\kappa} \cdot \mathbf{u}_{i\kappa}}{2} - \left(\frac{E_\kappa}{\rho_\kappa} + K_{E\kappa} \right) \right] M_{i\kappa \rightarrow i\alpha} \right\} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$						
$\Phi_{\kappa \rightarrow \alpha} = \sum_{j \in \mathcal{J}_s} \sum_{i \in \mathcal{J}_s} \left\{ \Phi_{j\kappa \rightarrow i\alpha} + \delta_{ij} \left[\frac{\eta_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} - \frac{\eta_\kappa}{\rho_\kappa} \right] M_{i\kappa \rightarrow i\alpha} \right\} \quad \text{for } \kappa \in \mathcal{J}_{c\alpha}^+$						
$\mathbf{T}_{\kappa \rightarrow \alpha}^* = -\mathbf{n}_\kappa \cdot \mathbf{t}_\kappa^* = \sum_{i \in \mathcal{J}_s} \sum_{j \in \mathcal{J}_s} \mathbf{T}_{j\kappa \rightarrow i\alpha}^* \quad \text{for } \beta \in \mathcal{J}_{c\alpha}^+, \kappa \in \mathcal{J}_{c\beta}^+$						
$Q_{\kappa \rightarrow \alpha}^* = -\mathbf{n}_\kappa \cdot (\mathbf{t}_\kappa^* \cdot \mathbf{v}_\kappa + \mathbf{q}_\kappa^*) = \sum_{i \in \mathcal{J}_s} \sum_{j \in \mathcal{J}_s} \left[(\mathbf{v}_{j\kappa} - \mathbf{v}_\kappa) \cdot \mathbf{T}_{j\kappa \rightarrow i\alpha}^* + Q_{j\kappa \rightarrow i\alpha}^* \right] \quad \text{for } \beta \in \mathcal{J}_{c\alpha}^+, \kappa \in \mathcal{J}_{c\beta}^+$						
$\Phi_{\kappa \rightarrow \alpha}^* = -\mathbf{n}_\kappa \cdot \boldsymbol{\varphi}_\kappa^* = \sum_{i \in \mathcal{J}_s} \sum_{j \in \mathcal{J}_s} \Phi_{j\kappa \rightarrow i\alpha}^* \quad \text{for } \beta \in \mathcal{J}_{c\alpha}^+, \kappa \in \mathcal{J}_{c\beta}^+$						

$$-\frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \mathbf{T}_{\kappa \rightarrow \alpha}^* - \nabla'' \cdot (\mathbf{l}_\alpha'' \cdot \mathbf{t}_\alpha) = \mathbf{0} \quad \text{for } \alpha \in \mathcal{J}_C. \quad (2.107)$$

The species-based and entity-based conservation of energy equations for a common curve, extracted from Tables 2.5 and 2.6 are, respectively,

$$\begin{aligned}
 \mathcal{E}_{i\alpha} = & \frac{\partial''}{\partial t} \left(E_{i\alpha} + \rho_\alpha \omega_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2} \right) + \nabla'' \cdot \left[\left(E_{i\alpha} + \rho_\alpha \omega_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2} \right) \mathbf{v}_{i\alpha} \right] \\
 & - \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha} - h_{i\alpha} \\
 & - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} \left[\delta_{ij} \left(\frac{E_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} + \frac{\mathbf{v}_{i\kappa} \cdot \mathbf{v}_{i\kappa}}{2} \right) \frac{M}{i\kappa \rightarrow i\alpha} + \mathbf{v}_{j\kappa} \cdot \frac{\mathbf{T}}{j\kappa \rightarrow i\alpha} + \frac{Q}{j\kappa \rightarrow i\alpha} \right] \\
 & - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \sum_{j \in \mathcal{J}_s} \left(\mathbf{v}_{j\kappa} \cdot \frac{\mathbf{T}^*}{j\kappa \rightarrow i\alpha} + \frac{Q^*}{j\kappa \rightarrow i\alpha} \right) \\
 & - \nabla'' \cdot [\mathbf{l}_\alpha'' \cdot (\mathbf{t}_{i\alpha} \cdot \mathbf{v}_{i\alpha} + \mathbf{q}_{i\alpha})] - e_{i\alpha} - \mathbf{p}_{i\alpha} \cdot \mathbf{v}_{i\alpha} - r_{i\alpha} \frac{\mathbf{v}_{i\alpha} \cdot \mathbf{v}_{i\alpha}}{2} = 0 \\
 & \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C \quad (2.108)
 \end{aligned}$$

and

$$\begin{aligned}
 \mathcal{E}_\alpha = & \frac{\partial''}{\partial t} \left[E_\alpha + \rho_\alpha \left(\frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} + K_{E\alpha} \right) \right] + \nabla'' \cdot \left\{ \left[E_\alpha + \rho_\alpha \left(\frac{\mathbf{v}_\alpha \cdot \mathbf{v}_\alpha}{2} + K_{E\alpha} \right) \right] \mathbf{v}_\alpha \right\} \\
 & - \rho_\alpha \mathbf{g}_\alpha \cdot \mathbf{v}_\alpha - \sum_{i \in \mathcal{J}_s} \rho_\alpha \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{u}_{i\alpha} - h_\alpha \\
 & - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \left[\left(\frac{E_\kappa}{\rho_\kappa} + \frac{\mathbf{v}_\kappa \cdot \mathbf{v}_\kappa}{2} \right) \frac{M}{\kappa \rightarrow \alpha} + \mathbf{v}_\kappa \cdot \frac{\mathbf{T}}{\kappa \rightarrow \alpha} + \frac{Q}{\kappa \rightarrow \alpha} \right] \\
 & - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \left(\mathbf{v}_\kappa \cdot \frac{\mathbf{T}^*}{\kappa \rightarrow \alpha} + \frac{Q^*}{\kappa \rightarrow \alpha} \right) - \nabla'' \cdot [\mathbf{l}_\alpha'' \cdot (\mathbf{t}_\alpha \cdot \mathbf{v}_\alpha + \mathbf{q}_\alpha)] = 0 \quad \text{for } \alpha \in \mathcal{J}_C. \quad (2.109)
 \end{aligned}$$

The balance of entropy equation for a species in a common curve-based on Table 2.5 is

$$\begin{aligned}
 \mathcal{S}_{i\alpha} = & \frac{\partial'' \eta_{i\alpha}}{\partial t} + \nabla'' \cdot (\eta_{i\alpha} \mathbf{v}_{i\alpha}) - b_{i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \sum_{j \in \mathcal{J}_s} \left(\delta_{ij} \frac{\eta_{i\kappa}}{\rho_\kappa \omega_{i\kappa}} \frac{M}{i\kappa \rightarrow i\alpha} + \frac{\Phi}{j\kappa \rightarrow i\alpha} \right) \\
 & - \frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \sum_{j \in \mathcal{J}_s} \frac{\Phi^*}{j\kappa \rightarrow i\alpha} - \nabla'' \cdot (\mathbf{l}_\alpha'' \cdot \boldsymbol{\phi}_{i\alpha}) = \Lambda_{i\alpha} \\
 & \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C. \quad (2.110)
 \end{aligned}$$

The entropy balance summed over all species is

$$\mathcal{S}_\alpha = \frac{\partial'' \eta_\alpha}{\partial t} + \nabla'' \cdot (\eta_\alpha \mathbf{v}_\alpha) - b_\alpha - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \left(\frac{\eta_\kappa}{\rho_\kappa} \frac{M}{\kappa \rightarrow \alpha} + \frac{\Phi}{\kappa \rightarrow \alpha} \right)$$

$$-\frac{1}{2} \sum_{\beta \in \mathcal{J}_{c\alpha}^+} \sum_{\kappa \in \mathcal{J}_{c\beta}^+} \Phi^*_{\kappa \rightarrow \alpha} - \nabla'' \cdot (\mathbf{l}''_{\alpha} \cdot \boldsymbol{\varphi}_{\alpha}) = \Lambda_{\alpha} \quad \text{for } \alpha \in \mathcal{J}_C. \quad (2.111)$$

Finally, the expression for the derivative of the body force potential on a curve that appears in Table 2.5 may be inferred from Table 2.3 for an interface or derived in a manner similar to that used to obtain the entry in that table. The resulting equation is

$$\begin{aligned} \mathcal{G}_{*i\alpha} &= \frac{D_{i\alpha} \Psi_{i\alpha}}{Dt} + \Psi_{i\alpha} \mathbf{l}''_{\alpha} \cdot \mathbf{d}''_{i\alpha} + \rho_{\alpha} \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{v}_{i\alpha} - \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \frac{M}{i\kappa \rightarrow i\alpha} \Psi_{i\alpha} \\ &\quad - \rho_{\alpha} \omega_{i\alpha} \frac{\partial'' \Psi_{i\alpha}}{\partial t} - \rho_{\alpha} \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot (\mathbf{l} - \mathbf{l}''_{\alpha}) \cdot \mathbf{v}_{i\alpha} - r_{i\alpha} \Psi_{i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C. \end{aligned} \quad (2.112)$$

For the common curve entity, the expression for $\mathcal{G}_{*\alpha}$ is obtained as

$$\begin{aligned} \mathcal{G}_{*\alpha} &= \frac{D_{\alpha} \Psi_{\alpha}}{Dt} + \Psi_{\alpha} \mathbf{l}''_{\alpha} \cdot \mathbf{d}''_{\alpha} + \nabla'' \cdot \left(\sum_{i \in \mathcal{J}_s} \rho_{\alpha} \omega_{i\alpha} \Psi_{i\alpha} \mathbf{l}''_{\alpha} \cdot \mathbf{u}_{i\alpha} \right) \\ &\quad + \rho_{\alpha} \mathbf{g}_{\alpha} \cdot \mathbf{v}_{\alpha} + \sum_{i \in \mathcal{J}_s} \rho_{\alpha} \omega_{i\alpha} \mathbf{g}_{i\alpha} \cdot \mathbf{l}''_{\alpha} \cdot \mathbf{u}_{i\alpha} - \sum_{i \in \mathcal{J}_s} \sum_{\kappa \in \mathcal{J}_{c\alpha}^+} \frac{M}{i\kappa \rightarrow i\alpha} \Psi_{i\alpha} \\ &\quad - \sum_{i \in \mathcal{J}_s} \rho_{\alpha} \omega_{i\alpha} \frac{\partial'' \Psi_{i\alpha}}{\partial t} - \sum_{i \in \mathcal{J}_s} \rho_{\alpha} \mathbf{g}_{\alpha} \cdot (\mathbf{l} - \mathbf{l}''_{\alpha}) \cdot \mathbf{v}_{\alpha} \\ &\quad - \sum_{i \in \mathcal{J}_s} r_{i\alpha} \Psi_{i\alpha} = 0 \quad \text{for } i \in \mathcal{J}_s, \alpha \in \mathcal{J}_C. \end{aligned} \quad (2.113)$$

Additionally, the expressions for $\mathcal{T}_{\mathcal{G}*i\alpha}$ and $\mathcal{T}_{\mathcal{G}*}\alpha$ for the common curve are the same in appearance as the corresponding expressions for phases and interfaces, Eqs. (2.45) and (2.48), respectively. When applied to a common curve, the densities that appear in these expressions are mass per common curve length.

2.6 General Multispecies Formulation for a Common Point

Common points are the fourth type of entity of interest in the development of conservation and balance equations. Common points are the regions in a multiphase system that exist where four phases meet, which is also the confluence of four common curves. Common points are zero-dimensional objects that do not occupy any volume, area, or length in a system. The measure of the extent of a common point entity is the number of these points in the system.

The notion of conservation and balance principles for common points parallels the notion of these principles for an interface and common curve, with some notable differences. Small regions exist in a system composed of four or more phases where

material properties undergo sharp changes due to the coalescence of these phases. Such a region of transition is treated conceptually as a common point.

Common points also play a role as locations at the end of common curves where mass, momentum, energy, and entropy can be exchanged among common curves that meet. The density of common points thus affects property exchanges and is a quantity of interest. Conventional multiphase porous medium models do not explicitly consider common point properties or their evolution with time. Here, conservation and balance equations for common points will be formulated so that they will be available for use in explicitly analyzing their impact on system behavior. We note that these points typically are of higher order importance in comparison to interfaces and common curves. Although they are difficult to model, only exist in systems composed of four or more phases, and have limited impact, the formulation of a comprehensive model requires that they be included at the onset. If it is desired to exclude these entities from a model, then an explicit assumption or set of assumptions can be employed and then examined in hindsight.

2.6.1 General Microscale Point Form

The equations for conservation or balance of a common point property apply to a domain, Ω_α , where $\alpha \in \mathcal{J}_{\text{Pt}}$ and \mathcal{J}_{Pt} is the index set of the various types of common points as determined by which phases meet at the point. Thus α is in the index set of common points for which $\Omega_\alpha \subset \mathbb{R}^0$ and whose extent is equal to the number of points in the system denoted \mathbb{N}_α . Because common points are zero dimensional, they do not have boundaries. This makes them different from the other entity types. Rather common points are formed where four phases meet such that $\Omega_\alpha = \bar{\Omega}_\beta \cap \bar{\Omega}_\gamma \cap \bar{\Omega}_\delta \cap \bar{\Omega}_\varepsilon$ where β, γ, δ , and $\varepsilon \in \mathcal{J}_p$.⁸

The easiest way to obtain the form of the microscale point conservation equation is by inference based on the form of Eq. (2.13) for a phase, Eq. (2.67) for an interface, and Eq. (2.100) for a common curve. We note a progression of increase in the primes in the equation as the dimensionality decreases such that the general species-based microscale equation for a common point is inferred to be

$$\frac{\partial''' F_{i\alpha}}{\partial t} + \nabla''' \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega T i \alpha} - \text{div}''' (\mathbf{S}_{\Gamma i \alpha} \cdot \mathbf{l}''') - G_{\Omega i \alpha} = 0$$

for $i \in \mathcal{J}_s, \alpha \in \mathcal{J}_{\text{Pt}}$. (2.114)

In this equation, the partial time derivative with three primes is an evaluation while holding none of the three spatial coordinates fixed. In other words, it is a time derivative evaluated moving with the common point. Note that a common point moves at

⁸ A common point is also the confluence of four common curves. When the common curves exist at the locations where three phases come together and the indexes of the four phases are β, γ, δ and ε , the indexes of the common curves can be denoted as $\beta\gamma\delta, \beta\gamma\varepsilon, \beta\delta\varepsilon$, and $\gamma\delta\varepsilon$. The domain of the common point can alternatively be indicated as $\Omega_\alpha = \bar{\Omega}_{\beta\gamma\delta} \cap \bar{\Omega}_{\beta\gamma\varepsilon} \cap \bar{\Omega}_{\beta\delta\varepsilon} \cap \bar{\Omega}_{\gamma\delta\varepsilon}$.

the same velocity as the material in the point and all species in the point. Therefore

$$\frac{\partial'''}{\partial t} = \frac{d}{dt} = \frac{D_{i\alpha}}{Dt} = \frac{D_\alpha}{Dt}. \quad (2.115)$$

In addition, ∇''' and div''' indicate divergence operators with all coordinates held constant. Therefore, the terms involving these operators are zero. From a physical perspective, a property constrained to exist only at a point cannot vary in space. Therefore, Eq. (2.114) reduces to

$$\frac{\partial''' F_{i\alpha}}{\partial t} - S_{\Omega T i \alpha} - G_{\Omega i \alpha} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_{\text{Pt}}. \quad (2.116)$$

Specific forms for this equation can be developed by inserting symbols from Table 2.3 or Table 2.4. However, the meanings of the symbols are such that the items chosen for $F_{i\alpha}$ have units of quantity per point while $S_{\Omega i \alpha}$ and $G_{\Omega i \alpha}$ have units of the quantity per point per time. When the common point has no properties, the surviving terms provide a jump condition for common curve properties at the point such that what leaves one curve must enter the other curves.

As an example, the microscale conservation equation for a chemical species at a common point is obtained, based on Eqs. (2.115) and (2.116) and Table 2.3 as

$$\mathcal{M}_{*i\alpha} = \frac{D_{i\alpha}(\rho_\alpha \omega_{i\alpha})}{Dt} - \sum_{\kappa \in \mathcal{I}_{c\alpha}^+} M_{i\kappa \rightarrow i\alpha} - r_{i\alpha} = 0 \quad \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}_{\text{Pt}}, \quad (2.117)$$

where $\rho_\alpha \omega_{i\alpha}$ is the mass of species i at common point α . In this equation, we have not allowed for concentrated direct mass exchange between the common point and phases or interfaces. The values that κ takes on are the index values of the four common curves that terminate at the common point. Thus the summation term is the net flux of species i from the common curves to the common point. This sum will be zero if the mass of i at the common point does not change with time and there is no net reaction or set of reactions $r_{i\alpha}$ that produce species i .

For the momentum equation, the form taken is slightly more complex if one includes the concentrated non-advective fluxes in the equation. A common point can interact with a phase directly if the point lies on the boundary of a phase at a location where the normal to the boundary is unique. Additionally, if the point lies at the edge of an interface where the normal to the edge of the interface that is also tangent to the interface is unique a term needs to be included that accounts for the interaction with the interface. The entity-based general form of the body source term is

$$S_{\Omega T \alpha} = S_{\Omega \alpha} + \sum_{\kappa \in \mathcal{I}_{c\alpha}^+} X_{\kappa \rightarrow \alpha} + \frac{1}{2} \sum_{\beta \in \mathcal{I}_{c\alpha}^+} \sum_{\kappa \in \mathcal{I}_{c\beta}^+} X_{\kappa \rightarrow \alpha}^* + \frac{1}{6} \sum_{\chi \in \mathcal{I}_{c\alpha}^+} \sum_{\beta \in \mathcal{I}_{c\chi}^+} \sum_{\kappa \in \mathcal{I}_{c\beta}^+} X_{\kappa \rightarrow \alpha}^* \quad \text{for } \alpha \in \mathcal{I}_{\text{Pt}}, \quad (2.118)$$

where the single summation accounts for exchanges with the common curves, the double sum accounts for exchanges with interfaces, and the triple sum accounts for exchanges with phases. These latter two groups can be employed when the normal to the entity is unique at the common point. Thus, for example, the momentum equation for a common point entity is

$$\begin{aligned} \mathcal{P}_{*\alpha} = & \frac{D_\alpha(\rho_\alpha \mathbf{v}_\alpha)}{Dt} - \rho_\alpha \mathbf{g}_\alpha - \sum_{\kappa \in \mathcal{I}_{c\alpha}^+} \left(\mathbf{v}_\kappa M_{\kappa \rightarrow \alpha} + \mathbf{T}_{\kappa \rightarrow \alpha} \right) \\ & - \frac{1}{2} \sum_{\beta \in \mathcal{I}_{c\alpha}^+} \sum_{\kappa \in \mathcal{I}_{c\beta}^+} \mathbf{T}_{\kappa \rightarrow \alpha}^* - \frac{1}{6} \sum_{\chi \in \mathcal{I}_{c\alpha}^+} \sum_{\beta \in \mathcal{I}_{c\chi}^+} \sum_{\kappa \in \mathcal{I}_{c\beta}^+} \mathbf{T}_{\kappa \rightarrow \alpha}^* = \mathbf{0} \quad \text{for } \alpha \in \mathcal{I}_{pt}. \end{aligned} \quad (2.119)$$

Listing of the remaining conservation equations of mass, momentum, and energy and of the entropy balance equation for species-based and entity-based quantities is straightforward based on Eqs. (2.116) and (2.119) along with the notation for quantities given in the tables for interfaces and common curves. Note that the meanings of the quantities is altered for the common point equations. The explicit conservation statements are not listed here simply because, except for the inclusion of the concentrated flux from a phase to the common point, the equations are redundant with previous equations and listings. Additionally, we will not be exploring systems with four or more phases such that common point dynamics will not enter our analyses.

2.7 Summary

A cornerstone of mechanistic modeling is the continuum equations for conservation of mass, momentum, and energy, along with the balance equation of entropy. TCAT builds upon microscale conservation and balance equations as a foundation for formulation of larger-scale models. The purpose of this chapter was to develop the general point-form microscale conservation equations for a phase, an interface, a common curve, and a common point. These general point-form conservation equations were expressed for a species in an entity and for an overall entity that includes all species in the entity.

The general conservation and balance equations account for the different dimensionality of the entities and for the fact that higher dimensional entities serve as body sources for lower dimensional entities. The general conservation or balance equation for a species property can be written as

$$\begin{aligned} \mathcal{F}_{i\alpha} = & \frac{\partial^{(n)} F_{i\alpha}}{\partial t} + \nabla^{(n)} \cdot (\mathbf{v}_{i\alpha} F_{i\alpha}) - S_{\Omega T i\alpha} - \text{div}^{(n)} \left(\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}_\alpha^{(n)} \right) - G_{\Omega i\alpha} = 0 \\ & \text{for } i \in \mathcal{I}_s, \alpha \in \mathcal{I}, n = 3 - \dim \alpha, \end{aligned} \quad (2.120)$$

or

$$\mathcal{F}_{*i\alpha} = \frac{D_{i\alpha} F_{i\alpha}}{Dt} + F_{i\alpha} \mathbf{l}_{\alpha}^{(n)} \cdot \mathbf{d}^{(n)} - S_{\Omega T i\alpha} - \text{div}^{(n)} \left(\mathbf{S}_{\Gamma i\alpha} \cdot \mathbf{l}_{\alpha}^{(n)} \right) - G_{\Omega i\alpha} = 0$$

for $i \in \mathcal{I}_s, \alpha \in \mathcal{I}, n = 3 - \dim \alpha$, (2.121)

where $\dim \alpha$ is the integer dimensionality of entity α such that $0 \leq \dim \alpha \leq 3$, (n) indicates the number of primes that appear in the equation with the primed time derivative, divergence operator, and strain tensor previously defined. We have adopted the convention of using the leftmost quantity to indicate an equation type (e.g., $\mathcal{F} = \mathcal{M}$ for mass conservation), and a specific form in terms of a partial derivative is indicated when there is no “*” in the subscript while a particular material derivative form corresponds to a designation with the “*” in the subscript. The body source $S_{\Omega T i\alpha}$ includes contributions from the next higher dimensional entity when $\dim \alpha = 0, 1$, or 2 , from an entity two dimensions higher when $\dim \alpha = 0$ or 1 , and from a phase entity to a common point when $\dim \alpha = 0$. The conservation or balance equation for an entity-based quantity is identical to Eq. (2.120) and Eq. (2.121) with the subscript i deleted. This is obtained by summing Eq. (2.120) over all species in the entity, and then rearranging if the material derivative form is desired. One needs to recognize, however, that although the sum of the species-based conservation equation in an entity provides the entity-based equation, the sum of an individual species-based variable does not always equal the corresponding variable for the entity.

Specific conservation and balance equations for each entity are formulated by mapping the physical variables for a given conservation or balance statement to the placeholder variables in the general equations. This approach allows for the simple identification of all microscale conservation and balance equations that will be built upon in this work. Exercises at the end of this chapter provide opportunities to master the concepts important to the derivations here.

Lastly, derivation of the conservation of angular momentum equations has not been included here because the role of this equation is primarily to demonstrate whether or not a stress tensor is symmetric. In this book, which is only an introduction to the TCAT approach, we will consider the stress tensor for an entity to be symmetric but allow the stress tensor for a species in an entity to be non-symmetric [1, 2, 14].

Exercises

2.1. Show that Eq. (2.37) may be written in the equivalent form:

$$\begin{aligned} \mathbf{q}_{\alpha} = & \sum_{i \in \mathcal{I}_s} \left[\mathbf{q}_{i\alpha} + (\mathbf{t}_{i\alpha}^T - \omega_{i\alpha} \mathbf{t}_{\alpha}^T) \cdot (\mathbf{v}_{i\alpha} - \mathbf{v}_{\alpha}) \right] \\ & - \sum_{i \in \mathcal{I}_s} \left[(E_{i\alpha} - \omega_{i\alpha} E_{\alpha}) + \rho_{\alpha} \omega_{i\alpha} \frac{(\mathbf{v}_{i\alpha} - \mathbf{v}_{\alpha}) \cdot (\mathbf{v}_{i\alpha} - \mathbf{v}_{\alpha})}{2} \right] (\mathbf{v}_{i\alpha} - \mathbf{v}_{\alpha}) . \end{aligned}$$

(2.122)

This form, though a bit lengthier, shows that the difference between \mathbf{q}_α and the sum over all species of $\mathbf{q}_{i\alpha}$ is a set of terms that are all products of deviations.

2.2. Show that Eq. (2.33) may equivalently be written

$$\sum_{i \in \mathcal{J}_s} \left(e_{i\alpha} + \mathbf{p}_{i\alpha} \cdot \mathbf{u}_{i\alpha} + r_{i\alpha} \frac{\mathbf{u}_{i\alpha} \cdot \mathbf{u}_{i\alpha}}{2} \right) = 0.$$

2.3. Show that the following definitions of a material derivative are equivalent:

$$\frac{D_\alpha}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}_\alpha \cdot \nabla = \frac{\partial'}{\partial t} + \mathbf{v}_\alpha \cdot \nabla' = \frac{\partial''}{\partial t} + \mathbf{v}_\alpha \cdot \nabla'' . \quad (2.123)$$

2.4. Show that in the summation of Eq. (2.73) over $i \in \mathcal{J}_s$ to obtain Eq. (2.74), one obtains

$$\begin{aligned} & \sum_{i \in \mathcal{J}_s} \sum_{j \in \mathcal{J}_s} \mathbf{n}_\kappa \cdot \left[\delta_{ij} \rho_\kappa \omega_{i\kappa} \mathbf{v}_{i\kappa} (\mathbf{v}_{i\kappa} - \mathbf{v}_\alpha) - \sum_{j\kappa \rightarrow i\alpha} z_T \mathbf{t}_{j\kappa}^T \right] \\ &= \mathbf{n}_\kappa \cdot [\rho_\kappa \mathbf{v}_\kappa (\mathbf{v}_\kappa - \mathbf{v}_\alpha) - \mathbf{t}_\kappa] \quad \text{for } \alpha \in \mathcal{J}, \kappa \in \mathcal{J}_{c\alpha}^+, \end{aligned} \quad (2.124)$$

where \mathbf{t}_κ is defined as in Eq. (2.30) and \mathbf{v}_κ is the barycentric velocity.

2.5. Show the following:

- a.** Equation (2.79) can be obtained as the sum of Eq. (2.78) over all species i in interface entity α .
- b.** The definitions of \mathbf{t}_α where $\alpha \in \mathcal{J}_I$ and \mathbf{t}_κ where $\kappa \in \mathcal{J}_{c\alpha}$ used in Eq. (2.79) satisfy Eq. (2.30).
- c.** The definitions of \mathbf{q}_α where $\alpha \in \mathcal{J}_I$ and \mathbf{q}_κ where $\kappa \in \mathcal{J}_{c\alpha}$ used in Eq. (2.79) satisfy Eq. (2.37).

2.6. Equation (2.30) defines the surface stress tensor in terms of species stress tensor. Show that for a surface, this equation also satisfies

$$\mathbf{t}_\alpha \cdot \mathbf{l}'_\alpha = \sum_{i \in \mathcal{J}_s} [\mathbf{t}_{i\alpha} \cdot \mathbf{l}'_\alpha - \rho_\alpha \omega_{i\alpha} \mathbf{l}'_\alpha \cdot (\mathbf{v}_{i\alpha} - \mathbf{v}_\alpha) (\mathbf{v}_{i\alpha} - \mathbf{v}_\alpha) \cdot \mathbf{l}'_\alpha] \quad \text{for } \alpha \in \mathcal{J}_I.$$

2.7. Prove Eq. (2.96) which states

$$\text{div}'' \mathbf{f} + \mathbf{f} \cdot (\nabla'' \cdot \mathbf{l}''_\alpha) = \text{div}'' (\mathbf{f} \cdot \mathbf{l}''_\alpha) \quad \text{for } \alpha \in \mathcal{J}_C.$$

2.8. Show that for an α entity composed of two chemical species, designated as A and B , the general form of $K_{E\alpha}$ given in Eq. (2.35) may be simplified to

$$K_{E\alpha} = \omega_{A\alpha} \omega_{B\alpha} \frac{(\mathbf{v}_{A\alpha} - \mathbf{v}_{B\alpha}) \cdot (\mathbf{v}_{A\alpha} - \mathbf{v}_{B\alpha})}{2}.$$

2.9. Write the explicit form of the momentum equation for a massless common point and provide a physical explanation for the terms in this equation.

2.10. The body force potential for a species, $\psi_{i\alpha}$, and the body force per mass of the species, $\mathbf{g}_{i\alpha}$, are related for all entities as given by Eq. (2.50) for a phase such that

$$\nabla \psi_{i\alpha} + \mathbf{g}_{i\alpha} = 0 \quad \text{for } i \in \mathcal{I}.$$

a. Show that for a phase the entity-based identity is

$$\nabla \psi_{\alpha} + \mathbf{g}_{\alpha} = \sum_{i \in \mathcal{I}_s} \nabla \omega_{i\alpha} (\psi_{i\alpha} - \psi_{N\alpha}) \quad \text{for } \alpha \in \mathcal{I}_p,$$

where $N \in \mathcal{I}_s$ is a reference species and ψ_{α} is defined for any entity as in Eq. (2.46).

b. Obtain the corresponding relation between $\nabla' \psi_{\alpha}$ and \mathbf{g}_{α} when $\alpha \in \mathcal{I}_l$.

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