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Macroscale continuum mechanics for multiphase porous-media flow including phases, interfaces, common lines and common points

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This paper provides the tools needed for analysis of multiphase flow in porous media. Contributions are in four areas. First, theorems are provided that allow global scale integral equations to be localized at the porous medium scale. This is a more general approach than the traditional averaging of microscale point equations. Second, conservation equations for mass, momentum, energy and entropy for phases, interfaces, common lines, and common points are obtained. The inclusion of common lines and common points completes the full description of multiphase flow in porous media. Third, the entropy inequality is developed for the full multiphase system. The interaction terms between phases, interfaces, common lines, and common points provide a clear direction as to whether the entropy equation for each of these components may be used in the development of a constitutive theory or if the constitutive theory will depend on a combined entropy inequality statement. Fourth, the simplification of the system of equations is presented for the case of massless interfaces and common lines where these constituents are still capable of sustaining stress and containing energy. These latter forms are particularly useful in consideration of capillary pressure terms when the mass of the interface may be considered negligible.

Key words: multiphase flow, porous media, averaging theory.

1 INTRODUCTION

During the past few decades significant progress has been made in developing general theories describing thermodynamic processes in general multiphase systems and in porous media. The primary aim of these derivations has been to obtain equations valid at a useful length scale of observation. Commonly, this scale is much larger than the scale of the minute structure and detailed occupation of space within the multiphase system. Two different approaches have been most often employed in these studies: mixture theories of continuum mechanics and averaging methods. The basic premises of these approaches have been to employ systematic procedures while retaining rigor such that arbitrariness and empiricism are avoided in the developments. Moreover, it has been the goal of these theories to avoid unwarranted simplifications and to include major features of the often complex multiphase systems. Thus, for example, multiphase theories have been developed that account for the presence of interfacial regions separating various phases at the microscale.

Early theories, however, considered these interfaces to be singular surfaces devoid of thermodynamic quantities. In these older approaches, the interfaces were simply modeled as surfaces of discontinuity in phase properties unable to affect thermodynamic processes on their own (e.g. in Refs 2, 3, 8, 15, 16, 27). Subsequent theories have assigned thermodynamic properties to the interfaces and thus include the effects of interfaces on the medium behavior at the macroscale (e.g. 9, 17, 20). These newer theories have been employed to derive basic equations describing two-phase flow processes and flow in unsaturated media[10,11,18,19] and flow in clayey materials.[1] The results of these studies have shown that inclusion of interfacial properties is essential if gross errors in the description of some multiphase systems are to be avoided. Based on these advances, it has become evident that all features of a multiphase system that may affect the thermodynamic behavior of the system must be accounted for.

One feature of multiphase systems that cannot necessarily be dismissed as unimportant is the common lines that exist in a system consisting of three or more phases. Common lines are regions of transition among three neighboring phases. It is well known that the properties of common lines influence the movement of neighboring menisci and phases.[21,24] However, in the theories presented to this point, common lines have been assumed to be devoid of thermodynamic properties. They are modeled as singular lines at which interfacial properties undergo jump discontinuities. Thus, equations of balance for these common lines are simply jump conditions for interfacial properties.[9,20] In the present work, common lines are modeled as one-dimensional regions with their own thermodynamic properties, such as mass, velocity, energy and entropy. Macroscale equations of balance for a multiphase system are developed and the effects of thermodynamic properties of common lines, as well as phase interfaces, are accounted for. In a three-phase system, such as a porous medium saturated with two fluids, only one common line type may exist. In a four-phase system, four different common line types may exist; and these lines may come together at a common point. Thus, a common point is a singular point where properties of common lines undergo jump discontinuities. To account for this type of discontinuity, jump conditions for common line properties must be provided that ensure the balance of conservative entities at a common point. In principle, it is possible to assume that matter and energy may accumulate at a common point. But that possibility is not explored here. However, the methodology employed can be easily extended to handle those cases.

Cases of practical interest exist where the amount of excess mass associated with an interface or a common line is negligible compared to the mass storage and transport within the phases. In these cases, the interface or common lines may be treated as massless. However, such an interface or common line may still sustain surface or line forces, and associated surface or line energy, with considerable influence on the dynamics of the system. In the present work, the treatment of massless interfaces and common lines is introduced; and appropriate balance laws are developed. These equations have potential utility in the description of a broad class of multiphase systems.

Another important feature of the approach employed here is a novel way of deriving equations of balance at the macroscale in the framework of averaging methods. The derivation of equations used in the description of porous media flow and transport has been, in some sense, disconnected from the derivation for flow of a simple continuum fluid, as explained subsequently. In the current presentation, a unity in the theoretical development is achieved.

The standard way to develop governing equations for a single-phase continuum is to pose the integral balance laws at a global scale for the system as a whole, apply the transport and divergence theorems, and then localize the integrands of the resulting expressions. The resulting differential equations are also called 'point' balance equations. Implicit in this derivation is the fact that quantities appearing in the integrands are written for a particular small scale, referred to here as the microscale, and that the localized point equations are also equations at the microscale. The microscale quantities are actually the average of molecular properties over a representative elementary volume containing a large number of molecules. Therefore, in reality, a finite volume is associated with each microscale point. Thus, for a single-phase continuum two length scales may be readily defined: a microscale on the order of the representative volume and a global scale. Similar scales may be defined for a multiphase medium. However, the microscale is too small and too detailed to be useful for the description of multiphase systems. For such systems, a length scale intermediate between the microscale and the global scale needs to be defined. This scale is commonly referred to as the macroscale. Let the characteristic lengths associated with microscale, macroscale, and global scale be denoted by d, l and L, respectively. Then the following restriction must be satisfied for a physically meaningful description of a multiphase system[15]

$$L \gg l \gg d \tag{1}$$

Balance equations for a multiphase system have to be developed at the macroscale. One approach, employed in the continuum theories of mixtures, is to assume the existence of macroscale field properties. Global balance equations are then written in terms of macroscale properties such that the integrands are macroscale quantities. These global equations can then be localized to obtain macroscale point equations. This approach has two drawbacks. One is that there is no connection between a macroscale property and pore properties. The second is that the extension to multiphase systems with interfacial and common line properties is not straightforward.

A second approach, commonly employed in the development of porous media theories, is to assume that the microscale point equations are valid for the single-phase continuum filling the interstitial spaces. Macroscale porous medium equations can be obtained by application of some integral theorems to the microscale point equations integrated over a volume with length scale l. The result of this manipulation is another set of point equations where the point is observed at a larger scale than in the microscopic perspective. This procedure thus scales down the global balance equations to microscale point equations, which are subsequently scaled up to macroscale point equations.

In the present work, a third, more appealing, approach is proposed and implemented. In this approach, which is physically more consistent, the derivation of porous media equations simply involves a direct scale-down of global balance equations to the macroscale. To begin this approach, global integral balance equations for each phase are written in terms of microscale properties of that phase such that the integrands are microscale quantities. Then macroscale point equations are obtained directly through the application of appropriate mathematical theorems. Similar procedures can also be applied to the derivation of macroscale balance laws for interfaces between material phases and balance laws for properties of common lines where three phases come together.

Here, the first and second upscaling alternatives are discussed briefly before providing the necessary framework for development and application of the third alternative. Subsequently, balance equations for mass, momentum, energy, and entropy for phases, interfaces, common lines, and common points are derived. Simplifications appropriate for massless interfaces and common lines are also presented.

Finally in this work, the second law of thermodynamics for individual components of a multiphase system will be discussed. Appropriate forms for the development of constitutive equations will be obtained.

2 PHASE EQUATIONS

2.1 Standard derivation for a single phase fluid

Consider a single phase continuum occupying a non-material global volume V at a given instant t. The boundary of V, denoted by S, may have a velocity $\boldsymbol{w}_{\mathrm{b}}$. Consider a phase property ψ defined per unit mass of the phase at the microscale. The general conservation equation for the single fluid phase property, ψ may be stated as[6]

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\psi\,\mathrm{d}V + \int_S \boldsymbol{n}^* \cdot [\rho(\boldsymbol{v} - \boldsymbol{w}_{\mathrm{b}})\psi - \boldsymbol{i}]\,\mathrm{d}S - \int_V \rho f\,\mathrm{d}V = \int_V G\,\mathrm{d}V \tag{2}$$

where ρ is the fluid density, $\boldsymbol{v}$ is the fluid velocity, $\boldsymbol{i}$ is the diffusive flux of ψ across the boundary, $\boldsymbol{n}^*$ is the unit vector normal to S and pointing outward from V, f is the external supply of ψ, and G is the term accounting for production of ψ within the volume. This equation is a mathematical statement of the physical principle that the rate of change of some property in a volume is equal to the net flux of that property across the boundary of the volume plus the external supply plus production of the property. All properties are considered to be the average of molecular properties over a representative element of volume containing a large number of molecules and having a characteristic size of d, the usual continuum scale used in fluid mechanical derivations. Here, the length scale of the volume is designated as L. The length scale constraint specified in eqn (1) is considered to be satisfied.

To transform the global balance eqn (2) to a point form, where the point is actually of length scale d, two mathematical theorems are typically applied to the integrals in this equation, the transport theorem and the divergence theorem. These two theorems are classical relations and are available in virtually all undergraduate mathematical and fluid mechanics text books. A novel procedure for derivation of these and other theorems used subsequently here is found in Gray *et al.*[13] Their notation has been modified for the present exposition, and their shorthand name for each theorem is presented along with the standard name. The transport theorem, written for some function F and the global volume V, is as follows.

Transport theorem $T[3,(0,0),3]$

$$\int_V \frac{\partial F}{\partial t}\,\mathrm{d}V = \frac{\mathrm{d}}{\mathrm{d}t}\int_V F\,\mathrm{d}V - \int_S \boldsymbol{n}^* \cdot \boldsymbol{w}_{\mathrm{b}} F\,\mathrm{d}S \tag{3}$$

The divergence theorem for a vector function $\boldsymbol{B}$ is as follows.

Divergence theorem $D[3,(0,0),3]$

$$\int_V \nabla \cdot \boldsymbol{B}\,\mathrm{d}V = \int_S \boldsymbol{n}^* \cdot \boldsymbol{B}\,\mathrm{d}S \tag{4}$$

Application of these theorems to eqn (2) brings the time derivative inside the integral and converts the surface integrals to volume integrals. The equation obtained is equivalent to eqn (2) but less intuitive

$$\int_V \left[\frac{\partial(\rho\psi)}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}\psi) - \nabla \cdot \boldsymbol{i} - \rho f\right]\mathrm{d}V = \int_V G\,\mathrm{d}V \tag{5}$$

Because the size of the volume is arbitrary, as long as eqn (1) is satisfied, the integrands themselves in eqn (5) must be equal so that the point equation is obtained as follows.[6]

Point microscale balance equation

$$\frac{\partial(\rho\psi)}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}\psi) - \nabla \cdot \boldsymbol{i} - \rho f = G \tag{6}$$

This point equation makes use of quantities at scale d; the same scale as in the integrand of eqn (2).

2.2 Continuum mixture theories for multiphase flow

Mixture theories provide one approach for deriving macroscopic balance laws for a multiphase system. In these theories, the multiphase system is envisaged as a superposition in space of a number of single-phase continua. No microscale presentation of the system is provided and microscale quantities are not defined. Phase properties are introduced at a larger scale. At every point all phases are considered to be present. Thus, a 'point' consists of a mixture of phases. For this approach, a global balance analogous to eqn (2) may be written with the integrand properties observed at a larger scale, l. For this case, the general conservation equation for a property of the α-phase may be written[7]

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho^\alpha \epsilon^\alpha \psi^\alpha \,\mathrm{d}V + \int_S \boldsymbol{n}^* \cdot [\rho^\alpha \epsilon^\alpha (\boldsymbol{v}^\alpha - \boldsymbol{w}_\mathrm{b})\psi^\alpha - \epsilon^\alpha \boldsymbol{i}^\alpha]\,\mathrm{d}S - \int_V \rho^\alpha \epsilon^\alpha f^\alpha \,\mathrm{d}V = \int_V \epsilon^\alpha G^\alpha \,\mathrm{d}V \quad (7)$$

The main differences between this equation and eqn (2) are the use of the superscript α to designate that the property being considered is associated with the α-phase at the macroscopic point and the introduction of the quantity ϵ^α, the volume fraction of the macroscopic point that is occupied by the α-phase. As should be expected, for the special case of single phase flow of the α-phase such that $\epsilon^\alpha = 1$, eqns (2) and (7) are identical in appearance. Note, however, that eqn (7) is written with integrand quantities at a larger scale, l, than the integrand quantities in eqn (2), at scale d. As long as both constraints in eqn (1) are satisfied, the balance laws both apply. Nevertheless, the integrand quantities in eqn (7) may require a different interpretation and may represent different physical quantities from those in eqn (2). For example, the production term G in eqn (2) will be zero for equations of mass, momentum, and energy conservation; whereas G^α in eqn (7) may be non-zero for these balance laws to account for the interaction among phases present at a given 'point'.

Transformation of eqn (7) to a differential form is analogous to the transformation for a single-phase continuum. Transport theorem (3) and divergence theorem (4) must be applied. Use of these mathematical relations again brings the time derivative inside the integral and converts the boundary integral to a volume integral so that the balance equation becomes

$$\int_V \left[\frac{\partial(\rho^\alpha \epsilon^\alpha \psi^\alpha)}{\partial t} + \nabla\cdot(\rho^\alpha \epsilon^\alpha \boldsymbol{v}^\alpha \psi^\alpha) - \nabla\cdot(\epsilon^\alpha \boldsymbol{i}^\alpha) - \rho^\alpha \epsilon^\alpha f^\alpha\right]\mathrm{d}V = \int_V \epsilon^\alpha G^\alpha \,\mathrm{d}V \quad (8)$$

In this equation, the size of the integration volume is arbitrary. As long as the length scale of this volume satisfies eqn (1), the integrands themselves in eqn (8) must be equal so that the point equation is obtained as follows.

Point macroscale balance equation

$$\frac{\partial(\rho^\alpha \epsilon^\alpha \psi^\alpha)}{\partial t} + \nabla\cdot(\rho^\alpha \epsilon^\alpha \boldsymbol{v}^\alpha \psi^\alpha) - \nabla\cdot(\epsilon^\alpha \boldsymbol{i}^\alpha) - \rho^\alpha \epsilon^\alpha f^\alpha = \epsilon^\alpha G^\alpha \quad (9)$$

This point equation makes use of quantities at the same scale, l, as in the integrand of eqn (7).

This approach may be applied to interfaces and common lines if appropriate macroscale properties can be identified. However, this is a difficult task and may lead to inconsistencies in the development. For example, some continuum mixture theories do not take the existence of interfaces into account; yet the fluid phases are considered to be immiscible.[4,25]

Another difficulty with this approach is that, because eqn (9) is written at a length scale $l > d$, it does not describe the conservation balance in as much small-scale detail as eqn (6). In fact, eqn (9) is, in some sense, an average representation of eqn (6) and the quantities that appear in the two equations must be somehow related. However, the precise correspondence between the terms and quantities in the two equations is not obvious; and it is not clear, for example, how to obtain the larger scale value of ρ^α for a macroscale point from the microscale values of density of the α-phase in the vicinity of that point. Correspondence between macroscale and microscale quantities may be accomplished through use of averaging theorems as described in the next section.

2.3 Averaging of microscale equations

An alternative method for developing continuum equations at the appropriate scale is to average microscale equations. Consider a porous medium consisting of a solid phase and a number of fluid phases. The phases are supposed to be immiscible and to have distinct thermodynamic properties. The phases are separated by very thin transition regions which are modeled as two-dimensional interfacial surfaces. Each interface has its own thermodynamic properties distinct from those of phases and other interface types. When a system consists of three or more phases, common lines may also exist. These are regions of transition where three interfaces come together. Common lines are one-dimensional regions with thermodynamic properties of their own. The space is occupied by phases, interfaces, and common lines which exist in mutually exclusive domains. This conceptualization of a multiphase system is referred to as the microscopic picture.

In principle, the conservation eqn (6) is applicable at each and every point within any particular phase. Other conservation equations are needed for interfaces and common lines to describe thermodynamic processes at the microscopic scale. However, microscopic details in a complex system are often not needed and are almost impossible to model. Therefore, the microscopic picture needs to be replaced with an averaged description of processes. Commonly, averaged, or macroscale, properties are defined through the integral of microscale properties over a Representative Elementary Volume (REV). The concepts behind the REV and its properties are discussed by many authors.[3,5,15] Of particular importance are the features that the size and shape of the REV do not vary with space or time. Also its length scale, l, must be much greater than the pore scale, d, but much less than the scale, L, of the full system under study as prescribed by restriction (1). If the REV is designated as δV, the portion of this volume that is occupied by the α-phase is indicated as δV^{α}. The union of interfacial regions within the REV between the α-phase and the β-phase is designated as $S_{\alpha\beta}$ and the unit vector normal to this surface oriented outward from the α-phase is designated as $\boldsymbol{n}^{\alpha}$. Within this framework, governing equations can be developed by averaging microscopic balance laws, such as eqn (6), over the REV.

To average eqn (6), two theorems are commonly employed that transform the average of a derivative to the derivative of an average. The first of these theorems is applied to a time derivative and may be stated as follows.

Time averaging theorem $T[3,(3,0),0]$

$$\int_{\delta V^{\alpha}} \frac{\partial F}{\partial t}\,\mathrm{d}V = \frac{\partial}{\partial t}\int_{\delta V^{\alpha}} F\,\mathrm{d}V - \sum_{\beta\neq\alpha}\int_{S_{\alpha\beta}} \boldsymbol{n}^{\alpha}\cdot\boldsymbol{w}_{\mathrm{b}}F|_{\alpha}\,\mathrm{d}S \tag{10}$$

The second theorem is applied to the divergence operator and is given as follows.

Divergence averaging theorem $D[3,(3,0),0]$

$$\int_{\delta V^{\alpha}} \nabla\cdot\boldsymbol{B}\,\mathrm{d}V = \nabla\cdot\int_{\delta V^{\alpha}} \boldsymbol{B}\,\mathrm{d}V + \sum_{\beta\neq\alpha}\int_{S_{\alpha\beta}} \boldsymbol{n}^{\alpha}\cdot\boldsymbol{B}|_{\alpha}\,\mathrm{d}S \tag{11}$$

where $F|_{\alpha}$ and $\boldsymbol{B}|_{\alpha}$ indicate that the quantities F and $\boldsymbol{B}$ are microscale properties of the α-phase (i.e. properties defined using length scale d) that are being integrated over the $\alpha\beta$-interface, and $\sum_{\beta\neq\alpha}$ denotes a summation over all phases except the α-phase.

Integration of eqn (6) over δV^{α} and application of eqns (10) and (11) to the appropriate derivatives yields

$$\begin{aligned}\frac{\partial}{\partial t}\int_{\delta V^{\alpha}} \rho\psi\,\mathrm{d}V &+ \nabla\cdot\int_{\delta V^{\alpha}}[\rho\boldsymbol{v}\psi - \boldsymbol{i}]\,\mathrm{d}V \\ &+ \sum_{\beta\neq\alpha}\int_{S_{\alpha\beta}} \boldsymbol{n}^{\alpha}\cdot[\rho(\boldsymbol{v}-\boldsymbol{w})\psi - \boldsymbol{i}]|_{\alpha}\,\mathrm{d}S \\ &- \int_{\delta V^{\alpha}} \rho f\,\mathrm{d}V = \int_{\delta V^{\alpha}} G\,\mathrm{d}V\end{aligned} \tag{12}$$

This equation may be written in terms of average quantities after dividing by δV. However, this will not be done at this point. Rather, eqn (12) will be re-derived in Section 2.4 from a different starting point, and the equation derived there, eqn (16), will then be manipulated to obtain an expression in terms of average quantities.

Gray and Hassanizadeh[9] have provided averaging theorems for interface balance equations as well as for phases. Marle[20] has also developed an approach for obtaining averaged equations for phases and interfaces. However, rather than integrating over an REV, he obtains average quantities by convolution with a weight function. Averaged equations for common lines that have thermodynamic properties have not appeared, although averaging theorems that facilitate the change in scale for common line balance laws can be found in Gray *et al.*[13]

The disadvantage of the averaging approach used to develop eqn (12) is that the starting point is the microscale differential equations such as eqn (6) instead of the global integral equations that are more fundamental relations. Thus, if a microscale quantity, such as the stress tensor, is non-local, then the global equation involving this quantity may not be localized to the microscale. However, it may still be localized to the REV scale, provided that the non-local scale is less than the REV scale. An averaging approach that requires a microscale differential equation as a starting point would not be usable in this instance. In the next section, an alternative is presented that is devoid of this drawback.

2.4 Derivation of macroscale equations from global balance laws

The starting point for this approach is the microscale conceptualization of a multiphase system as described in the first paragraph of Section 2.3. To begin this derivation, a 'global' balance equation will be written for a volume of α-phase δV^{α} that is a portion of a multiphase spherical volume, δV. In turn, δV is a small portion of a much larger volume of the multiphase system. The length scale of the large system is L, and the length scale of δV and δV^{α} is l with $L \gg l$. The quantities in the integrand are at length scale d with $d \ll l$. For convenience, the boundary of δV^{α} will be divided into two parts, δS^{α}, which accounts for portions of the surface that intersect the α-phase and is coincident with the boundary of δV, and $S_{\alpha\beta}$ which is the portion of the boundary that is an interface between the α-phase and all other phases. The volume δV is fixed in space and non-deforming such that the normal velocity of the boundary δS^{α} is zero. However, due to the phase change and deformation, the $S_{\alpha\beta}$ boundary between phases inside δV may have a normal component of velocity. With this notation, eqn (2) takes the form

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}t}\int_{\delta V^{\alpha}} \rho\psi\,\mathrm{d}V &+ \int_{\delta S^{\alpha}} \boldsymbol{n}^{*}\cdot[\rho\boldsymbol{v}\psi - \boldsymbol{i}]\,\mathrm{d}S \\ &+ \sum_{\beta\neq\alpha}\int_{S_{\alpha\beta}} \boldsymbol{n}^{\alpha}\cdot[\rho(\boldsymbol{v}-\boldsymbol{w}_{\mathrm{b}})\psi - \boldsymbol{i}]|_{\alpha}\,\mathrm{d}S \\ &- \int_{\delta V^{\alpha}} \rho f\,\mathrm{d}V = \int_{\delta V^{\alpha}} G\,\mathrm{d}V\end{aligned} \tag{13}$$

where the unit normal vector $\boldsymbol{n}^\alpha$ is directed outward from the α-phase on the phase interface.

Since the external boundaries of δV are fixed, a correspondence may be made between the total time derivative in eqn (13) and the partial time derivative that applies when considering an averaged equation at a point. This correspondence is obtained by combining equations $T[3,(0,0),3]$, the transport theorem, and $T[3,(3,0),0]$, the averaging theorem for a partial time derivative in space, as found in Gray *et al.*,[12] to obtain the following relation.

Transport theorem for use with macroscale phase equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{\delta V^\alpha} F\,\mathrm{d}V = \frac{\partial}{\partial t}\int_{\delta V^\alpha} F\,\mathrm{d}V \tag{14}$$

It should be understood that this conversion requires that the volume δV^α under consideration be the volume of the α-phase within a particular δV located at a particular point in space. Although δV^α may change with time and may assume different shapes within different δVs located at different positions, each δV is fixed in space; and the shape of δV is independent of position.

The integral over δS^α in eqn (13) may be converted to a divergence of an integral using the relation[12,23,26] that may be obtained by comparing alternative forms[13] of the averaging theorems $D[3,(3,0),0]$ and $D[3,(0,3),0]$. This theorem makes use of the fact that sampling of the global system may be accomplished using the volume δV at any point in space. Thus, the divergence of the integral that appears in the following equation is a divergence of summed values associated with each point in space.

Divergence theorem for use with macroscale phase equations

$$\int_{\delta S^\alpha} \boldsymbol{n}^* \cdot \boldsymbol{B}\,\mathrm{d}S = \nabla \cdot \int_{\delta V^\alpha} \boldsymbol{B}\,\mathrm{d}V \tag{15}$$

Application of eqns (14) and (15) to eqn (13) produces a macroscale point balance equation written in terms of microscale quantities that is identical to eqn (12)

$$\frac{\partial}{\partial t}\int_{\delta V^\alpha} \rho\psi\,\mathrm{d}V + \nabla \cdot \int_{\delta V^\alpha} [\rho \boldsymbol{v}\psi - \boldsymbol{i}]\,\mathrm{d}V + \sum_{\beta\neq\alpha}\int_{S_{\alpha\beta}} \boldsymbol{n}^\alpha \cdot [\rho(\boldsymbol{v}-\boldsymbol{w})\psi - \boldsymbol{i}]\big|_\alpha\,\mathrm{d}S - \int_{\delta V^\alpha} \rho f\,\mathrm{d}V = \int_{\delta V^\alpha} G\,\mathrm{d}V \tag{16}$$

The objective of this derivation is to obtain a relation between the macroscale quantities that appear in eqn (9) and microscale quantities. This is accomplished by dividing eqn (16) by the constant macroscale volume $\delta V = \delta V^\alpha/\epsilon^\alpha$, where ϵ^α is the α-phase volume fraction, to obtain:

$$\frac{\partial(\epsilon^\alpha\langle\rho\psi\rangle^\alpha)}{\partial t} + \nabla\cdot(\epsilon^\alpha\langle\rho\boldsymbol{v}\psi\rangle^\alpha) - \nabla\cdot(\epsilon^\alpha\langle\boldsymbol{i}\rangle^\alpha) + \frac{\epsilon^\alpha}{\delta V^\alpha}\sum_{\beta\neq\alpha}\int_{S_{\alpha\beta}} \boldsymbol{n}^*\cdot[\rho(\boldsymbol{v}-\boldsymbol{w})\psi - \boldsymbol{i}]\big|_\alpha\,\mathrm{d}S - \epsilon^\alpha\langle\rho f\rangle^\alpha = \epsilon^\alpha\langle G\rangle^\alpha \tag{17}$$

where the notation to indicate an average over a volume has been introduced such that

$$\langle F\rangle^\alpha = \frac{1}{\delta V^\alpha}\int_{\delta V^\alpha} F\,\mathrm{d}V \tag{18a}$$

It is also useful to introduce the mass weighted average given by

$$\bar{F}^\alpha = \frac{1}{\langle\rho\rangle^\alpha\delta V^\alpha}\int_{\delta V^\alpha}\rho F\,\mathrm{d}V = \frac{\langle\rho F\rangle^\alpha}{\langle\rho\rangle^\alpha} \tag{18b}$$

and to define the deviation of a microscopic quantity from the macroscopic mean value as

$$\tilde{F}^\alpha = F - \bar{F}^\alpha. \tag{18c}$$

where this relation applies only for a microscale point in the α-phase. Introduction of the notation in eqns (18b) and (18c) into eqn (17) yields the macroscale balance equation in the following form.

Macroscale balance equation in terms of averaged quantities

$$\frac{\partial(\epsilon^\alpha\langle\rho\rangle^\alpha\bar{\psi}^\alpha)}{\partial t} + \nabla\cdot(\epsilon^\alpha\langle\rho\rangle^\alpha\bar{\boldsymbol{v}}^\alpha\bar{\psi}^\alpha) - \nabla\cdot\{\epsilon^\alpha[\langle\boldsymbol{i}\rangle^\alpha - \langle\rho\rangle^\alpha(\overline{\bar{\boldsymbol{v}}^\alpha\tilde{\psi}^\alpha}^\alpha + \overline{\tilde{\boldsymbol{v}}^\alpha\bar{\psi}^\alpha}^\alpha + \overline{\tilde{\boldsymbol{v}}^\alpha\tilde{\psi}^\alpha}^\alpha)]\} - \epsilon^\alpha\langle\rho\rangle^\alpha\bar{f}^\alpha = \epsilon^\alpha\langle G\rangle^\alpha + \sum_{\beta\neq\alpha}(\hat{e}^\alpha_{\alpha\beta}\bar{\psi}^\alpha + \hat{\boldsymbol{I}}^\alpha_{\alpha\beta}) \tag{19a}$$

where

$$\hat{e}^i_{\alpha\beta} = \frac{1}{\delta V}\int_{S_{\alpha\beta}} \boldsymbol{n}^i\cdot[\rho(\boldsymbol{w}-\boldsymbol{v})]\big|_i\,\mathrm{d}S; \qquad i=\alpha,\beta \tag{19b}$$

and

$$\hat{\boldsymbol{I}}^i_{\alpha\beta} = \frac{1}{\delta V}\int_{S_{\alpha\beta}} \boldsymbol{n}^i\cdot[\boldsymbol{i} - \rho(\boldsymbol{v}-\boldsymbol{w})\tilde{\psi}^i]\big|_i\,\mathrm{d}S; \qquad i=\alpha,\beta \tag{19c}$$

The quantity $\hat{e}^i_{\alpha\beta}$ accounts for mass exchange between the i-phase ($i=\alpha,\beta$) and the $\alpha\beta$-interface. The term $\hat{\boldsymbol{I}}^i_{\alpha\beta}$ deals with non-convective interaction of the i-phase ($i=\alpha,\beta$) with the interface.

Correspondence between the averaged microscale quantities in eqn (19a) and the directly written macroscale eqn (9) proposed in continuum mixture theories may now be determined by direct comparison of these two equations. The results, are as follows

$$\rho^\alpha = \langle\rho\rangle^\alpha \tag{20a}$$

$$\boldsymbol{v}^\alpha = \bar{\boldsymbol{v}}^\alpha \tag{20b}$$

$$\psi^\alpha = \bar{\psi}^\alpha \tag{20c}$$

$$f^\alpha = \bar{f}^\alpha \tag{20d}$$

$$\boldsymbol{i}^\alpha = \langle \boldsymbol{i} \rangle^\alpha - \langle \rho \rangle^\alpha (\overline{\bar{\boldsymbol{v}}^\alpha \tilde{\psi}^\alpha}^\alpha + \overline{\tilde{\boldsymbol{v}}^\alpha \bar{\psi}^\alpha}^\alpha + \overline{\tilde{\boldsymbol{v}}^\alpha \tilde{\psi}^\alpha}^\alpha) \tag{20e}$$

$$\epsilon^\alpha G^\alpha = \epsilon^\alpha \langle G \rangle^\alpha + \sum_{\beta \neq \alpha} (\hat{e}^\alpha_{\alpha\beta} \bar{\psi}^\alpha + \hat{\boldsymbol{I}}^\alpha_{\alpha\beta}) \tag{20f}$$

When $l \gg d$, the correlation between average quantities at length scale l and deviation quantities at length scale d is negligible such that the first two terms in parentheses in eqn (20e) are negligible and this expression simplifies to

$$\boldsymbol{i}^\alpha = \langle \boldsymbol{i} \rangle^\alpha - \langle \rho \rangle^\alpha \overline{\tilde{\boldsymbol{v}}^\alpha \tilde{\psi}^\alpha}^\alpha \tag{21}$$

In eqn (21), the second term on the right-hand side is an average of a product of spatial deviations that is analogous to the average of products of temporal deviations that gives rise to the Reynolds stresses in turbulence theory. Inclusion of the integral accounting for interface processes with the definition of a macroscopic source in eqn (20f) is based on the fact that microscale convection and diffusion processes at the interface are source terms for the property under consideration in the α-phase.

The purpose of this derivation has been to obtain the macroscale balance eqn (9) while providing a link between macroscale and microscale quantities. Such a link is given by eqns (20a) through (20f) and (21). Then, it can be easily verified that the introduction of these equations into eqn (19a) yields eqn (9). By appropriate choice of quantities ψ, $\boldsymbol{i}$, f and G, specific equations of balance can be obtained. This has been accomplished in the rest of this section.

2.5 Conservation of mass

For conservation of mass in the α-phase, $\psi = 1$, $\boldsymbol{i} = 0$, $f = 0$ and $G = 0$. Substitution into eqn (19a) gives the following.

Macroscale mass conservation for the α-phase

$$\frac{\partial(\epsilon^\alpha \rho^\alpha)}{\partial t} + \nabla \cdot (\epsilon^\alpha \rho^\alpha \boldsymbol{v}^\alpha) = \sum_{\beta \neq \alpha} \hat{e}^\alpha_{\alpha\beta} \tag{22}$$

where the right-hand side source term accounts for exchange of mass due to phase change. Note that because all phases are considered to be composed of a single component in this study, the only mechanism of mass transfer between phases and interfaces would be through phase change.

2.6 Conservation of momentum

For conservation of momentum in the α-phase, $\psi = \boldsymbol{v}$, $\boldsymbol{i} = \mathbf{t}$, $f = \boldsymbol{g}$, and $G = 0$ where $\mathbf{t}$ is the stress tensor and $\boldsymbol{g}$ is the body force per unit mass. Substitution into eqn (19a) gives

$$\frac{\partial(\epsilon^\alpha \rho^\alpha \boldsymbol{v}^\alpha)}{\partial t} + \nabla \cdot (\epsilon^\alpha \rho^\alpha \boldsymbol{v}^\alpha \boldsymbol{v}^\alpha) - \nabla \cdot (\epsilon^\alpha \mathbf{t}^\alpha) - \epsilon^\alpha \rho^\alpha \boldsymbol{g}^\alpha = \sum_{\beta \neq \alpha} (\hat{e}^\alpha_{\alpha\beta} \boldsymbol{v}^\alpha + \hat{\boldsymbol{T}}^\alpha_{\alpha\beta}) \tag{23a}$$

where

$$\mathbf{t}^\alpha = \langle \mathbf{t} \rangle^\alpha - \rho^\alpha \overline{\tilde{\boldsymbol{v}}^\alpha \tilde{\boldsymbol{v}}^\alpha}^\alpha \tag{23b}$$

and

$$\hat{\boldsymbol{T}}^\alpha_{\alpha\beta} = \frac{\epsilon^\alpha}{\delta V^\alpha} \int_{S_{\alpha\beta}} \boldsymbol{n}^\alpha \cdot [\mathbf{t} - \rho(\boldsymbol{v} - \boldsymbol{w})\tilde{\boldsymbol{v}}^\alpha]\big|_\alpha \,\mathrm{d}S \tag{23c}$$

Note that the macroscopic stress, $\mathbf{t}^\alpha$, is composed of components that, due to the average microscopic stress and velocity fluctuations occurring at the sub-macroscale, serve to dissipate momentum. The integral in eqn (23c) accounts for dissipation of momentum due to interaction of the α-phase with the boundary of that phase.

The continuity eqn (22) may be multiplied by $\boldsymbol{v}^\alpha$ and subtracted from eqn (23a) to yield the momentum equation in the following form.

Macroscale momentum conservation for the α-phase

$$\epsilon^\alpha \rho^\alpha \frac{D^\alpha \boldsymbol{v}^\alpha}{Dt} - \nabla \cdot (\epsilon^\alpha \mathbf{t}^\alpha) - \epsilon^\alpha \rho^\alpha \boldsymbol{g}^\alpha = \sum_{\beta \neq \alpha} \hat{\boldsymbol{T}}^\alpha_{\alpha\beta} \tag{24}$$

where the α-phase material time derivative is defined by

$$\frac{D^\alpha}{Dt} = \frac{\partial}{\partial t} + \boldsymbol{v}^\alpha \cdot \nabla \tag{25}$$

2.7 Conservation of angular momentum

A full global conservation of angular momentum (or moment of momentum) equation may be written and reduced to a macroscale point equation analogously to the derivation of the linear momentum equation. Then, combination of the angular and linear momentum equations will yield the result that the macroscale stress tensor, as defined by eqn (23b), is symmetric for a microscopically non-polar medium. Alternatively, the fact that the microscale stress tensor is symmetric for microscopically non-polar media may be employed directly. By this approach, because $\rho^\alpha \overline{\tilde{\boldsymbol{v}}^\alpha \tilde{\boldsymbol{v}}^\alpha}^\alpha$ is symmetric, the macroscale stress tensor $\mathbf{t}^\alpha$ must also be symmetric such that

$$\mathbf{t}^\alpha = \mathbf{t}^{\alpha T} \tag{26}$$

2.8 Conservation of energy

The full equation of conservation of energy accounts for both internal and kinetic energy. This balance for the α-phase makes use of $\psi = E + v^2/2$, $\boldsymbol{i} = \mathbf{t} \cdot \boldsymbol{v} + \boldsymbol{q}$, $f = \boldsymbol{g} \cdot \boldsymbol{v} + h$ and $G = 0$. In these definitions, E is internal energy per unit mass, $\boldsymbol{q}$ is the heat conduction flux vector, and h accounts for external supply such as radiation. Substitution into eqn (19a) gives

$$\frac{\partial\{\epsilon^\alpha\rho^\alpha[E^\alpha+(v^\alpha)^2/2]\}}{\partial t}+\nabla\cdot\{\epsilon^\alpha\rho^\alpha\boldsymbol{v}^\alpha[E^\alpha+(v^\alpha)^2/2]\}$$
$$-\nabla\cdot[\epsilon^\alpha(\mathbf{t}^\alpha\cdot\boldsymbol{v}^\alpha+\boldsymbol{q}^\alpha)]-\epsilon^\alpha\rho^\alpha(\boldsymbol{g}^\alpha\cdot\boldsymbol{v}^\alpha+h^\alpha)$$
$$=\sum_{\beta\neq\alpha}\{\hat{e}^\alpha_{\alpha\beta}[E^\alpha+(v^\alpha)^2/2]+\hat{\boldsymbol{T}}^\alpha_{\alpha\beta}\cdot\boldsymbol{v}^\alpha+\hat{Q}^\alpha_{\alpha\beta}\} \tag{27a}$$

where

$$E^\alpha=\bar{E}^\alpha+\overline{(\tilde{v}^\alpha)^2}^\alpha/2 \tag{27b}$$

$$\boldsymbol{q}^\alpha=\langle\boldsymbol{q}\rangle^\alpha+\langle\mathbf{t}\cdot\tilde{\boldsymbol{v}}^\alpha\rangle^\alpha-\langle\rho\rangle^\alpha\overline{\tilde{\boldsymbol{v}}^\alpha(\tilde{E}^\alpha+(\tilde{v}^\alpha)^2/2)}^\alpha \tag{27c}$$

$$h^\alpha=\bar{h}^\alpha+\overline{\boldsymbol{g}\cdot\tilde{\boldsymbol{v}}^\alpha}^\alpha \tag{27d}$$

and

$$\hat{Q}^\alpha_{\alpha\beta}=\frac{1}{\delta V}\int_{S_{\alpha\beta}}\boldsymbol{n}^\alpha\cdot[\boldsymbol{q}+\mathbf{t}\cdot\tilde{\boldsymbol{v}}^\alpha$$
$$-\rho(\boldsymbol{v}-\boldsymbol{w})(\tilde{E}^\alpha+(\tilde{v}^\alpha)^2/2)]|_\alpha\,\mathrm{d}S \tag{27e}$$

Thus, the macroscopic internal energy is composed of the average microscopic internal energy plus the sub-macroscale deviations of the fluid velocity that contribute to internal energy at the macroscale. For most porous media systems where the velocity is small, the contribution of the fluid motion to the internal energy through the average of the deviation terms is small. Similarly, the macroscopic external supply of energy to the system, h^α, is composed of the average microscale energy supply plus the work of microscale external forces due to deviations in flow velocity. The transfer of heat at the macroscale is due to the average heat flux plus an additional flux due to subscale energy transfer caused by fluid motion. The integral in eqn (27e) accounts for energy transfer between the α-phase and the interfaces at the boundary of that phase.

Multiplication of continuity eqn (22) by $E^\alpha+(v^\alpha)^2/2$ and subtraction from eqn (27a) followed by subtraction of the scalar product of $\boldsymbol{v}^\alpha$ with momentum eqn (24) reduces the energy equation to the following form.

Macroscale energy conservation for the α-phase

$$\epsilon^\alpha\rho^\alpha\frac{D^\alpha E^\alpha}{Dt}-\nabla\cdot(\epsilon^\alpha\boldsymbol{q}^\alpha)-\epsilon^\alpha\mathbf{t}^\alpha:\nabla\boldsymbol{v}^\alpha-\epsilon^\alpha\rho^\alpha h^\alpha$$
$$=\sum_{\beta\neq\alpha}\hat{Q}^\alpha_{\alpha\beta} \tag{28}$$

2.9 Balance equation for entropy

Entropy is conserved only for a reversible process. However, an entropy balance may be written for the α-phase with $\psi=\eta$, $\boldsymbol{i}=\boldsymbol{\varphi}$, $f=b$ and $G=\Lambda$. Here, η is the entropy per unit mass, $\boldsymbol{\varphi}$ is the entropy flux, b is the entropy supply term, and Λ is the net rate of production of entropy. By the second law of thermodynamics, the entropy generation term, Λ, has the property that $\Lambda\geq 0$. The non-negativity of Λ means that the time rate of change of entropy of a body is never less than the sum of the net influx of entropy through the surface and the entropy supplied by body sources.[6] Substitution into eqn (19a) gives

$$\frac{\partial(\epsilon^\alpha\rho^\alpha\eta^\alpha)}{\partial t}+\nabla\cdot(\epsilon^\alpha\rho^\alpha\boldsymbol{v}^\alpha\eta^\alpha)-\nabla\cdot(\epsilon^\alpha\boldsymbol{\varphi}^\alpha)-\epsilon^\alpha\rho^\alpha b^\alpha$$
$$=\epsilon^\alpha\Lambda^\alpha+\sum_{\beta\neq\alpha}(\hat{\Phi}^\alpha_{\alpha\beta}+\hat{e}^\alpha_{\alpha\beta}\eta^\alpha) \tag{29a}$$

where

$$\eta^\alpha=\bar{\eta}^\alpha \tag{29b}$$

$$\boldsymbol{\varphi}^\alpha=\langle\boldsymbol{\varphi}\rangle^\alpha-\rho^\alpha\overline{\tilde{\boldsymbol{v}}^\alpha\tilde{\eta}^\alpha}^\alpha \tag{29c}$$

$$b^\alpha=\bar{b}^\alpha \tag{29d}$$

$$\Lambda^\alpha=\langle\Lambda\rangle^\alpha \tag{29e}$$

and:

$$\hat{\Phi}^\alpha_{\alpha\beta}=\frac{\epsilon^\alpha}{\delta V^\alpha}\int_{S_{\alpha\beta}}\boldsymbol{n}^\alpha\cdot[\boldsymbol{\varphi}-\rho(\boldsymbol{v}-\boldsymbol{w})\tilde{\eta}^\alpha]|_\alpha\,\mathrm{d}S \tag{29f}$$

Subtraction of continuity eqn (22) multiplied by η^α from eqn (29a) yields the entropy balance equation in the following form.

Macroscopic entropy balance for the α-phase

$$\epsilon^\alpha\rho^\alpha\frac{D^\alpha\eta^\alpha}{Dt}-\nabla\cdot(\epsilon^\alpha\boldsymbol{\varphi}^\alpha)-\epsilon^\alpha\rho^\alpha b^\alpha=\epsilon^\alpha\Lambda^\alpha+\sum_{\beta\neq\alpha}\hat{\Phi}^\alpha_{\alpha\beta} \tag{30}$$

3 INTERFACE EQUATIONS

The bulk phases in a multiphase system are separated by interfaces. At the microscale, interfacial regions are modeled as two-dimensional continua that may have thermodynamic properties different from those of the neighboring bulk phases. The thermodynamic quantities associated with the interfaces are called, after a model due to Gibbs, surface excess properties (see e.g. Miller and Neogi[21]). In continuum mechanics of single phase continua, general conservation equations are given for surface properties.

The general conservation equation for an $\alpha\beta$-interface property when this interface is located in a volume, δV, is

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{S_{\alpha\beta}}(\rho\psi)|_{\alpha\beta}\,\mathrm{d}S+\int_{C_{\alpha\beta}}\boldsymbol{\nu}^*\cdot[\rho(\boldsymbol{v}-\boldsymbol{w}_\mathrm{b})\psi-\boldsymbol{i}]|_{\alpha\beta}\,\mathrm{d}C$$
$$+\sum_{\gamma\neq\alpha,\beta}\int_{C_{\alpha\beta\gamma}}\boldsymbol{\nu}^{\alpha\beta}\cdot[\rho(\boldsymbol{v}-\boldsymbol{u}_\mathrm{b})\psi-\boldsymbol{i}]|_{\alpha\beta}\,\mathrm{d}C$$
$$-\sum_{i=\alpha,\beta}\int_{S_{\alpha\beta}}\boldsymbol{n}^i\cdot[\rho(\boldsymbol{v}-\boldsymbol{w})\psi-\boldsymbol{i}]|_i\,\mathrm{d}S$$
$$-\int_{S_{\alpha\beta}}(\rho f)|_{\alpha\beta}\,\mathrm{d}S=\int_{S_{\alpha\beta}}G|_{\alpha\beta}\,\mathrm{d}S \tag{31}$$

where the notation $|_{\alpha\beta}$ is used to indicate a microscopic surficial property of the $\alpha\beta$-interface, $S_{\alpha\beta}$ is the two-dimensional spatial region occupied by the interface, $C_{\alpha\beta}$ is the intersection of the $\alpha\beta$-interface with the boundary of δV, $C_{\alpha\beta\gamma}$ is the common line formed at the intersection of $\alpha\beta$, $\alpha\gamma$ and $\beta\gamma$ interfaces, $\rho|_i$ is the mass density of the α or β phase on the side of the interface indicated with the vertical bar $[M/L^3]$, $\rho|_{\alpha\beta}$ is the excess mass density of the interface $[M/L^2]$, ψ is the property of interest per unit excess mass of the interface, $\boldsymbol{v}$ is the velocity of the material in the interface, $\boldsymbol{u}_b$ is the velocity of the internal boundary of the interface (i.e. a common line), $\boldsymbol{w}$ is the velocity of the interface, $\boldsymbol{w}_b$ is the velocity of the bounding edge of the interface on the boundary of δV, $\boldsymbol{i}$ is a non-convective flux from the interphase into an adjacent phase or a non-convective flux from the curve bounding the interface, $\boldsymbol{\nu}^*$ is a unit normal vector of $C_{\alpha\beta}$ that is also tangent to $S_{\alpha\beta}$ and oriented outward (with respect to the REV), $\boldsymbol{\nu}^{\alpha\beta}$ is a unit normal vector of $C_{\alpha\beta\gamma}$ that is tangent to $S_{\alpha\beta}$ pointing outward, f is the external supply of ψ, G accounts for the net production of ψ within the $\alpha\beta$-interface, and $\sum_{\gamma\neq\alpha,\beta}$ denotes a summation over all common lines bounding the $\alpha\beta$-interface.

The first term in eqn (31) is the rate of accumulation of ψ on the surface. The second and third integrals account for flux out of the surface across the exterior boundary of the volume where it intersects the surface (i.e. on the curve $C_{\alpha\beta}$) and at a common line forming the boundary of the surface in the interior of the volume (i.e. on the $C_{\alpha\beta\gamma}$ common line), respectively. The fourth integral accounts for addition of ψ to the interface from the phases on the two sides of the interface. The last integral on the left-hand side of the equation is the external supply term, and the right-hand side of the equation is the net production term.

The volume δV in which the surface exists for eqn (31) is an REV and therefore is independent of space and time. However, the surfaces and common lines within the volume may deform and grow. Because the volume is required to be an REV at a particular position in space such that its external boundaries are fixed, a correspondence between the time derivative in eqn (31) and the partial time derivative that appears in a macroscopic averaged equation may be obtained. Combination of equations $T[2,(0,0),2]$, the transport theorem for a surface, and $T[2,(3,0),0]$, the averaging theorem for a partial time derivative on a surface,[13] provides the following useful relation.

Transport theorem for use with macroscale interface equations

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{S_{\alpha\beta}} F|_{\alpha\beta}\,\mathrm{d}S - \int_{C_{\alpha\beta}} \boldsymbol{\nu}^*\cdot\boldsymbol{w}_b F|_{\alpha\beta}\,\mathrm{d}C = \frac{\partial}{\partial t}\int_{S_{\alpha\beta}} F|_{\alpha\beta}\,\mathrm{d}S + \nabla\cdot\int_{S_{\alpha\beta}} \boldsymbol{n}^\alpha\boldsymbol{n}^\alpha\cdot(\boldsymbol{w}F)|_{\alpha\beta}\,\mathrm{d}S \tag{32}$$

The integral over $C_{\alpha\beta}$ in eqn (31) can be converted to the divergence of an integral by combination of the averaging theorems for surface divergence operators, eqns $D[2,(3,0),0]$ and $D[2,(0,3),0]$ in Gray *et al.*[13] to obtain the following.

Divergence theorem for use with macroscale interface equations

$$\int_{C_{\alpha\beta}} \boldsymbol{\nu}^*\cdot\boldsymbol{B}|_{\alpha\beta}\,\mathrm{d}C = \nabla\cdot\int_{S_{\alpha\beta}} \boldsymbol{B}^{\mathrm{s}}|_{\alpha\beta}\,\mathrm{d}S \tag{33a}$$

where

$$\boldsymbol{B}^{\mathrm{s}}|_{\alpha\beta} = \boldsymbol{B}|_{\alpha\beta} - \boldsymbol{n}^\alpha\boldsymbol{n}^\alpha\cdot\boldsymbol{B}|_{\alpha\beta} \tag{33b}$$

such that $\boldsymbol{B}^{\mathrm{s}}|_{\alpha\beta}$ is the three-dimensional representation of a vector that is tangent to $S_{\alpha\beta}$.

Application of eqns (32) and (33a) to eqn (31) yields

$$\frac{\partial}{\partial t}\int_{S_{\alpha\beta}}(\rho\psi)|_{\alpha\beta}\,\mathrm{d}S + \nabla\cdot\int_{S_{\alpha\beta}}[\rho\boldsymbol{v}\psi - \boldsymbol{i}^{\mathrm{s}}]|_{\alpha\beta}\,\mathrm{d}S + \sum_{\gamma\neq\alpha,\beta}\int_{C_{\alpha\beta\gamma}}\boldsymbol{\nu}^{\alpha\beta}\cdot[\rho(\boldsymbol{v}-\boldsymbol{u})\psi - \boldsymbol{i}]|_{\alpha\beta}\,\mathrm{d}C - \sum_{i=\alpha,\beta}\int_{S_{\alpha\beta}}\boldsymbol{n}^i\cdot[\rho(\boldsymbol{v}-\boldsymbol{w})\psi - \boldsymbol{i}]|_i\,\mathrm{d}S - \int_{S_{\alpha\beta}}(\rho f)|_{\alpha\beta}\,\mathrm{d}S = \int_{S_{\alpha\beta}} G|_{\alpha\beta}\,\mathrm{d}S \tag{34}$$

where use has been made of the fact that $\boldsymbol{v}|_{\alpha\beta} = \boldsymbol{v}^{\mathrm{s}}|_{\alpha\beta} + \boldsymbol{n}^\alpha\boldsymbol{n}^\alpha\cdot\boldsymbol{w}|_{\alpha\beta}$. This equation can be written in a more convenient form by dividing by the constant averaging volume, δV, to obtain

$$\frac{\partial(a^{\alpha\beta}\langle\rho\psi\rangle^{\alpha\beta})}{\partial t} + \nabla\cdot(a^{\alpha\beta}\langle\rho\boldsymbol{v}\psi\rangle^{\alpha\beta}) - \nabla\cdot(a^{\alpha\beta}\langle\boldsymbol{i}^{\mathrm{s}}\rangle^{\alpha\beta}) + \frac{1}{\delta V}\sum_{\gamma\neq\alpha,\beta}\int_{C_{\alpha\beta\gamma}}\boldsymbol{\nu}^{\alpha\beta}\cdot[\rho(\boldsymbol{v}-\boldsymbol{u})\psi - \boldsymbol{i}]_{\alpha\beta}\,\mathrm{d}C + \sum_{i=\alpha,\beta}(\hat{e}^i_{\alpha\beta}\psi^i + \hat{\boldsymbol{I}}^i_{\alpha\beta}) - a^{\alpha\beta}\langle\rho f\rangle^{\alpha\beta} = a^{\alpha\beta}\langle G\rangle^{\alpha\beta} \tag{35}$$

where $\hat{e}_{\alpha\beta}$ and $\hat{\boldsymbol{I}}_{\alpha\beta}$ are defined by eqns (19b) and (19c), and the notation of an average over an area has been used for properties defined on a per unit area basis with

$$\langle F\rangle^{\alpha\beta} = \frac{1}{S_{\alpha\beta}}\int_{S_{\alpha\beta}} F|_{\alpha\beta}\,\mathrm{d}S \tag{36a}$$

and

$$a^{\alpha\beta} = \frac{1}{\delta V}\int_{S_{\alpha\beta}}\mathrm{d}S = \frac{S_{\alpha\beta}}{\delta V} \tag{36b}$$

The specific surface, $a^{\alpha\beta}$, is the amount of $\alpha\beta$-interface per unit volume. As with the phase properties, it is useful to introduce a mass weighted area average and the deviation of the microscopic property from the macroscopic mean, respectively, as

$$\bar{F}^{\alpha\beta} = \frac{1}{\langle\rho\rangle^{\alpha\beta}S_{\alpha\beta}}\int_{S_{\alpha\beta}}(\rho F)|_{\alpha\beta}\,\mathrm{d}S = \frac{\langle\rho F\rangle^{\alpha\beta}}{\langle\rho\rangle^{\alpha\beta}} \tag{36c}$$

and

$$\tilde{F}^{\alpha\beta} = F - \bar{F}^{\alpha\beta} \tag{36d}$$

Substitution of these definitions into eqn (35) yields the following.

Macroscale surface balance equation in terms of averaged quantities

$$\frac{\partial(a^{\alpha\beta}\langle\rho\rangle^{\alpha\beta}\bar{\psi}^{\alpha\beta})}{\partial t} + \nabla\cdot(a^{\alpha\beta}\langle\rho\rangle^{\alpha\beta}\bar{\boldsymbol{v}}^{\alpha\beta}\bar{\psi}^{\alpha\beta})$$
$$- \nabla\cdot[a^{\alpha\beta}(\langle \boldsymbol{i}^s\rangle^{\alpha\beta} - \langle\rho\rangle^{\alpha\beta}\overline{\tilde{\boldsymbol{v}}^{\alpha\beta}\tilde{\psi}^{\alpha\beta}}^{\alpha\beta})]$$
$$- a^{\alpha\beta}\langle\rho\rangle^{\alpha\beta}\bar{f}^{\alpha\beta} = a^{\alpha\beta}\langle G\rangle^{\alpha\beta} - \sum_{i=\alpha,\beta}(\hat{e}^i_{\alpha\beta}\psi^i + \hat{\boldsymbol{I}}^i_{\alpha\beta})$$
$$+ \sum_{\gamma\neq\alpha,\beta}(\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\bar{\psi}^{\alpha\beta} + \hat{\boldsymbol{I}}^{\alpha\beta}_{\alpha\beta\gamma}) \tag{37a}$$

where

$$\hat{e}^{ij}_{\alpha\beta\gamma} = \frac{1}{\delta V}\int_{C_{\alpha\beta\gamma}} \boldsymbol{\nu}^{ij}\cdot[\rho(\boldsymbol{u}-\boldsymbol{v})]\big|_{ij}\,\mathrm{d}C;$$
$$ij = \alpha\beta, \alpha\gamma, \beta\gamma \tag{37b}$$

and

$$\hat{\boldsymbol{I}}^{ij}_{\alpha\beta\gamma} = \frac{1}{\delta V}\int_{C_{\alpha\beta\gamma}} \boldsymbol{\nu}^{ij}\cdot[\boldsymbol{i} - \rho(\boldsymbol{v}-\boldsymbol{u})\tilde{\psi}^{ij}]\big|_{ij}\,\mathrm{d}C;$$
$$ij = \alpha\beta, \alpha\gamma, \beta\gamma \tag{37c}$$

These last two terms account for interactions of an ij-interface with a bounding common line. The notation in eqn (37a) can be simplified by defining surface macroscale properties in terms of averages analogous to the definitions in eqns (20a) through (20f) for phase properties to obtain

$$\frac{\partial(a^{\alpha\beta}\rho^{\alpha\beta}\psi^{\alpha\beta})}{\partial t} + \nabla\cdot(a^{\alpha\beta}\rho^{\alpha\beta}\boldsymbol{v}^{\alpha\beta}\psi^{\alpha\beta})$$
$$- \nabla\cdot[a^{\alpha\beta}\boldsymbol{i}^{\alpha\beta}] - a^{\alpha\beta}\rho^{\alpha\beta}f^{\alpha\beta}$$
$$= a^{\alpha\beta}G^{\alpha\beta} - \sum_{i=\alpha,\beta}(\hat{e}^i_{\alpha\beta}\psi^i + \hat{\boldsymbol{I}}^i_{\alpha\beta})$$
$$+ \sum_{\gamma\neq\alpha,\beta}(\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\psi^{\alpha\beta} + \hat{\boldsymbol{I}}^{\alpha\beta}_{\alpha\beta\gamma}) \tag{38}$$

This equation may be used, as was done with the general phase equation, to obtain specific macroscale balances. This will be done here.

3.1 Conservation of mass

For the $\alpha\beta$-interface, mass conservation is obtained when the microscale properties are given by $\psi|_{\alpha\beta} = 1$, $\boldsymbol{i}^s|_{\alpha\beta} = 0, f|_{\alpha\beta} = 0$ and $G|_{\alpha\beta} = 0$. The resulting equation is as follows.

Macroscale mass conservation for the $\alpha\beta$-interface

$$\frac{\partial(a^{\alpha\beta}\rho^{\alpha\beta})}{\partial t} + \nabla\cdot(a^{\alpha\beta}\rho^{\alpha\beta}\boldsymbol{v}^{\alpha\beta})$$
$$= -(\hat{e}^{\alpha}_{\alpha\beta} + \hat{e}^{\beta}_{\alpha\beta}) + \sum_{\gamma\neq\alpha,\beta}\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} \tag{39}$$

The two terms on the right account, respectively, for the exchange of mass with the neighbouring phases and with the bounding common curve.

3.2 Conservation of momentum

For an $\alpha\beta$-interface, momentum conservation is obtained from eqn (38) with microscale properties defined such that $\psi|_{\alpha\beta} = \boldsymbol{v}|_{\alpha\beta}$, $\boldsymbol{i}|_{\alpha\beta} = \mathbf{t}|_{\alpha\beta}$, $f|_{\alpha\beta} = \boldsymbol{g}|_{\alpha\beta}$ and $G|_{\alpha\beta} = 0$

$$\frac{\partial(a^{\alpha\beta}\rho^{\alpha\beta}\boldsymbol{v}^{\alpha\beta})}{\partial t} + \nabla\cdot(a^{\alpha\beta}\rho^{\alpha\beta}\boldsymbol{v}^{\alpha\beta}\boldsymbol{v}^{\alpha\beta})$$
$$- \nabla\cdot[a^{\alpha\beta}\mathbf{S}^{\alpha\beta}] - a^{\alpha\beta}\rho^{\alpha\beta}\boldsymbol{g}^{\alpha\beta}$$
$$= -\sum_{i=\alpha,\beta}(\hat{e}^i_{\alpha\beta}\boldsymbol{v}^i + \hat{\boldsymbol{T}}^i_{\alpha\beta})$$
$$+ \sum_{\gamma\neq\alpha,\beta}(\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\boldsymbol{v}^{\alpha\beta} + \hat{\boldsymbol{T}}^{\alpha\beta}_{\alpha\beta\gamma}) \tag{40a}$$

where

$$\mathbf{S}^{\alpha\beta} = \langle\mathbf{t}^s\rangle^{\alpha\beta} - \rho^{\alpha\beta}\overline{\tilde{\boldsymbol{v}}^{\alpha\beta}\tilde{\boldsymbol{v}}^{\alpha\beta}}^{\alpha\beta} \tag{40b}$$

with

$$\mathbf{t}^s|_{\alpha\beta} = \mathbf{t}|_{\alpha\beta} - \boldsymbol{n}^\alpha\boldsymbol{n}^\alpha\cdot\mathbf{t}|_{\alpha\beta}\cdot\boldsymbol{n}^\alpha\boldsymbol{n}^\alpha \tag{40c}$$

and

$$\hat{\boldsymbol{T}}^{ij}_{\alpha\beta\gamma} = \frac{1}{\delta V}\int_{C_{\alpha\beta\gamma}} \boldsymbol{\nu}^{ij}\cdot[\mathbf{t}^s - \rho(\boldsymbol{v}-\boldsymbol{u})\tilde{\boldsymbol{v}}^{ij}]\big|_{ij}\,\mathrm{d}C;$$
$$ij = \alpha\beta, \alpha\gamma, \beta\gamma \tag{40d}$$

Note that although $\mathbf{t}^s$ is a tensor acting over the two-dimensional space of the surface such that it has no constituents normal to the surface (i.e. $\boldsymbol{n}^\alpha\cdot\mathbf{t}^s|_{\alpha\beta} = \mathbf{t}^s|_{\alpha\beta}\cdot\boldsymbol{n}^\alpha = 0$), when averaged over the surfaces within an REV with the surfaces not oriented in any particular direction, the macroscale stress tensor, $\mathbf{S}^{\alpha\beta}$, will have components in all three dimensions of macrospace.

Multiplication of mass conservation eqn (39) by $\boldsymbol{v}^{\alpha\beta}$ and subtraction from eqn (40a) yields the momentum equation in the following form.

Macroscale momentum conservation for the $\alpha\beta$-interface

$$a^{\alpha\beta}\rho^{\alpha\beta}\frac{D^{\alpha\beta}\boldsymbol{v}^{\alpha\beta}}{Dt} - \nabla\cdot(a^{\alpha\beta}\mathbf{S}^{\alpha\beta}) - a^{\alpha\beta}\rho^{\alpha\beta}\boldsymbol{g}^{\alpha\beta}$$
$$= -\sum_{i=\alpha,\beta}(\hat{e}^i_{\alpha\beta}\boldsymbol{v}^{i,\alpha\beta} + \hat{\boldsymbol{T}}^i_{\alpha\beta}) + \sum_{\gamma\neq\alpha,\beta}\hat{\boldsymbol{T}}^{\alpha\beta}_{\alpha\beta\gamma} \tag{41}$$

where the $\alpha\beta$-interface material time derivative is defined by

$$\frac{D^{\alpha\beta}}{Dt} = \frac{\partial}{\partial t} + \boldsymbol{v}^{\alpha\beta}\cdot\nabla \tag{42}$$

and $\boldsymbol{v}^{i,\alpha\beta}$ denotes the relative macroscopic velocity of phase i with respect to the velocity of the material in the

$\alpha\beta$-interface

$$\boldsymbol{v}^{i,\alpha\beta} = \boldsymbol{v}^{i} - \boldsymbol{v}^{\alpha\beta} \tag{43}$$

3.3 Conservation of angular momentum

The conservation of angular momentum equation may be used to demonstrate that the macroscale surface stress tensor is symmetric. The derivation proceeds similarly as would be done with the spatial stress tensor. Moeckel[22] has shown that the microscale stress tensor, $\mathbf{t}^{s}$, is symmetric for a non-polar medium and has no normal components. Then from definition (40b), it follows that $\mathbf{S}^{\alpha\beta}$ is also symmetric

$$\mathbf{S}^{\alpha\beta} = \mathbf{S}^{\alpha\beta^{\mathrm{T}}} \tag{44}$$

3.4 Conservation of energy

The energy balance equation for the $\alpha\beta$-interface makes use of averages of the microscopic quantities $\psi|_{\alpha\beta} = (E + v^2/2)|_{\alpha\beta}$, $\boldsymbol{i}_{\alpha\beta} = (\mathbf{t}\cdot\boldsymbol{v} + \boldsymbol{q})|_{\alpha\beta}$, $f|_{\alpha\beta} = (\boldsymbol{g}\cdot\boldsymbol{v} + h)|_{\alpha\beta}$ and $G|_{\alpha\beta} = 0$. For these parameters, eqn (38) becomes

$$\begin{aligned}
&\frac{\partial\{a^{\alpha\beta}\rho^{\alpha\beta}[E^{\alpha\beta} + (v^{\alpha\beta})^2/2]\}}{\partial t} \\
&\quad + \nabla\cdot\{a^{\alpha\beta}\rho^{\alpha\beta}\boldsymbol{v}^{\alpha\beta}[E^{\alpha\beta} + (v^{\alpha\beta})^2/2]\} \\
&\quad - \nabla\cdot[a^{\alpha\beta}(\mathbf{S}^{\alpha\beta}\cdot\boldsymbol{v}^{\alpha\beta} + \boldsymbol{q}^{\alpha\beta})] \\
&\quad - a^{\alpha\beta}\rho^{\alpha\beta}(\boldsymbol{g}^{\alpha\beta}\cdot\boldsymbol{v}^{\alpha\beta} + h^{\alpha\beta}) \\
&= -\sum_{i=\alpha,\beta}\{\hat{e}^{i}_{\alpha\beta}[E^{i} + (v^{i})^2/2] + \hat{\boldsymbol{T}}^{i}_{\alpha\beta}\cdot\boldsymbol{v}^{i} + \hat{Q}^{i}_{\alpha\beta}\} \\
&\quad + \sum_{\gamma\neq\alpha,\beta}\{\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}[E^{\alpha\beta} + (v^{\alpha\beta})^2/2] \\
&\quad + \hat{\boldsymbol{T}}^{\alpha\beta}_{\alpha\beta\gamma}\cdot\boldsymbol{v}^{\alpha\beta} + \hat{Q}^{\alpha\beta}_{\alpha\beta\gamma}\}
\end{aligned} \tag{45a}$$

where

$$E^{\alpha\beta} = \bar{E}^{\alpha\beta} + \overline{(\tilde{v}^{\alpha\beta})^2}^{\alpha\beta}/2 \tag{45b}$$

$$\begin{aligned}
\boldsymbol{q}^{\alpha\beta} &= \langle\boldsymbol{q}\rangle^{\alpha\beta} + \langle\mathbf{t}\cdot\tilde{\boldsymbol{v}}^{\alpha\beta}\rangle^{\alpha\beta} \\
&\quad - \langle\rho\rangle^{\alpha\beta}\overline{\tilde{\boldsymbol{v}}^{\alpha\beta}(\tilde{E}^{\alpha\beta} + (\tilde{v}^{\alpha\beta})^2/2)}^{\alpha\beta}
\end{aligned} \tag{45c}$$

$$h^{\alpha\beta} = \bar{h}^{\alpha\beta} + \overline{\boldsymbol{g}\cdot\tilde{\boldsymbol{v}}^{\alpha\beta}}^{\alpha\beta} \tag{45d}$$

and

$$\begin{aligned}
\hat{Q}^{ij}_{\alpha\beta\gamma} &= \frac{1}{\delta V}\int_{C_{\alpha\beta\gamma}} \boldsymbol{\nu}^{ij}\cdot[\boldsymbol{q} + \mathbf{t}\cdot\tilde{\boldsymbol{v}}^{ij} - \rho(\boldsymbol{v} - \boldsymbol{u}) \\
&\quad \times (\tilde{E}^{ij} + (\tilde{v}^{ij})^2/2)]|_{ij}\,\mathrm{d}C; \qquad ij = \alpha\beta, \alpha\gamma, \beta\gamma
\end{aligned} \tag{45e}$$

Note that the two summations on the right-hand side account, respectively, for the exchange of energy with the adjacent phases and with the common lines that bound the interface within δV.

Continuity eqn (39) may be multiplied by $E^{\alpha\beta} + (v^{\alpha\beta})^2/2$ and then subtracted from energy eqn (45a). The scalar product of $\boldsymbol{v}^{\alpha\beta}$ with momentum eqn (41) may also be subtracted from the energy equation. The result of these operations is the following.

Macroscale energy conservation for the $\alpha\beta$-interface

$$\begin{aligned}
&a^{\alpha\beta}\rho^{\alpha\beta}\frac{D^{\alpha\beta}E^{\alpha\beta}}{Dt} - \nabla\cdot(a^{\alpha\beta}\boldsymbol{q}^{\alpha\beta}) \\
&\quad - a^{\alpha\beta}\mathbf{S}^{\alpha\beta} : \nabla\boldsymbol{v}^{\alpha\beta} - a^{\alpha\beta}\rho^{\alpha\beta}h^{\alpha\beta} \\
&= -v\sum_{i=\alpha,\beta}\{\hat{e}^{i}_{\alpha\beta}[E^{i,\alpha\beta} + (\nu^{i,\alpha\beta})^2/2] \\
&\quad + \hat{\boldsymbol{T}}^{i}_{\alpha\beta}\cdot\boldsymbol{v}^{i,\alpha\beta} + \hat{Q}^{i}_{\alpha\beta}\} + \sum_{\gamma\neq\alpha,\beta}\hat{Q}^{\alpha\beta}_{\alpha\beta\gamma}
\end{aligned} \tag{46}$$

where: $E^{i,\alpha\beta} = E^{i} - E^{\alpha\beta}$.

3.5 Balance equation for entropy

For the $\alpha\beta$-interface, the balance equation for entropy can be obtained from eqn (38) when the microscale quantities have been defined as $\psi|_{\alpha\beta} = \eta|_{\alpha\beta}$, $\boldsymbol{i}|_{\alpha\beta} = \boldsymbol{\varphi}|_{\alpha\beta}$, $f|_{\alpha\beta} = b|_{\alpha\beta}$, and $G|_{\alpha\beta} = \Lambda|_{\alpha\beta}$ where the entropy, $\eta|_{\alpha\beta}$, is on a per unit mass basis. If the appropriate definition of macroscale quantities in terms of averages of microscale counterparts are invoked, the resulting balance equation is

$$\begin{aligned}
&\frac{\partial(a^{\alpha\beta}\rho^{\alpha\beta}\eta^{\alpha\beta})}{\partial t} + \nabla\cdot(a^{\alpha\beta}\rho^{\alpha\beta}\boldsymbol{v}^{\alpha\beta}\eta^{\alpha\beta}) \\
&\quad - \nabla\cdot[a^{\alpha\beta}\boldsymbol{\varphi}^{\alpha\beta}] - a^{\alpha\beta}\rho^{\alpha\beta}b^{\alpha\beta} \\
&= a^{\alpha\beta}\Lambda^{\alpha\beta} - \sum_{i=\alpha,\beta}(\hat{e}^{i}_{\alpha\beta}\eta^{i} + \hat{\Phi}^{i}_{\alpha\beta}) \\
&\quad + \sum_{\gamma\neq\alpha,\beta}(\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\eta^{\alpha\beta} + \hat{\Phi}^{\alpha\beta}_{\alpha\beta\gamma})
\end{aligned} \tag{47a}$$

where

$$\eta^{\alpha\beta} = \bar{\eta}^{\alpha\beta} \tag{47b}$$

$$\boldsymbol{\varphi}^{\alpha\beta} = \langle\boldsymbol{\varphi}^{s}\rangle^{\alpha\beta} - \rho^{\alpha\beta}\overline{\tilde{\boldsymbol{v}}^{\alpha\beta}\tilde{\eta}^{\alpha\beta}}^{\alpha\beta} \tag{47c}$$

$$b^{\alpha\beta} = \bar{b}^{\alpha\beta} \tag{47d}$$

$$\Lambda^{\alpha\beta} = \langle\Lambda\rangle^{\alpha\beta} \tag{47e}$$

and

$$\begin{aligned}
&\hat{\Phi}^{ij}_{\alpha\beta\gamma} = \frac{1}{\delta V}\int_{C_{\alpha\beta\gamma}} \boldsymbol{\nu}^{ij}\cdot[\boldsymbol{\varphi}^{s} - \rho(\boldsymbol{v} - \boldsymbol{u})\tilde{\eta}^{ij}]|_{ij}\,\mathrm{d}C; \\
&ij = \alpha\beta, \alpha\gamma, \beta\gamma
\end{aligned} \tag{47f}$$

Multiplication of macroscale interface mass conservation eqn (39), by $\eta^{\alpha\beta}$ and subtraction from eqn (47a) yields the entropy balance in the following form.

Macroscopic entropy balance for the αβ-interface

$$a^{\alpha\beta}\rho^{\alpha\beta}\frac{D^{\alpha\beta}\eta^{\alpha\beta}}{Dt}-\nabla\cdot(a^{\alpha\beta}\varphi^{\alpha\beta})-a^{\alpha\beta}\rho^{\alpha\beta}b^{\alpha\beta}$$
$$=a^{\alpha\beta}\Lambda^{\alpha\beta}-\sum_{i=\alpha,\beta}(\hat{e}^{i}_{\alpha\beta}\eta^{i,\alpha\beta}+\hat{\Phi}^{i}_{\alpha\beta})+\sum_{\gamma\neq\alpha,\beta}\hat{\Phi}^{\alpha\beta}_{\alpha\beta\gamma} \tag{48}$$

4 COMMON LINE EQUATIONS

At the microscale, common lines are regions where three phases (and, thus, three interfaces) come together. Common lines are modeled as one-dimensional continua which may have thermodynamic properties different from those of the neighboring bulk phases and interfaces. Similar to the case of interfaces, line excess properties may be associated with common lines.

The general conservation equation in terms of microscopic properties for an $\alpha\beta\gamma$-common-line property when this curve is located in a volume, δV, is

$$\frac{d}{dt}\int_{C_{\alpha\beta\gamma}}(\rho\psi)|_{\alpha\beta\gamma}\,dC+\sum_{C_{\alpha\beta\gamma_{\text{ends}}}}\boldsymbol{\lambda}^{*}\cdot[\rho(\boldsymbol{v}-\boldsymbol{w}_{\text{b}})\psi-\boldsymbol{i}]|_{\alpha\beta\gamma}$$
$$+\sum_{\epsilon\neq\alpha,\beta,\gamma}\{\boldsymbol{\lambda}^{\alpha\beta\gamma}\cdot[\rho(\boldsymbol{v}-\boldsymbol{u}_{\text{p}})\psi-\boldsymbol{i}]|_{\alpha\beta\gamma}\}|_{P_{\alpha\beta\gamma\epsilon}}$$
$$-\sum_{ij=\alpha\beta,\beta\gamma,\alpha\gamma}\int_{C_{\alpha\beta\gamma}}\boldsymbol{\nu}^{ij}\cdot[\rho(\boldsymbol{v}-\boldsymbol{u}_{\text{b}})\psi-\boldsymbol{i}]|_{ij}\,dC$$
$$-\int_{C_{\alpha\beta\gamma}}(\rho f)|_{\alpha\beta\gamma}\,dC=\int_{C_{\alpha\beta\gamma}}G|_{\alpha\beta\gamma}\,dC \tag{49}$$

where $C_{\alpha\beta\gamma_{\text{ends}}}$ denotes the intersection of the common line with the boundary of the REV; $P_{\alpha\beta\gamma\epsilon}$ denotes the common point formed at the intersection of the common lines $\alpha\beta\gamma$, $\alpha\beta\epsilon$, $\alpha\gamma\epsilon$ and $\beta\gamma\epsilon$; $\rho|_{\alpha\beta\gamma}$ is the excess mass density of the common line, $[M/L]$, $\psi|_{\alpha\beta\gamma}$ is the property of interest per unit mass, $\boldsymbol{v}|_{\alpha\beta\gamma}$ is the velocity of the common line material, $\boldsymbol{u}_{\text{p}}$ is the velocity of the common point where different common lines terminate, $\boldsymbol{w}_{\text{b}}$ is the velocity of the bounding point of a common line at the exterior boundary of δV, $\boldsymbol{i}|_{\alpha\beta\gamma}$ is a non-convective flux, $\boldsymbol{\lambda}^{*}$ is the unit vector tangent to the curve $C_{\alpha\beta\gamma}$, oriented outward, at a point on the external boundary of δV, $\boldsymbol{\lambda}^{\alpha\beta\gamma}$ is the unit vector tangent to $C_{\alpha\beta\gamma}$ oriented outward from the line at a common point $P_{\alpha\beta\gamma\epsilon}$, $f|_{\alpha\beta\gamma}$ is the external supply of $\psi|_{\alpha\beta\gamma}$, $G|_{\alpha\beta\gamma}$ accounts for the net production of $\psi|_{\alpha\beta\gamma}$ within the $\alpha\beta\gamma$-common line, and the summation in the second term is over all common points formed at the intersection of $C_{\alpha\beta\gamma}$ and all other common lines.

The first term in eqn (49) is the rate of accumulation of ψ on the common line. The second and third summations account for flux out of the common line across the exterior boundary of the volume where it intersects the surface (i.e. on the points where a common line pierces the shell of the volume) and at common points interior to the volume where four phases coincide (i.e. on the $P_{\alpha\beta\gamma\epsilon}$ points), respectively. The fourth term accounts for addition of ψ to the common line from the three surfaces that intersect to form the line. The last integral on the left-hand side of the equation is the external supply term, and the right side of the equation accounts for net production.

The volume δV in which the common line exists is restricted to be an REV at a particular position in space such that its external boundaries are fixed. Therefore, the time derivative in eqn (49) may be related to a partial time derivative at the macroscale. An important relation is obtained by combination of equation $T[1,(0,0,1]$, the transport theorem for a curve, and $T[1,(3,0),0]$, the averaging theorem for a partial time derivative for a property on a curve, as found in Gray *et al.*[13] to obtain the following.

Transport theorem for use with macroscale common line equation

$$\frac{d}{dt}\int_{C_{\alpha\beta\gamma}}F|_{\alpha\beta\gamma}\,dC-\sum_{C_{\alpha\beta\gamma_{\text{ends}}}}\boldsymbol{\lambda}^{*}\cdot\boldsymbol{w}_{\text{b}}F|_{\alpha\beta\gamma}$$
$$=\frac{\partial}{\partial t}\int_{C_{\alpha\beta\gamma}}F|_{\alpha\beta\gamma}\,dC+\nabla\cdot\int_{C_{\alpha\beta\gamma}}(\boldsymbol{u}^{\text{s}}F)|_{\alpha\beta\gamma}\,dC \tag{50}$$

where $\boldsymbol{u}^{\text{s}}|_{\alpha\beta\gamma}=\boldsymbol{v}|_{\alpha\beta\gamma}-\boldsymbol{\lambda}^{\alpha\beta\gamma}\boldsymbol{\lambda}^{\alpha\beta\gamma}\cdot\boldsymbol{v}|_{\alpha\beta\gamma}$. The summation over the end points at the boundary of δV may be converted to a divergence of an integral over the common line by a combination of the averaging theorems for lineal divergence operators, equations $D[1,(3,0),0]$ and $D[1,(0,3),0]$ in Gray *et al.*[13]

Divergence theorem for use with macroscale common line equation

$$\sum_{C_{\alpha\beta\gamma_{\text{ends}}}}\boldsymbol{\lambda}^{*}\cdot\boldsymbol{B}|_{\alpha\beta\gamma}=\nabla\cdot\int_{C_{\alpha\beta\gamma}}\boldsymbol{B}^{\text{c}}|_{\alpha\beta\gamma}\,dC \tag{51a}$$

where

$$\boldsymbol{B}^{\text{c}}|_{\alpha\beta\gamma}=\boldsymbol{\lambda}^{\alpha\beta\gamma}\boldsymbol{\lambda}^{\alpha\beta\gamma}\cdot\boldsymbol{B}|_{\alpha\beta\gamma} \tag{51b}$$

such that $\boldsymbol{B}^{\text{c}}|_{\alpha\beta\gamma}$ is tangent to $C_{\alpha\beta\gamma}$.

Application of eqns (50) and (51a) to eqn (49) provides the general balance equation for a common line in the form

$$\frac{\partial}{\partial t}\int_{C_{\alpha\beta\gamma}}(\rho\psi)|_{\alpha\beta\gamma}\,dC+\nabla\cdot\int_{C_{\alpha\beta\gamma}}[\rho\boldsymbol{v}\psi-\boldsymbol{i}^{\text{c}}]|_{\alpha\beta\gamma}\,dC$$
$$+\sum_{\epsilon\neq\alpha,\beta,\gamma}\{\boldsymbol{\lambda}^{\alpha\beta\gamma}\cdot[\rho(\boldsymbol{v}-\boldsymbol{u}_{\text{p}})\psi-\boldsymbol{i}]|_{\alpha\beta\gamma}\}|_{P_{\alpha\beta\gamma\epsilon}}$$
$$-\sum_{ij=\alpha\beta,\beta\gamma,\alpha\gamma}\int_{C_{\alpha\beta\gamma}}\boldsymbol{\nu}^{ij}\cdot[\rho(\boldsymbol{v}-\boldsymbol{u})\psi-\boldsymbol{i}]|_{ij}\,dC$$
$$-\int_{C_{\alpha\beta\gamma}}(\rho f)|_{\alpha\beta\gamma}\,dC=\int_{C_{\alpha\beta\gamma}}G|_{\alpha\beta\gamma}\,dC \tag{52}$$

where use has been made of the fact that $v|_{\alpha\beta\gamma} = u^{s}|_{\alpha\beta\gamma} + v^{c}|_{\alpha\beta\gamma}$. This equation can be written in terms of averages over the common line after dividing by the averaging volume, δV, to obtain

$$\frac{\partial(l^{\alpha\beta\gamma}\langle\rho\psi\rangle^{\alpha\beta\gamma})}{\partial t} + \nabla\cdot(l^{\alpha\beta\gamma}\langle\rho v\psi\rangle^{\alpha\beta\gamma}) - \nabla\cdot(l^{\alpha\beta\gamma}\langle i^{c}\rangle^{\alpha\beta\gamma}) + \frac{1}{\delta V}\sum_{\epsilon\neq\alpha,\beta,\gamma}\{\lambda^{\alpha\beta\gamma}\cdot[\rho(v-u_{p})\psi - i]|_{\alpha\beta\gamma}\}|_{P_{\alpha\beta\gamma\epsilon}} + \sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}(\hat{e}^{ij}_{\alpha\beta\gamma}\psi^{ij} + \hat{I}^{ij}_{\alpha\beta\gamma}) - l^{\alpha\beta\gamma}\langle\rho f\rangle^{\alpha\beta\gamma} = l^{\alpha\beta\gamma}\langle G\rangle^{\alpha\beta\gamma} \quad (53)$$

where the notation employed to designate averages is such that

$$\langle F\rangle^{\alpha\beta\gamma} = \frac{1}{C_{\alpha\beta\gamma}}\int_{C_{\alpha\beta\gamma}} F|_{\alpha\beta\gamma}\,\mathrm{d}C \quad (54a)$$

and

$$l^{\alpha\beta\gamma} = \frac{1}{\delta V}\int_{C_{\alpha\beta\gamma}}\mathrm{d}C = \frac{C_{\alpha\beta\gamma}}{\delta V} \quad (54b)$$

where $l^{\alpha\beta\gamma}$ is the specific length, the length of $\alpha\beta\gamma$ common line per averaging volume. As with the phase and interface properties, a mass weighted common line average and the deviation of the microscopic property from the macroscopic mean are introduced, respectively, as

$$\bar{F}^{\alpha\beta\gamma} = \frac{1}{\langle\rho\rangle^{\alpha\beta\gamma}C_{\alpha\beta\gamma}}\int_{C_{\alpha\beta\gamma}}(\rho F)|_{\alpha\beta\gamma}\,\mathrm{d}C = \frac{\langle\rho F\rangle^{\alpha\beta\gamma}}{\langle\rho\rangle^{\alpha\beta\gamma}} \quad (54c)$$

and

$$\tilde{F}^{\alpha\beta\gamma} = F|_{\alpha\beta\gamma} - \bar{F}^{\alpha\beta\gamma} \quad (54d)$$

Substitution of these definitions into eqn (53) yields the following.

Macroscale common line balance equation in terms of averaged quantities

$$\frac{\partial(l^{\alpha\beta\gamma}\langle\rho\rangle^{\alpha\beta\gamma}\bar{\psi}^{\alpha\beta\gamma})}{\partial t} + \nabla\cdot(l^{\alpha\beta\gamma}\langle\rho\rangle^{\alpha\beta\gamma}\bar{v}^{\alpha\beta\gamma}\bar{\psi}^{\alpha\beta\gamma}) - \nabla\cdot[l^{\alpha\beta\gamma}(\langle i^{c}\rangle^{\alpha\beta\gamma} - \langle\rho\rangle^{\alpha\beta\gamma}\overline{\tilde{v}^{\alpha\beta\gamma}\tilde{\psi}^{\alpha\beta\gamma}}^{\alpha\beta\gamma})] - \sum_{\epsilon\neq\alpha,\beta,\gamma}(\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}\bar{\psi}^{\alpha\beta\gamma} + \hat{I}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}) + \sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}(\hat{e}^{ij}_{\alpha\beta\gamma}\psi^{ij} + \hat{I}^{ij}_{\alpha\beta\gamma}) - l^{\alpha\beta\gamma}\langle\rho\rangle^{\alpha\beta\gamma}\bar{f}^{\alpha\beta\gamma} = l^{\alpha\beta\gamma}\langle G\rangle^{\alpha\beta\gamma} \quad (55a)$$

where

$$\hat{e}^{ijk}_{\alpha\beta\gamma\epsilon} = \frac{1}{\delta V}\sum_{\epsilon\neq\alpha,\beta,\gamma}\{\lambda^{ijk}\cdot[\rho(u_{p}-v)]|_{ijk}\}|_{P_{\alpha\beta\gamma\epsilon}};$$
$$ijk = \alpha\beta\gamma, \alpha\beta\epsilon, \alpha\gamma\epsilon, \beta\gamma\epsilon \quad (55b)$$

and

$$\hat{I}^{ijk}_{\alpha\beta\gamma\epsilon} = \frac{1}{\delta V}\sum_{\epsilon\neq\alpha,\beta,\gamma}\{\lambda^{ijk}\cdot[i - \rho(v-u_{p})\tilde{\psi}^{ijk}]|_{ijk}\}|_{P_{\alpha\beta\gamma\epsilon}};$$
$$ijk = \alpha\beta\gamma, \alpha\beta\epsilon, \alpha\gamma\epsilon, \beta\gamma\epsilon \quad (55c)$$

The last two equations provide expressions for the interaction of the common line with the points at the end of the line within the averaging volume. The notation in eqn (55a) will be simplified analogously to the procedure for the phase and interface equations using definitions similar to eqns (20a) through (20e) to obtain

$$\frac{\partial(l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\psi^{\alpha\beta\gamma})}{\partial t} + \nabla\cdot(l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}v^{\alpha\beta\gamma}\psi^{\alpha\beta\gamma}) - \nabla\cdot[l^{\alpha\beta\gamma}i^{\alpha\beta\gamma}] - l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}f^{\alpha\beta\gamma} = l^{\alpha\beta\gamma}G^{\alpha\beta\gamma} - \sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}(\hat{e}^{ij}_{\alpha\beta\gamma}\psi^{ij} + \hat{I}^{ij}_{\alpha\beta\gamma}) + \sum_{\epsilon\neq\alpha,\beta,\gamma}(\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}\psi^{\alpha\beta\gamma} + \hat{I}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}) \quad (56)$$

This equation will be used to obtain the macroscale common curve conservation equations for various properties.

4.1 Conservation of mass

For the $\alpha\beta\gamma$-common line, mass conservation is obtained when the microscale properties are given by $\psi|_{\alpha\beta\gamma} = 1$, $i^{c}|_{\alpha\beta\gamma} = 0$, $f|_{\alpha\beta\gamma} = 0$ and $G|_{\alpha\beta\gamma} = 0$. The equation that results from eqn (56) is as follows.

Macroscale mass conservation for the $\alpha\beta\gamma$-common line

$$\frac{\partial(l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma})}{\partial t} + \nabla\cdot(l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}v^{\alpha\beta\gamma}) = -(\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} + \hat{e}^{\alpha\gamma}_{\alpha\beta\gamma} + \hat{e}^{\beta\gamma}_{\alpha\beta\gamma}) + \sum_{\epsilon\neq\alpha,\beta,\gamma}\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon} \quad (57)$$

The two terms on the right-hand side of this equation account, respectively, for the exchange of mass with the interfaces that meet at the common line and with the points at the end of the common line.

4.2 Conservation of momentum

For the $\alpha\beta\gamma$-common line, the momentum equation is obtained from eqn (56) when the microscale properties are such that $\psi|_{\alpha\beta\gamma} = v|_{\alpha\beta\gamma}$, $i|_{\alpha\beta\gamma} = \mathbf{t}|_{\alpha\beta\gamma}$, $f|_{\alpha\beta\gamma} = g|_{\alpha\beta\gamma}$

and $G|_{\alpha\beta\gamma} = 0$ so that

$$\frac{\partial(l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\boldsymbol{v}^{\alpha\beta\gamma})}{\partial t} + \nabla\cdot(l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\boldsymbol{v}^{\alpha\beta\gamma}\boldsymbol{v}^{\alpha\beta\gamma}) - \nabla\cdot[l^{\alpha\beta\gamma}\mathbf{C}^{\alpha\beta\gamma}] - l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\boldsymbol{g}^{\alpha\beta\gamma} = -\sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}(\hat{e}^{ij}_{\alpha\beta\gamma}\boldsymbol{v}^{ij} + \hat{\boldsymbol{T}}^{ij}_{\alpha\beta\gamma}) + \sum_{\epsilon\neq\alpha,\beta,\gamma}(\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}\boldsymbol{v}^{\alpha\beta\gamma} + \hat{\boldsymbol{T}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}) \quad (58a)$$

where

$$\mathbf{C}^{\alpha\beta\gamma} = \langle\mathbf{t}^{c}\rangle^{\alpha\beta\gamma} - \rho^{\alpha\beta\gamma}\overline{\tilde{\boldsymbol{v}}^{\alpha\beta\gamma}\tilde{\boldsymbol{v}}^{\alpha\beta\gamma}}^{\alpha\beta\gamma} \quad (58b)$$

with:

$$\mathbf{t}^{c}|_{\alpha\beta\gamma} = \boldsymbol{\lambda}^{\alpha\beta\gamma}\boldsymbol{\lambda}^{\alpha\beta\gamma}\cdot\mathbf{t}|_{\alpha\beta\gamma}\cdot\boldsymbol{\lambda}^{\alpha\beta\gamma}\boldsymbol{\lambda}^{\alpha\beta\gamma} \quad (58c)$$

and

$$\hat{\boldsymbol{T}}^{ijk}_{\alpha\beta\gamma\epsilon} = \frac{1}{\delta V}\sum_{\epsilon\neq\alpha,\beta,\gamma}\{\boldsymbol{\lambda}^{ijk}\cdot[\mathbf{t}^{c} - \rho(\boldsymbol{v}-\boldsymbol{u}_{\mathrm{p}})\tilde{\boldsymbol{v}}^{ijk}]|_{ijk}\}|_{P_{\alpha\beta\gamma\epsilon}};$$

$$ijk = \alpha\beta\gamma, \alpha\beta\epsilon, \alpha\gamma\epsilon, \beta\gamma\epsilon \quad (58d)$$

Multiplication of the conservation of mass eqn (57) by $\boldsymbol{v}^{\alpha\beta\gamma}$ and subtraction from eqn (58a) yields the macroscopic momentum balance of a common line.

Macroscale momentum balance for the $\alpha\beta\gamma$-common line

$$l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\frac{D^{\alpha\beta\gamma}\boldsymbol{v}^{\alpha\beta\gamma}}{Dt} - \nabla\cdot[l^{\alpha\beta\gamma}\mathbf{C}^{\alpha\beta\gamma}] - l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\boldsymbol{g}^{\alpha\beta\gamma} = -\sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}(\hat{e}^{ij}_{\alpha\beta\gamma}\boldsymbol{v}^{ij,\alpha\beta\gamma} + \hat{\boldsymbol{T}}^{ij}_{\alpha\beta\gamma}) + \sum_{\epsilon\neq\alpha,\beta,\gamma}\hat{\boldsymbol{T}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon} \quad (59)$$

where the $\alpha\beta\gamma$-common line material time derivative is defined by

$$\frac{D^{\alpha\beta\gamma}}{Dt} = \frac{\partial}{\partial t} + \boldsymbol{v}^{\alpha\beta\gamma}\cdot\nabla \quad (60)$$

and $\boldsymbol{v}^{ij,\alpha\beta\gamma}$ denotes the relative macroscopic velocity of the material in interface ij with respect to the $\alpha\beta\gamma$-common line

$$\boldsymbol{v}^{ij,\alpha\beta\gamma} = \boldsymbol{v}^{ij} - \boldsymbol{v}^{\alpha\beta\gamma} \quad (61)$$

4.3 Conservation of angular momentum

Application of conservation of angular momentum to the common line demonstrates that the macroscale stress tensor is symmetric, such that

$$\mathbf{C}^{\alpha\beta\gamma} = \mathbf{C}^{\alpha\beta\gamma^{\mathrm{T}}} \quad (62)$$

4.4 Conservation of energy

For the $\alpha\beta\gamma$-common line, the energy balance equation is obtained from eqn (56) with $\psi|_{\alpha\beta\gamma} = (E + v^2/2)|_{\alpha\beta\gamma}$, $\boldsymbol{i}|_{\alpha\beta\gamma} = (\mathbf{t}\cdot\boldsymbol{v} + \boldsymbol{q})|_{\alpha\beta\gamma}$, $f|_{\alpha\beta\gamma} = (\boldsymbol{g}\cdot\boldsymbol{v} + h)|_{\alpha\beta\gamma}$ and $G|_{\alpha\beta\gamma} = 0$

$$\frac{\partial\{l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}[E^{\alpha\beta\gamma} + (v^{\alpha\beta\gamma})^2/2]\}}{\partial t} + \nabla\cdot\{l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\boldsymbol{v}^{\alpha\beta\gamma}[E^{\alpha\beta\gamma} + (v^{\alpha\beta\gamma})^2/2]\} - \nabla\cdot[l^{\alpha\beta\gamma}(\mathbf{C}^{\alpha\beta\gamma}\cdot\boldsymbol{v}^{\alpha\beta\gamma} + \boldsymbol{q}^{\alpha\beta\gamma})] - l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}(\boldsymbol{g}^{\alpha\beta\gamma}\cdot\boldsymbol{v}^{\alpha\beta\gamma} + h^{\alpha\beta\gamma}) = -\sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}\{\hat{e}^{ij}_{\alpha\beta\gamma}[E^{ij} + (v^{ij})^2/2] + \hat{\boldsymbol{T}}^{ij}_{\alpha\beta\gamma}\cdot\boldsymbol{v}^{ij} + \hat{Q}^{ij}_{\alpha\beta\gamma}\} + \sum_{\epsilon\neq\alpha,\beta,\gamma}\{\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}[E^{\alpha\beta\gamma} + (v^{\alpha\beta\gamma})^2/2] + \hat{\boldsymbol{T}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}\cdot\boldsymbol{v}^{\alpha\beta\gamma} + \hat{Q}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}\} \quad (63a)$$

where

$$E^{\alpha\beta\gamma} = \bar{E}^{\alpha\beta\gamma} + \overline{(\tilde{v}^{\alpha\beta\gamma})^2}^{\alpha\beta\gamma}/2 \quad (63b)$$

$$\boldsymbol{q}^{\alpha\beta\gamma} = \langle\boldsymbol{q}\rangle^{\alpha\beta\gamma} + \langle\mathbf{t}|_{\alpha\beta\gamma}\cdot\tilde{\boldsymbol{v}}^{\alpha\beta\gamma}\rangle^{\alpha\beta\gamma} - \rho^{\alpha\beta\gamma}\overline{\tilde{\boldsymbol{v}}^{\alpha\beta\gamma}(\tilde{E}^{\alpha\beta\gamma} + (\tilde{v}^{\alpha\beta\gamma})^2/2)}^{\alpha\beta\gamma} \quad (63c)$$

$$h^{\alpha\beta\gamma} = \bar{h}^{\alpha\beta\gamma} + \overline{\boldsymbol{g}\cdot\tilde{\boldsymbol{v}}^{\alpha\beta\gamma}}^{\alpha\beta\gamma} \quad (63d)$$

and:

$$\hat{Q}^{ijk}_{\alpha\beta\gamma\epsilon} = \frac{1}{\delta V}\{\boldsymbol{\lambda}^{ijk}\cdot[\boldsymbol{q} + \mathbf{t}\cdot\tilde{\boldsymbol{v}}^{ijk} - \rho(\boldsymbol{v}-\boldsymbol{u}_{\mathrm{p}})(\tilde{E}^{ijk} + (\tilde{v}^{ijk})^2/2)]|_{ijk}\}|_{P_{\alpha\beta\gamma\epsilon}};$$

$$ijk = \alpha\beta\gamma, \alpha\beta\epsilon, \alpha\gamma\epsilon, \beta\gamma\epsilon \quad (63e)$$

The two summations on the right-hand side of eqn (63a) account, respectively, for the exchange of energy with the adjacent interfaces and with the end points of the $\alpha\beta\gamma$ common lines with δV.

Continuity eqn (57) may be multiplied by $E^{\alpha\beta\gamma} + (v^{\alpha\beta\gamma})^2/2$ and then subtracted from energy eqn (63a). The scalar product of $\boldsymbol{v}^{\alpha\beta\gamma}$ with momentum eqn (59) may also be subtracted from the energy equation. The result of these operations is as follows.

Macroscale energy conservation for the $\alpha\beta\gamma$-common line

$$l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\frac{D^{\alpha\beta\gamma}E^{\alpha\beta\gamma}}{Dt} - \nabla\cdot(l^{\alpha\beta\gamma}\boldsymbol{q}^{\alpha\beta\gamma}) - l^{\alpha\beta\gamma}\mathbf{C}^{\alpha\beta\gamma}:\nabla\boldsymbol{v}^{\alpha\beta\gamma} - l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}h^{\alpha\beta\gamma} = -\sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}\{\hat{e}^{ij}_{\alpha\beta\gamma}[E^{ij,\alpha\beta\gamma} + (v^{ij,\alpha\beta\gamma})^2/2] + \hat{\boldsymbol{T}}^{ij}_{\alpha\beta\gamma}\cdot\boldsymbol{v}^{ij,\alpha\beta\gamma} + \hat{Q}^{ij}_{\alpha\beta\gamma}\} + \sum_{\epsilon\neq\alpha,\beta,\gamma}\hat{Q}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon} \quad (64)$$

where $E^{ij,\alpha\beta\gamma} = E^{ij} - E^{\alpha\beta\gamma}$ and $\boldsymbol{v}^{ij,\alpha\beta\gamma} = \boldsymbol{v}^{ij} - \boldsymbol{v}^{\alpha\beta\gamma}$.

4.5 Balance equation for entropy

For the $\alpha\beta\gamma$-common line, the balance equation for entropy can be obtained from eqn (56) when the microscale quantities have been defined as $\psi|_{\alpha\beta\gamma} = \eta|_{\alpha\beta\gamma}$, $\boldsymbol{i}|_{\alpha\beta\gamma} = \boldsymbol{\varphi}|_{\alpha\beta\gamma}, f|_{\alpha\beta\gamma} = b|_{\alpha\beta\gamma}$, and $G|_{\alpha\beta\gamma} = \Lambda|_{\alpha\beta\gamma}$ where the entropy, $\eta|_{\alpha\beta\gamma}$, is on a per unit mass basis. If the appropriate definition of macroscale quantities in terms of averages of microscale counterparts are invoked, the resulting balance equation is

$$\frac{\partial(l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\eta^{\alpha\beta\gamma})}{\partial t} + \nabla\cdot(l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\boldsymbol{v}^{\alpha\beta\gamma}\eta^{\alpha\beta\gamma}) - \nabla\cdot[l^{\alpha\beta\gamma}\boldsymbol{\varphi}^{\alpha\beta\gamma}] - l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}b^{\alpha\beta\gamma} = l^{\alpha\beta\gamma}\Lambda^{\alpha\beta\gamma} - \sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}(\hat{e}^{ij}_{\alpha\beta\gamma}\eta^{ij} + \hat{\Phi}^{ij}_{\alpha\beta\gamma}) + \sum_{\epsilon\neq\alpha,\beta,\gamma}(\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}\eta^{\alpha\beta\gamma} + \hat{\Phi}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}) \tag{65a}$$

where

$$\eta^{\alpha\beta\gamma} = \bar{\eta}^{\alpha\beta\gamma} \tag{65b}$$

$$\boldsymbol{\varphi}^{\alpha\beta\gamma} = \langle\boldsymbol{\varphi}^{c}\rangle^{\alpha\beta\gamma} - \rho^{\alpha\beta\gamma}\overline{\tilde{\boldsymbol{v}}^{\alpha\beta\gamma}\tilde{\eta}^{\alpha\beta\gamma}}^{\alpha\beta\gamma} \tag{65c}$$

$$b^{\alpha\beta\gamma} = \bar{b}^{\alpha\beta\gamma} \tag{65d}$$

$$\Lambda^{\alpha\beta\gamma} = \langle\Lambda\rangle^{\alpha\beta\gamma} \tag{65e}$$

and:

$$\hat{\Phi}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon} = \frac{1}{\delta V}\{\boldsymbol{\lambda}^{\alpha\beta\gamma}\cdot[\boldsymbol{\varphi}^{c} - \rho(\boldsymbol{v} - \boldsymbol{u}_{p})\tilde{\eta}^{\alpha\beta\gamma}]|_{\alpha\beta\gamma}\}|_{P_{\alpha\beta\gamma\epsilon}} \tag{65f}$$

where the evaluation in eqn (65f) is over all points $P_{\alpha\beta\gamma\epsilon}$ in the REV. Multiplication of the macroscale common line mass conservation equation, eqn (57), by $\eta^{\alpha\beta\gamma}$ and subtraction from eqn (65a) yields the entropy balance in the following form.

Macroscopic entropy balance for the $\alpha\beta\gamma$-common line

$$l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\frac{D^{\alpha\beta\gamma}\eta^{\alpha\beta\gamma}}{Dt} - \nabla\cdot(l^{\alpha\beta\gamma}\boldsymbol{\varphi}^{\alpha\beta\gamma}) - l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}b^{\alpha\beta\gamma} = l^{\alpha\beta\gamma}\Lambda^{\alpha\beta\gamma} - \sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}(\hat{e}^{ij}_{\alpha\beta\gamma}\eta^{ij,\alpha\beta\gamma} + \hat{\Phi}^{ij}_{\alpha\beta\gamma}) + \sum_{\epsilon\neq\alpha,\beta,\gamma}\hat{\Phi}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon} \tag{66}$$

5 COMMON POINT EQUATIONS

Common points that are the loci of the convergence of common lines are considered to have no properties. These points act merely as discontinuities between common lines and give rise to jump conditions for the conservation laws. The following point conditions will have to apply.

Common point condition for mass

$$\sum_{ijk=\alpha\beta\gamma,\alpha\beta\epsilon,\alpha\gamma\epsilon,\beta\gamma\epsilon}\hat{e}^{ijk}_{\alpha\beta\gamma\epsilon} = 0 \tag{67}$$

Common point condition for momentum

$$\sum_{ijk=\alpha\beta\gamma,\alpha\beta\epsilon,\alpha\gamma\epsilon,\beta\gamma\epsilon}(\hat{e}^{ijk}_{\alpha\beta\gamma\epsilon}\boldsymbol{v}^{ijk} + \hat{\boldsymbol{T}}^{ijk}_{\alpha\beta\gamma\epsilon}) = 0 \tag{68}$$

Common point condition for energy

$$\sum_{ijk=\alpha\beta\gamma,\alpha\beta\epsilon,\alpha\gamma\epsilon,\beta\gamma\epsilon}\{\hat{e}^{ijk}_{\alpha\beta\gamma\epsilon}[E^{ijk} + (v^{ijk})^2/2] + \hat{\boldsymbol{T}}^{ijk}_{\alpha\beta\gamma\epsilon}\cdot\boldsymbol{v}^{ijk} + \hat{Q}^{ijk}_{\alpha\beta\gamma\epsilon}\} = 0 \tag{69}$$

Common point condition for entropy generation

$$\Lambda^{\alpha\beta\gamma\epsilon} - \sum_{ijk=\alpha\beta\gamma,\alpha\beta\epsilon,\alpha\gamma\epsilon,\beta\gamma\epsilon}(\hat{e}^{ijk}_{\alpha\beta\gamma\epsilon}\eta^{ijk} + \hat{\Phi}^{ijk}_{\alpha\beta\gamma\epsilon}) = 0 \tag{70}$$

6 THE SECOND LAW OF THERMODYNAMICS

The development of macroscopic balance laws for a multiphase system is not complete without an appropriate form of the second law of thermodynamics. The starting point is the general statement of the second law for a system. The second law prescribes that the net rate of production of entropy of a system must be non-negative. In terms of microscopic quantities, this may be written as

$$\int_V \Lambda\, dV \geq 0 \tag{71}$$

This equation is a statement that the right-hand side of general balance eqn (2) is non-negative for the entropy balance. As with the other macroscopic balance laws, two approaches for the derivation of the macroscopic form of the second law are possible.

One approach is to follow the procedure employed in this work and write eqn (71) for the REV. Because the system in the REV consists of phases, interfaces, common lines, and common points, eqn (71) for the REV becomes

$$\sum_{\alpha}\int_{\delta V^{\alpha}}\Lambda\, dV + \sum_{\alpha\beta}\int_{S^{\alpha\beta}}\Lambda\, dS + \sum_{\alpha\beta\gamma}\int_{C^{\alpha\beta\gamma}}\Lambda\, dC + \sum_{P_{\alpha\beta\gamma\epsilon}}\Lambda^{\alpha\beta\gamma\epsilon} \geq 0 \tag{72}$$

Division of this by δV and the use of averaging definitions yields the macroscopic form of the second law

$$\sum_{\alpha}\epsilon^{\alpha}\Lambda^{\alpha} + \sum_{\alpha\beta}a^{\alpha\beta}\Lambda^{\alpha\beta} + \sum_{\alpha\beta\gamma}l^{\alpha\beta\gamma}\Lambda^{\alpha\beta\gamma} + \sum_{P_{\alpha\beta\gamma\epsilon}}\Lambda^{\alpha\beta\gamma\epsilon} \geq 0 \tag{73}$$

We can now substitute for the individual net rates of production of entropy, Λ^{α}, $\Lambda^{\alpha\beta}$, $\Lambda^{\alpha\beta\gamma}$ and $\Lambda^{\alpha\beta\gamma\epsilon}$, from eqns (30), (48), (66) and (70), respectively. The resulting entropy inequality for the whole system at a given macroscopic point is

$$\sum_{\alpha}\left\{\epsilon^{\alpha}\rho^{\alpha}\frac{D^{\alpha}\eta^{\alpha}}{Dt}-\nabla\cdot(\epsilon^{\alpha}\varphi^{\alpha})-\epsilon^{\alpha}\rho^{\alpha}b^{\alpha}\right\}$$
$$+\sum_{\alpha\beta}\left\{a^{\alpha\beta}\rho^{\alpha\beta}\frac{D^{\alpha\beta}\eta^{\alpha\beta}}{Dt}-\nabla\cdot(a^{\alpha\beta}\varphi^{\alpha\beta})\right.$$
$$\left.-a^{\alpha\beta}\rho^{\alpha\beta}b^{\alpha\beta}+\sum_{i=\alpha,\beta}(\hat{e}^{i}_{\alpha\beta}\eta^{i,\alpha\beta})\right\}$$
$$+\sum_{\alpha\beta\gamma}\left\{l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\frac{D^{\alpha\beta\gamma}\eta^{\alpha\beta\gamma}}{Dt}-\nabla\cdot(l^{\alpha\beta\gamma}\varphi^{\alpha\beta\gamma})\right.$$
$$\left.-l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}b^{\alpha\beta\gamma}+\sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}(\hat{e}^{ij}_{\alpha\beta\gamma}\eta^{ij,\alpha\beta\gamma})\right\}$$
$$+\sum_{\alpha\beta\gamma\epsilon}\left\{\sum_{ijk=\alpha\beta\gamma,\alpha\beta\epsilon,\alpha\gamma\epsilon,\beta\gamma\epsilon}(\hat{e}^{ijk}_{\alpha\beta\gamma\epsilon}\eta^{ijk,r})\right\}\geq 0 \tag{74}$$

where η^{r} is a reference entropy that may be selected arbitrarily.

A second approach would be to localize the inequality (71) at the microscale to obtain

$$\Lambda\geq 0 \tag{75}$$

A microscale point may lie in a phase, on an interface, on a common line, or be a common point and inequality (75) holds at any of these points. Thus, this inequality can be averaged over a phase, an interface, a common line, or for a particular common point type within an REV to obtain

$$\Lambda^{\alpha}\geq 0 \tag{76a}$$
$$\Lambda^{\alpha\beta}\geq 0 \tag{76b}$$
$$\Lambda^{\alpha\beta\gamma}\geq 0 \tag{76c}$$
$$\Lambda^{\alpha\beta\gamma\epsilon}\geq 0 \tag{76d}$$

Thus, an entropy inequality may be written for each phase, interface, common line, or common point. However, further examination of the consequences of these inequalities will show that the individual entropy inequalities of eqns (76a) through (76d) are not useful in the development of the constitutive theory. To see this, combine the entropy balance (30) with (76a) to obtain

$$\epsilon^{\alpha}\rho^{\alpha}\frac{D^{\alpha}\eta^{\alpha}}{Dt}-\nabla\cdot(\epsilon^{\alpha}\varphi^{\alpha})-\epsilon^{\alpha}\rho^{\alpha}b^{\alpha}\geq\sum_{\beta\neq\alpha}\hat{\Phi}^{\alpha}_{\alpha\beta} \tag{77a}$$

For this to be a useful expression for determining constitutive relations, something must be known about the sign of the term $\hat{\Phi}^{\alpha}_{\alpha\beta}$. However, such information is not available; and this entropy exchange term may be positive, negative or zero. In other words, the macroscale entropy inequality cannot be applied to obtain constitutive relations for one phase that is a part of a multiphase system without accounting for the interaction of that phase with other phases, interfaces, and common lines. The same difficulty arises when considering the entropy inequalities for interfaces and common lines. For the interfaces, the common lines, and the common points, the following equations are obtained from eqns (48), (66) and (70), respectively

$$a^{\alpha\beta}\rho^{\alpha\beta}\frac{D^{\alpha\beta}\eta^{\alpha\beta}}{Dt}-\nabla\cdot(a^{\alpha\beta}\varphi^{\alpha\beta})-a^{\alpha\beta}\rho^{\alpha\beta}b^{\alpha\beta}$$
$$+\sum_{i=\alpha,\beta}(\hat{e}^{i}_{\alpha\beta}\eta^{i,\alpha\beta})\geq\sum_{\gamma\neq\alpha,\beta}\hat{\Phi}^{\alpha\beta}_{\alpha\beta\gamma}-\sum_{i=\alpha,\beta}\hat{\Phi}^{i}_{\alpha\beta} \tag{77b}$$

$$l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\frac{D^{\alpha\beta\gamma}\eta^{\alpha\beta\gamma}}{Dt}-\nabla\cdot(l^{\alpha\beta\gamma}\varphi^{\alpha\beta\gamma})-l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}b^{\alpha\beta\gamma}$$
$$+\sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}(\hat{e}^{ij}_{\alpha\beta\gamma}\eta^{ij,\alpha\beta\gamma})$$
$$\geq\sum_{\epsilon\neq\alpha,\beta,\gamma}\hat{\Phi}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}-\sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}\hat{\Phi}^{ij}_{\alpha\beta\gamma} \tag{77c}$$

and

$$\sum_{ijk=\alpha\beta\gamma,\alpha\beta\epsilon,\alpha\gamma\epsilon,\beta\gamma\epsilon}\hat{e}^{ijk}_{\alpha\beta\gamma\epsilon}\eta^{ijk}$$
$$\geq-\sum_{ijk=\alpha\beta\gamma,\alpha\beta\epsilon,\alpha\gamma\epsilon,\beta\gamma\epsilon}\hat{\Phi}^{ijk}_{\alpha\beta\gamma\epsilon} \tag{77d}$$

Unless a phase, interface, or common line does not interact with its adjacent interface, common line, or common point, the only way to eliminate the exchange terms from these individual entropy expressions is to sum inequalities (77a) through (77d). The resulting equation is the same as inequality (74) obtained via the first approach. This inequality is very important and has a central role in the derivation of constitutive equations.

To actually use eqn (74) in deriving constitutive equations, it is convenient to write it in terms of the rate of change of Helmholtz free energy rather than in terms of rate of change of entropy. For the phases, the free energy per unit mass will be employed such that:

$$A^{\alpha}=E^{\alpha}-\theta^{\alpha}\eta^{\alpha} \tag{78}$$

For the interfaces, it is convenient to work with thermodynamic properties defined on a per unit area basis such that

$$\hat{\mathscr{F}}^{\alpha\beta}=\rho^{\alpha\beta}\mathscr{F}^{\alpha\beta} \tag{79a}$$

where $\mathscr{F}^{\alpha\beta}$ is a thermodynamic property of an $\alpha\beta$ interface defined on a per unit mass basis and $\hat{\mathscr{F}}^{\alpha\beta}$ is the same property on a per unit area basis. With this notation, the Helmholtz free energy per unit area is

$$\hat{A}^{\alpha\beta}=\hat{E}^{\alpha\beta}-\theta^{\alpha\beta}\hat{\eta}^{\alpha\beta}=\rho^{\alpha\beta}E^{\alpha\beta}-\theta^{\alpha\beta}\rho^{\alpha\beta}\eta^{\alpha\beta} \tag{79b}$$

Similarly, the thermodynamic properties of the common line may be defined per unit length with

$$\hat{\mathscr{F}}^{\alpha\beta\gamma} = \rho^{\alpha\beta\gamma}\mathscr{F}^{\alpha\beta\gamma} \tag{80a}$$

where $\mathscr{F}^{\alpha\beta\gamma}$ is a thermodynamic property of an $\alpha\beta\gamma$ common line defined on a per unit mass basis and $\hat{\mathscr{F}}^{\alpha\beta\gamma}$ is the same property on a per unit length basis. The Helmholtz free energy per unit length is

$$\begin{aligned}\hat{A}^{\alpha\beta\gamma} &= \hat{E}^{\alpha\beta\gamma} - \theta^{\alpha\beta\gamma}\hat{\eta}^{\alpha\beta\gamma} \\ &= \rho^{\alpha\beta\gamma}E^{\alpha\beta\gamma} - \theta^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\eta^{\alpha\beta\gamma}\end{aligned} \tag{80b}$$

Material derivatives of the definitions of free energy can be related to material derivatives of entropy and substituted into eqn (74). Additionally, the energy and momentum equations can be employed to eliminate other terms that arise. The result of these algebraic manipulations is the entropy inequality in the following form.

Entropy inequality in terms of Helmholtz free energy

$$\begin{aligned}
&-\sum_{\alpha}\frac{\epsilon^\alpha\rho^\alpha}{\theta^\alpha}\left[\frac{D^\alpha A^\alpha}{Dt} + \eta^\alpha\frac{D^\alpha\theta^\alpha}{Dt}\right] + \sum_{\alpha}\frac{\epsilon^\alpha}{\theta^\alpha}\mathbf{t}^\alpha : \mathbf{d}^\alpha \\
&-\sum_{\alpha\beta}\frac{1}{\theta^{\alpha\beta}}\left[\frac{D^{\alpha\beta}(a^{\alpha\beta}\hat{A}^{\alpha\beta})}{Dt} + a^{\alpha\beta}\hat{\eta}^{\alpha\beta}\frac{D^{\alpha\beta}\theta^{\alpha\beta}}{Dt}\right] \\
&+\sum_{\alpha\beta}\frac{a^{\alpha\beta}}{\theta^{\alpha\beta}}(\mathbf{S}^{\alpha\beta} - \hat{A}^{\alpha\beta}\mathbf{I}) : \mathbf{d}^{\alpha\beta} - \sum_{\alpha\beta\gamma}\frac{1}{\theta^{\alpha\beta\gamma}} \\
&\times\left[\frac{D^{\alpha\beta\gamma}(l^{\alpha\beta\gamma}\hat{A}^{\alpha\beta\gamma})}{Dt} + l^{\alpha\beta\gamma}\hat{\eta}^{\alpha\beta\gamma}\frac{D^{\alpha\beta\gamma}\theta^{\alpha\beta\gamma}}{Dt}\right] \\
&+\sum_{\alpha\beta\gamma}\frac{l^{\alpha\beta\gamma}}{\theta^{\alpha\beta\gamma}}(\mathbf{C}^{\alpha\beta\gamma} - \hat{A}^{\alpha\beta\gamma}\mathbf{I}) : \mathbf{d}^{\alpha\beta\gamma} \\
&-\sum_{\alpha\beta}\sum_{\gamma\neq\alpha,\beta}\frac{1}{\theta^{\alpha\beta\gamma}}\hat{\boldsymbol{T}}^{\alpha\beta}_{\alpha\beta\gamma}\cdot\boldsymbol{v}^{\alpha\beta,\alpha\beta\gamma} \\
&-\sum_{\alpha}\sum_{\beta\neq\alpha}\frac{1}{\theta^{\alpha\beta}}\hat{\boldsymbol{T}}^{\alpha}_{\alpha\beta}\cdot\boldsymbol{v}^{\alpha,\alpha\beta} \\
&-\sum_{\alpha\beta\gamma}\sum_{\epsilon\neq\alpha,\beta,\gamma}\frac{1}{\theta^{\mathrm{r}}}\hat{\boldsymbol{T}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}\cdot\boldsymbol{v}^{\alpha\beta\gamma,\mathrm{r}} \\
&+\sum_{\alpha}\frac{\epsilon^\alpha}{(\theta^\alpha)^2}\boldsymbol{q}^\alpha\cdot\nabla\theta^\alpha + \sum_{\alpha\beta}\frac{a^{\alpha\beta}}{(\theta^{\alpha\beta})^2}\boldsymbol{q}^{\alpha\beta}\cdot\nabla\theta^{\alpha\beta} \\
&+\sum_{\alpha\beta\gamma}\frac{l^{\alpha\beta\gamma}}{(\theta^{\alpha\beta\gamma})^2}\boldsymbol{q}^{\alpha\beta\gamma}\cdot\nabla\theta^{\alpha\beta\gamma} \\
&-\sum_{\alpha}\nabla\cdot\left[\epsilon^\alpha\left(\varphi^\alpha - \frac{\boldsymbol{q}^\alpha}{\theta^\alpha}\right)\right] \\
&-\sum_{\alpha\beta}\nabla\cdot\left[a^{\alpha\beta}\left(\varphi^{\alpha\beta} - \frac{\boldsymbol{q}^{\alpha\beta}}{\theta^{\alpha\beta}}\right)\right] \\
&-\sum_{\alpha\beta\gamma}\nabla\cdot\left[l^{\alpha\beta\gamma}\left(\varphi^{\alpha\beta\gamma} - \frac{\boldsymbol{q}^{\alpha\beta\gamma}}{\theta^{\alpha\beta\gamma}}\right)\right] \\
&-\sum_{\alpha}\left[\epsilon^\alpha\rho^\alpha\left(b^\alpha - \frac{h^\alpha}{\theta^\alpha}\right)\right] - \sum_{\alpha\beta}\left[a^{\alpha\beta}\rho^{\alpha\beta}\left(b^{\alpha\beta} - \frac{h^{\alpha\beta}}{\theta^{\alpha\beta}}\right)\right] \\
&-\sum_{\alpha\beta\gamma}\left[l^{\alpha\beta\gamma}\rho^{\alpha\beta\gamma}\left(b^{\alpha\beta\gamma} - \frac{h^{\alpha\beta\gamma}}{\theta^{\alpha\beta\gamma}}\right)\right] \\
&-\sum_{\alpha}\sum_{\beta\neq\alpha}\frac{\hat{e}^{\alpha}_{\alpha\beta}}{\theta^{\alpha\beta}}[A^\alpha + \eta^\alpha\theta^{\alpha,\alpha\beta} + \tfrac{1}{2}(v^{\alpha,\alpha\beta})^2] \\
&-\sum_{\alpha\beta}\sum_{\gamma\neq\alpha,\beta}\frac{\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}}{\theta^{\alpha\beta\gamma}}\left[\frac{E^{\alpha\beta}\theta^{\alpha\beta,\alpha\beta\gamma}}{\theta^{\alpha\beta}} + \tfrac{1}{2}(v^{\alpha\beta,\alpha\beta\gamma})^2\right] \\
&-\sum_{\alpha\beta\gamma}\sum_{\epsilon\neq\alpha,\beta,\gamma}\frac{\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon}}{\theta^{\mathrm{r}}}\left[\frac{E^{\alpha\beta\gamma}\theta^{\alpha\beta\gamma,\mathrm{r}}}{\theta^{\alpha\beta\gamma}} + \tfrac{1}{2}(v^{\alpha\beta\gamma,\mathrm{r}})^2\right] \\
&-\sum_{\alpha}\sum_{\beta\neq\alpha}\frac{\theta^{\alpha,\alpha\beta}}{\theta^\alpha\theta^{\alpha\beta}}\hat{Q}^{\alpha}_{\alpha\beta} - \sum_{\alpha\beta}\sum_{\gamma\neq\alpha,\beta}\frac{\theta^{\alpha\beta,\alpha\beta\gamma}}{\theta^{\alpha\beta}\theta^{\alpha\beta\gamma}}\hat{Q}^{\alpha\beta}_{\alpha\beta\gamma} \\
&-\sum_{\alpha\beta\gamma}\sum_{\epsilon\neq\alpha,\beta,\gamma}\frac{\theta^{\alpha\beta\gamma,\mathrm{r}}}{\theta^{\alpha\beta\gamma}\theta^{\mathrm{r}}}\hat{Q}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon} \geq 0
\end{aligned} \tag{81}$$

where θ^{r} is an arbitrary reference temperature. After hypothesizing constitutive dependencies for the free energy, this equation may be used to develop constitutive forms and macroscale thermodynamic relations.

7 MASSLESS INTERFACES AND COMMON LINES

7.1 Interface and common line mass conservation equations

An interesting and important special case of an interface between phases is when the interface can be considered to be massless. For this case, $\rho^{\alpha\beta} \to 0$, and eqn (39) reduces to the following form.

Macroscale mass conservation at a massless $\alpha\beta$-interface

$$\hat{e}^{\alpha}_{\alpha\beta} + \hat{e}^{\beta}_{\alpha\beta} = 0 \tag{82a}$$

and

$$\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} = 0 \tag{82b}$$

Thus eqn (82a) indicates that the mass leaving a phase on one side of an interface is transferred directly to the phase on the other side of the interface such that the interface itself stores no mass. Equation (82b) indicates that no mass can be transferred between a massless interface and a common line.

When the common line is massless such that $\rho^{\alpha\beta\gamma} \to 0$, eqn (57) simplifies and provides restrictions on the exchange of mass between the common line and the surfaces that form the line and between the common line and common points.

Macroscale mass conservation for a massless $\alpha\beta\gamma$-common line

$$\hat{e}^{\alpha\beta}_{\alpha\beta\gamma} + \hat{e}^{\alpha\gamma}_{\alpha\beta\gamma} + \hat{e}^{\beta\gamma}_{\alpha\beta\gamma} = 0 \tag{83a}$$

and

$$\hat{e}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon} = 0 \tag{83b}$$

Equation (83a) states that the mass transferred among interfaces at a common line takes place such that the common line itself holds no mass. If the interfaces themselves are also massless, then constraint (83a) simplifies further so that each term on the left-hand side is zero as in eqn (82b). Equation (83b) indicates that a massless common line cannot transfer mass at a common point.

7.2 Interface and common line momentum conservation equations

When the interface is massless, it may nevertheless sustain a stress. So, in the limit where $\rho^{\alpha\beta} \to 0$, the momentum balance eqn (41) still provides a restriction on the interface as well as on its exchange of momentum with neighboring phases and common lines.

Macroscale momentum conservation for a massless $\alpha\beta$-interface

$$-\nabla \cdot (a^{\alpha\beta}\mathbf{S}^{\alpha\beta}) = -\hat{\boldsymbol{T}}^{\alpha}_{\alpha\beta} - \hat{\boldsymbol{T}}^{\beta}_{\alpha\beta} - \hat{e}^{\alpha}_{\alpha\beta}\boldsymbol{v}^{\alpha,\beta} + \sum_{\gamma\neq\alpha,\beta} \hat{\boldsymbol{T}}^{\alpha\beta}_{\alpha\beta\gamma} \tag{84}$$

where $\boldsymbol{v}^{\alpha,\beta} = \boldsymbol{v}^{\alpha} - \boldsymbol{v}^{\beta}$.

When the common line is massless and is also the location where massless interfaces come together, it may nevertheless sustain a stress. Thus, in the limit where $\rho^{\alpha\beta\gamma} \to 0$, the equation for stress in the common line is obtained from eqn (59) as the following.

Macroscale momentum conservation for a massless $\alpha\beta\gamma$-common line

$$-\nabla \cdot [l^{\alpha\beta\gamma}\mathbf{C}^{\alpha\beta\gamma}] = -\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\boldsymbol{v}^{\alpha\beta,\alpha\gamma} - \hat{e}^{\beta\gamma}_{\alpha\beta\gamma}\boldsymbol{v}^{\beta\gamma,\alpha\gamma} - \sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma} \hat{\boldsymbol{T}}^{ij}_{\alpha\beta\gamma} + \sum_{\epsilon\neq\alpha,\beta,\gamma} \hat{\boldsymbol{T}}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon} \tag{85}$$

Note that if the interfaces are massless, as well as the common line, the first two terms on the right-hand side of eqn (85) will also be zero by constraint (82b).

7.3 Interface and common line energy balance equations

For the situation where the interface may be considered massless, internal energy and the external source term must be converted from a per-unit-mass basis to a per-unit-area basis. This may be done directly by defining

$$\hat{E}^{\alpha\beta} = \lim_{\rho^{\alpha\beta}\to 0} (\rho^{\alpha\beta}E^{\alpha\beta}) \tag{86a}$$

and

$$\hat{h}^{\alpha\beta} = \lim_{\rho^{\alpha\beta}\to 0} (\rho^{\alpha\beta}h^{\alpha\beta}) \tag{86b}$$

Use of these definitions in eqn (45a), noting that the kinetic energy of the interface will be zero, use of momentum constraint (84), and application of the restrictions on the mass exchange terms through a massless interface given by eqn (82a) gives the following.

Macroscale energy conservation for a massless $\alpha\beta$-interface

$$\frac{D^{\alpha\beta}(a^{\alpha\beta}\hat{E}^{\alpha\beta})}{Dt} - a^{\alpha\beta}(\mathbf{S}^{\alpha\beta} - \hat{E}^{\alpha\beta}\mathbf{I}) : \nabla\boldsymbol{v}^{\alpha\beta} - a^{\alpha\beta}\hat{h}^{\alpha\beta} - \nabla\cdot(a^{\alpha\beta}\boldsymbol{q}^{\alpha\beta}) = \sum_{\gamma\neq\alpha,\beta} \hat{Q}^{\alpha\beta}_{\alpha\beta\gamma} - \hat{e}^{\alpha}_{\alpha\beta}[E^{\alpha,\beta} + 1/2(v^{\alpha,\beta})^2] - \sum_{i=\alpha,\beta}[\hat{\boldsymbol{T}}^{i}_{\alpha\beta}\cdot\boldsymbol{v}^{i,\alpha\beta} + \hat{Q}^{i}_{\alpha\beta}] \tag{87}$$

In similar fashion, when the common line may be considered massless, internal energy and the external source term must be converted from a 'per unit mass' basis to a 'per unit length' basis with the definitions

$$\hat{E}^{\alpha\beta\gamma} = \lim_{\rho^{\alpha\beta\gamma}\to 0} (\rho^{\alpha\beta\gamma}E^{\alpha\beta\gamma}) \tag{88a}$$

and

$$\hat{h}^{\alpha\beta\gamma} = \lim_{\rho^{\alpha\beta\gamma}\to 0} (\rho^{\alpha\beta\gamma}h^{\alpha\beta\gamma}) \tag{88b}$$

Use of these definitions in eqn (63a) and application of the restrictions on the mass exchange terms through a massless interface given by eqns (83a) and (83b) subject to momentum constraint (85) gives the following.

Macroscale energy conservation of a massless $\alpha\beta\gamma$-common line

$$\frac{D^{\alpha\beta\gamma}(l^{\alpha\beta\gamma}\hat{E}^{\alpha\beta\gamma})}{Dt} - l^{\alpha\beta\gamma}(\mathbf{C}^{\alpha\beta\gamma} - \hat{E}^{\alpha\beta\gamma}\mathbf{I}) : \nabla\boldsymbol{v}^{\alpha\beta\gamma} - l^{\alpha\beta\gamma}\hat{h}^{\alpha\beta\gamma} - \nabla\cdot(l^{\alpha\beta\gamma}\boldsymbol{q}^{\alpha\beta\gamma}) = -\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\{E^{\alpha\beta,\beta\gamma} + 1/2[v^{\alpha\beta,\beta\gamma}(v^{\alpha\beta,\alpha\beta\gamma} + v^{\beta\gamma,\alpha\beta\gamma})]^2\} - \hat{e}^{\alpha\gamma}_{\alpha\beta\gamma}\{E^{\alpha\gamma,\beta\gamma} + 1/2[v^{\alpha\gamma,\beta\gamma}(v^{\alpha\gamma,\alpha\beta\gamma} + v^{\beta\gamma,\alpha\beta\gamma})]^2\} + \sum_{\epsilon\neq\alpha,\beta,\gamma} \hat{Q}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon} - \sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma}[\hat{\boldsymbol{T}}^{ij}_{\alpha\beta\gamma}\cdot\boldsymbol{v}^{ij,\alpha\beta\gamma} + \hat{Q}^{ij}_{\alpha\beta\gamma}] \tag{89}$$

If the interfaces are also massless, the quantities $\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}$ and $\hat{e}^{\alpha\gamma}_{\alpha\beta\gamma}$ will also be zero because of constraint (82b).

7.4 Interface and common line entropy balance equations

For the case where the interface is essentially massless, entropy per unit area and a source term per unit area may be defined, respectively, as

$$\hat{\eta}^{\alpha\beta} = \lim_{\rho^{\alpha\beta}\to 0} (\rho^{\alpha\beta}\eta^{\alpha\beta}) \tag{90a}$$

$$\hat{b}^{\alpha\beta} = \lim_{\rho^{\alpha\beta}\to 0} (\rho^{\alpha\beta}b^{\alpha\beta}) \tag{90b}$$

Use of these relations, along with restrictions (83a) and (83b), in eqn (47a) yields the following entropy relation.

Macroscopic entropy balance for a massless $\alpha\beta$-interface

$$\frac{D^{\alpha\beta}(a^{\alpha\beta}\hat{\eta}^{\alpha\beta})}{Dt} + a^{\alpha\beta}\hat{\eta}^{\alpha\beta}\mathbf{I} : \nabla \boldsymbol{v}^{\alpha\beta} - \nabla\cdot(a^{\alpha\beta}\boldsymbol{\varphi}^{\alpha\beta}) - a^{\alpha\beta}\hat{b}^{\alpha\beta} = a^{\alpha\beta}\Lambda^{\alpha\beta} - \hat{e}^{\alpha}_{\alpha\beta}\eta^{\alpha,\beta} - \sum_{i=\alpha,\beta} \hat{\Phi}^{i}_{\alpha\beta} + \sum_{\gamma\neq\alpha,\beta} \hat{\Phi}^{\alpha\beta}_{\alpha\beta\gamma} \tag{91}$$

When the common line is massless, entropy per unit length and a source term per unit length are defined, respectively, as

$$\hat{\eta}^{\alpha\beta\gamma} = \lim_{\rho^{\alpha\beta\gamma}\to 0} (\rho^{\alpha\beta\gamma}\eta^{\alpha\beta\gamma}) \tag{92a}$$

and

$$\hat{b}^{\alpha\beta\gamma} = \lim_{\rho^{\alpha\beta\gamma}\to 0} (\rho^{\alpha\beta\gamma}b^{\alpha\beta\gamma}) \tag{92b}$$

Use of these relations, along with conditions and (83a) and (83b), in eqn (65a) yields the following entropy relation.

Macroscopic entropy balance for a massless $\alpha\beta\gamma$-common line

$$\frac{D^{\alpha\beta\gamma}(l^{\alpha\beta\gamma}\hat{\eta}^{\alpha\beta\gamma})}{Dt} + l^{\alpha\beta\gamma}\hat{\eta}^{\alpha\beta\gamma}\mathbf{I} : \nabla \boldsymbol{v}^{\alpha\beta\gamma} - \nabla\cdot(l^{\alpha\beta\gamma}\boldsymbol{\varphi}^{\alpha\beta\gamma}) - l^{\alpha\beta\gamma}\hat{b}^{\alpha\beta\gamma} = l^{\alpha\beta\gamma}\Lambda^{\alpha\beta\gamma} - \hat{e}^{\alpha\beta}_{\alpha\beta\gamma}\eta^{\alpha\beta,\beta\gamma} - \hat{e}^{\alpha\gamma}_{\alpha\beta\gamma}\eta^{\alpha\gamma,\beta\gamma} - \sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma} \hat{\Phi}^{ij}_{\alpha\beta\gamma} + \sum_{\epsilon\neq\alpha,\beta,\gamma} \hat{\Phi}^{\alpha\beta\gamma}_{\alpha\beta\gamma\epsilon} \tag{93}$$

If the interfaces are also massless, the quantities $\hat{e}^{\alpha\beta}_{\alpha\beta\gamma}$ and $\hat{e}^{\alpha\gamma}_{\alpha\beta\gamma}$ will also be zero because of constraint (82b).

8 JUMP CONDITIONS FOR INTERFACES WITHOUT PROPERTIES

When all properties of the interfaces and common lines are negligible, the interfaces act merely as surfaces of discontinuity between phases. These conditions give rise to the standard jump conditions for the conservation laws. These jump conditions are obtained by examination of the interface balance equations; and with all terms that relate to properties of the interface and to exchange with the common lines eliminated, the jump balance equations are obtained. The jump condition for mass conservation, from eqn (39), is as follows.

Jump condition for massless interface

$$\sum_{i=\alpha,\beta} \hat{e}^{i}_{\alpha\beta} = 0 \tag{94}$$

The jump condition for momentum conservation is obtained from eqn (40a).

Jump condition for a stress-free, massless interface

$$\sum_{i=\alpha,\beta} (\hat{e}^{i}_{\alpha\beta}\boldsymbol{v}^{i} + \hat{\boldsymbol{T}}^{i}_{\alpha\beta}) = 0 \tag{95}$$

For energy conservation, the jump condition is obtained from eqn (45a).

Jump condition for a massless interface that cannot store energy

$$\sum_{i=\alpha,\beta} \{\hat{e}^{i}_{\alpha\beta}[E^{i} + (v^{i})^2/2] + \hat{\boldsymbol{T}}^{i}_{\alpha\beta}\cdot\boldsymbol{v}^{i} + \hat{Q}^{i}_{\alpha\beta}\} = 0 \tag{96}$$

The jump condition for entropy can be most easily obtained by considering eqn (91). If the interface possesses no entropy, no entropy fluxes or body source terms exist in the interface, and the interface does not exchange entropy with a common line, eqn (91) reduces to the following.

Jump condition for the entropy balance for a singular interface

$$a^{\alpha\beta}\Lambda^{\alpha\beta} - \sum_{i=\alpha,\beta} (\hat{e}^{i}_{\alpha\beta}\eta^{i} + \hat{\Phi}^{i}_{\alpha\beta}) = 0 \tag{97}$$

9 JUMP CONDITIONS FOR COMMON LINES WITHOUT PROPERTIES

When all properties of the common lines (and accumulation points), though not necessarily of the interfaces, are negligible, the common lines act merely as discontinuities between interfaces. These conditions give rise to jump conditions for the conservation laws. They are obtained by setting the left side of the common line equations to zero and neglecting transport to accumulation points. The jump condition for mass conservation, from eqn (57), is as follows.

Jump condition for massless common line

$$\sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma} \hat{e}^{ij}_{\alpha\beta\gamma} = 0 \tag{98}$$

The jump condition for momentum conservation is obtained from eqn (59).

Jump condition for a stress-free, massless common line

$$\sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma} (\hat{e}^{ij}_{\alpha\beta\gamma}\boldsymbol{v}^{ij} + \hat{\boldsymbol{T}}^{ij}_{\alpha\beta\gamma}) = 0 \tag{99}$$

For energy conservation, the jump condition is obtained from eqn (63a) to yield the following.

Jump condition for a massless common line that cannot store energy

$$\sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma} \{\hat{e}^{ij}_{\alpha\beta\gamma}[E^{ij} + (v^{ij})^2/2] + \hat{\boldsymbol{T}}^{ij}_{\alpha\beta\gamma} \cdot \boldsymbol{v}^{ij} + \hat{Q}^{ij}_{\alpha\beta\gamma}\} = 0 \quad (100)$$

The jump condition for entropy when the interface between phases is considered to be merely a singular surface is obtained from eqn (93) as the following.

Jump condition for the entropy balance for a singular common line

$$l^{\alpha\beta\gamma}\Lambda^{\alpha\beta\gamma} - \sum_{ij=\alpha\beta,\alpha\gamma,\beta\gamma} (\hat{e}^{ij}_{\alpha\beta\gamma}\eta^{ij} + \hat{\Phi}^{ij}_{\alpha\beta\gamma}) = 0 \quad (101)$$

10 CONCLUSION

Global conservation equations written in terms of microscale continuum values can be localized to the macroscale by use of the theorems that have been developed here. The equations that result account for interphase transfer processes as source terms. Equations are obtained for interfaces, common lines, and common points as well as for phases. The coupling among phases, interfaces, and common lines is naturally accounted for. It is noted that the orientations of interfaces and common lines are lost when viewed at the macroscale. In fact, these regions are governed by equations similar to those for phases with the exchange terms modified appropriately. Additionally, the interface, common line, and common point equations are written for the case when these regions are massless but still capable of sustaining a stress or transporting energy.

The entropy exchange terms have been shown to be important when considering the form of the entropy inequality useful for development of constitutive equations. The entropy equations for each phase, interface, common line, and common point type must be combined to eliminate exchange terms among these different regions. The resulting form, or forms, may then be used to obtain constraints on an allowable dependence of constitutive functions on independent variables.

Equations for species transport in a multi-phase system may also be obtained as a special case of the general transport equations. However, incorporation of this phenomenon into the entropy inequality when phase change must be considered, requires that the momentum and energy equations also be developed for each species as in Hassanizadeh.[14] Consideration of this case will significantly complicate the process of exploitation of the entropy inequality in a systematic fashion.

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