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ON THE EXPLICIT INCORPORATION OF SURFACE EFFECTS INTO THE MULTIPHASE MIXTURE BALANCE LAWS

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Abstract—Interfacial conditions for multiphase flows are formulated on the microscale to include the possibility of surface effects. These conditions are then averaged to obtain macroscopic continuum equations which may be used in describing multiphase flows. A transformation is presented whereby the resultant macroscopic equations can be rewritten in a form identical to that which has been developed previously for a multiphase system not influenced by interfacial effects. This transformation is shown to have an impact on the forms of the intraphase stress tensor and heat flux vector in addition to the interphase stress and heat flux terms. Inclusion of interfacial effects is demonstrated to be essential to the proper understanding of phase interaction.

INTRODUCTION

Many past investigations have centered on the use of averaging theory to develop macroscopic balance equations for multiphase systems from the microscopic balance equations of continuum mechanics. A summary of these investigations is beyond the scope of this work. Those interested may refer to Bedford & Drumheller (1983) for a comprehensive review of significant contributions in this area. In most of the previous averaging theories (including Delhaye, 1977; Nigmatulin, 1979; Hassanizadeh & Gray, 1979a,b; and Ene, 1981) surface effects at interfaces were either explicitly or implicitly neglected. Surface properties (such as surface tension), however, are known to be important to many types of multiphase mixtures.

A few researchers have sought to include some of these surface effects in their derivations. Ishii (1975) used a time-averaging approach and employed a number of simplifying assumptions to develop a two-phase flow model which incorporated surface effects. A two-phase model was also developed by Drew (1971) and Drew & Segel (1971) by averaging local equations twice in space and time. Although surface momentum effects were considered in their formulation, energy and entropy interfacial effects were not examined. Resultant macroscopic equations in the foregoing theories are often quite complex and specification of a number of additional constitutive relations are required to complete the system.

This paper will focus on the explicit incorporation of surface properties into the multiphase macroscopic balance equations by a volume-averaging approach. It will be demonstrated that, if various terms are redefined, the form of these equations need not be more complex than the form of those equations which have been developed with no regard for surface effects. Thus, previous work in multiphase equation development could be reinterpreted and applied to mixtures for which surface phenomena play an important role.

The following development builds upon the work set forth in Hassanizadeh & Gray (1979a). In that paper, a general macroscopic balance equation was derived by averaging local balance equations over a representative elementary volume (REV). The macroscopic

balance law for a property ψ in a phase α is obtained as:

$$\frac{\partial}{\partial t}(\langle\rho\rangle_\alpha\bar{\psi}^\alpha) + \nabla\cdot(\langle\rho\rangle_\alpha\bar{\mathbf{v}}^\alpha\bar{\psi}^\alpha) - \nabla\cdot\mathbf{i}^\alpha - \langle\rho\rangle_\alpha\bar{f}^\alpha - \langle\rho\rangle_\alpha e^\alpha(\rho\psi) - \langle\rho\rangle_\alpha\hat{I}^\alpha = \langle\rho\rangle_\alpha\bar{G}^\alpha. \quad [1]$$

Here overbars and angle brackets are used to indicate mass weighted and phase volume averages, respectively. For convenience, notation has been summarized in the nomenclature section at the end of this paper.

Equation [1] is very general in that it accounts for the effects of mass exchange between the phases, net production of a property within a phase, and external supply of that property to a phase. This balance equation must be supplemented by an averaged conservation condition across the interfaces within a REV. Derivation of such a condition is the subject of the next section. Once this condition has been developed, the specific balance laws of mass, momentum, energy and entropy will be presented and examined to give new insight.

FORMULATION OF THE AVERAGED JUMP CONDITION

Local balance equations which govern mass, momentum, energy and entropy at an interface between two phases have been developed by a number of investigators. Scriven (1960) first examined the mass and momentum balances in moving surfaces for Newtonian fluids. His work was extended by Slattery (1964, 1967) to include the balance of energy and to account for exchange of mass with the adjacent phases. General local interfacial balance equations were later developed by Delhaye (1974), Ishii (1975) and Moeckel (1975). These equations incorporated surface properties, surface sources and mass exchange effects. Moeckel's development is the most general and will be used here as the starting point for the derivation of a macroscopic relation.

This discussion will be restricted to interfaces of negligibly small mass, such that interface momentum and mechanical energy may be neglected. In addition, external supplies of a property to an interface will not be considered. The phases of the multiphase system are assumed to be microscopically nonpolar (i.e. no internal spin momenta and no body or surface couples act on a body). For such a system, the general local balance equation for a property ψ at an α–β interface may be written as (Moeckel 1975):

$$\mathbf{n}^{\alpha\beta}\cdot[\rho(\mathbf{w}-\mathbf{v})\psi + \mathbf{i}]\,|_\alpha + \mathbf{n}^{\beta\alpha}\cdot[\rho(\mathbf{w}-\mathbf{v})\psi + \mathbf{i}]\,|_\beta = \nabla'\cdot\boldsymbol{\lambda}_s^{\alpha\beta'} + p_s^{\alpha\beta}. \quad [2]$$

Here $|_\alpha$ indicates that a term is to be evaluated in the limit as the interface is approached from the α-phase side, $\boldsymbol{\lambda}_s^{\alpha\beta'}$ is a surface flux and $p_s^{\alpha\beta}$ is a surface production term. In this paper, the subscript s means that the subscripted quantity pertains to an interfacial surface, a prime (′) designates a variable as a surface vector (two dimensional) in the interface, and ∇' denotes the two-dimensional surface gradient operator.

Equation [2] may be used to derive a constraint on the macroscopic balance equation [1]. The following development of this constraint has its roots in the work of Hassanizadeh (1979). In keeping with the averaging theory and criteria put forth in Hassanizadeh & Gray (1979a), eq [2] will be averaged over all α–β interfaces within an REV ($\delta A_{\alpha\beta}$) and then over the entire volume of the system (V) to produce the following global balance equation:

$$\int_V \frac{1}{\delta V}\int_{\delta A_{\alpha\beta}} \rho\psi(\mathbf{w}-\mathbf{v})\cdot\mathbf{n}^{\alpha\beta}\,|_\alpha\,\mathrm{d}a\,\mathrm{d}V + \int_V \frac{1}{\delta V}\int_{\delta A_{\alpha\beta}} \rho\psi(\mathbf{w}-\mathbf{v})\cdot\mathbf{n}^{\beta\alpha}\,|_\beta\,\mathrm{d}a\,\mathrm{d}V + \int_V \frac{1}{\delta V}\int_{\delta A_{\alpha\beta}} \mathbf{n}^{\alpha\beta}\cdot\mathbf{i}\,|_\alpha\,\mathrm{d}a\,\mathrm{d}V + \int_V \frac{1}{\delta V}\int_{\delta A_{\alpha\beta}} \mathbf{n}^{\beta\alpha}\cdot\mathbf{i}\,|_\beta\,\mathrm{d}a\,\mathrm{d}V = \int_V \frac{1}{\delta V}\int_{\delta A_{\alpha\beta}} \nabla'\cdot\boldsymbol{\lambda}_s^{\alpha\beta'}\,\mathrm{d}a\,\mathrm{d}V + \int_V \frac{1}{\delta V}\int_{\delta A_{\alpha\beta}} p_s^{\alpha\beta}\,\mathrm{d}a\,\mathrm{d}V. \quad [3]$$

Equation [3] may be manipulated to gain information about the exchange terms which appear in the general balance equation [1]. Summing [3] over all α and β yields:

$$2\int_V \sum_\alpha \langle\rho\rangle_\alpha [e^\alpha(\rho\psi) + \hat{I}^\alpha]\,\mathrm{d}V = \int_V \sum_\alpha \sum_{\beta\neq\alpha} \frac{1}{\delta V}\int_{\delta A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'}\,\mathrm{d}a\,\mathrm{d}V + \int_V \sum_\alpha \sum_{\beta\neq\alpha} \frac{1}{\delta V}\int_{\delta A_{\alpha\beta}} p_s^{\alpha\beta}\,\mathrm{d}a\,\mathrm{d}V. \quad [4]$$

A factor of two appears in the left-hand side of the abovementioned equation due to the double occurrence of integrals over the region $\delta A_{\alpha\beta}$ for each specific α–β combination. The form of equation [4] may be simplified by the application of Green's theorem in a surface to the first term on the right-hand side (see appendix A):

$$\int_V \sum_\alpha \sum_{\beta\neq\alpha} \frac{1}{\delta V}\int_{\delta A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'}\,\mathrm{d}a\,\mathrm{d}V = \int_A \sum_\alpha \frac{1}{\delta A}\int_{C_\alpha} \nu'_{\alpha\beta} \cdot \lambda_s^{\alpha\beta'}\,\mathrm{d}l\,\mathrm{d}A. \quad [5]$$

Here C_α is the curve formed by the intersection of all interfaces bordering the α phase ($\Sigma_{\beta\neq\alpha}\,\delta A_{\alpha\beta}$) with δA, an infinitesimal element of A and $\nu'_{\alpha\beta}$ is a unit surface vector lying tangent to the α–β interface and normal to C_α (see figure 1). The integral $\int_{C_\alpha} \nu'_{\alpha\beta} \cdot \lambda_s^{\alpha\beta'}\,\mathrm{d}l$ represents the flux of the property ψ through all α interfaces across the surface δA.

A macroscopic flux density contributed by all interfaces in contact with the α phase may

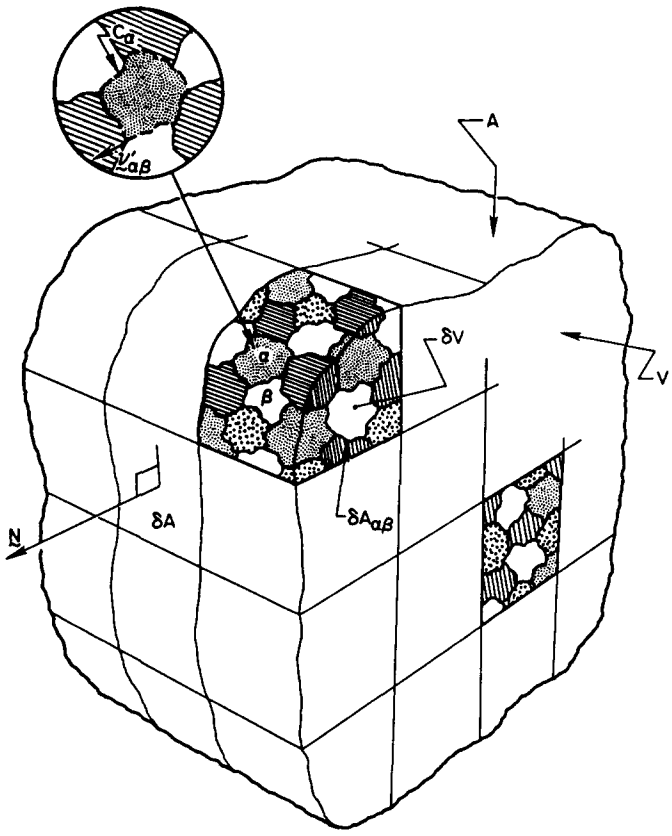

Figure 1. Schematic of multiphase system volume V. V is subdivided into volumes δV with total surface area A subdivided into δA and outward normal N. The interface between the α phase and all other phases is denoted by $\delta A_{\alpha\beta}$. The curve C_α marks the intersection of $\delta A_{\alpha\beta}$ with A. The unit vector $\nu'_{\alpha\beta}$ is normal to C_α and tangent to the α–β interface.

now be defined as:

$$\lambda_s^\alpha = \frac{1}{\delta A}\int_{C_\alpha} \nu'_{\alpha\beta} \cdot \lambda_s^{\alpha\beta'}\,\mathrm{d}l. \qquad [6]$$

Also definition of $\hat{p}_s^\alpha$ as

$$\hat{p}_s^\alpha = \frac{1}{\delta V}\sum_{\beta\neq\alpha}\int_{\delta A_{\alpha\beta}} p_s^{\alpha\beta}\,\mathrm{d}a \qquad [7]$$

and substitution of [5] and [6] into [4] yields:

$$2\int_V \sum_\alpha \langle\rho\rangle_\alpha[e^\alpha(\rho\psi) + \hat{I}^\alpha]\,\mathrm{d}V = \int_A \sum_\alpha \lambda_s^\alpha\,\mathrm{d}A + \int_V \sum_\alpha \hat{p}_s^\alpha\,\mathrm{d}V. \qquad [8]$$

A tetrahedron argument (see Hassanizadeh & Gray (1979a) appendix B) may be invoked at this point to prove the existence of a space flux vector λ_s^α such that $\mathbf{N}\cdot\lambda_s^\alpha = \lambda_s^\alpha$, where $\mathbf{N}$ is a unit normal to the surface δA. Application of the divergence theorem to the first term on the right-hand side of [8] and localization of this equation produces the final form:

$$2\sum_\alpha \langle\rho\rangle_\alpha[e^\alpha(\rho\psi) + \hat{I}^\alpha] = \sum_\alpha \nabla\cdot\lambda_s^\alpha + \sum_\alpha \hat{p}_s^\alpha. \qquad [9]$$

Equation [9] will serve as a constraint on the general balance equation [1].

PRESENTATION OF THE BALANCE EQUATIONS

Based on [1] and [9], individual macroscopic balance laws and their accompanying averaged interface conditions can now be developed. The balance laws have been derived previously by Hassanizadeh & Gray (1979b) and will merely be stated here. Constraints of the specific form [9], however, do not seem to have appeared in the literature and hence will be presented in some detail.

The balance equations for a phase α may be written as:

Mass

$$\frac{D^\alpha\langle\rho\rangle_\alpha}{Dt} + \langle\rho\rangle_\alpha(\nabla\cdot\bar{\mathbf{v}}^\alpha) - \langle\rho\rangle_\alpha e^\alpha(\rho) = 0. \qquad [10a]$$

Linear Momentum

$$\langle\rho\rangle_\alpha\frac{D^\alpha\bar{\mathbf{v}}^\alpha}{Dt} - \nabla\cdot\underline{t}^\alpha - \langle\rho\rangle_\alpha\bar{\mathbf{g}}^\alpha - \langle\rho\rangle_\alpha[\hat{\mathbf{T}}^\alpha + e^\alpha(\rho\tilde{\mathbf{v}})] = 0. \qquad [10b]$$

Angular Momentum

$$\underline{t}^\alpha = \underline{t}^{\alpha^T}. \qquad [10c]$$

Energy

$$\langle\rho\rangle_\alpha\frac{D^\alpha E^\alpha}{Dt} - \underline{t}^\alpha{:}\nabla\bar{\mathbf{v}}^\alpha - \nabla\cdot\mathbf{q}^\alpha - \langle\rho\rangle_\alpha h^\alpha - \langle\rho\rangle_\alpha[\hat{Q}^\alpha + e^\alpha(\rho\tilde{E})] = 0. \qquad [10d]$$

Entropy

$$\langle\rho\rangle_\alpha \frac{D^\alpha \bar{S}^\alpha}{Dt} - \nabla \cdot \phi^\alpha - \langle\rho\rangle_\alpha \bar{b}^\alpha - \langle\rho\rangle_\alpha[\hat{\Phi}^\alpha + e^\alpha(\rho\tilde{S})] = \langle\rho\rangle_\alpha \bar{\Gamma}^\alpha. \qquad [10e]$$

Definitions of terms which appear in [10] are enumerated in the nomenclature section of this paper.

An itemization of the local quantities which must be substituted into [2] to obtain the individual interface equations is given in table 1. For the mass balance, both $p_s^{\alpha\beta}$ and $\lambda_s^{\alpha\beta}$ are zero since the interface has been assumed massless. In addition, there is no nonadvective flux of mass. Thus, the averaged mass jump condition [9] becomes:

$$\sum_\alpha \langle\rho\rangle_\alpha e^\alpha(\rho) = 0. \qquad [11]$$

In the linear momentum balance at the interface, $\underset{\sim}{\sigma}_s^{\alpha\beta}$ represents a surface stress tensor which accounts for the effect of stress within the interface as well as surface tension. In indicial notation, $\underset{\sim}{\sigma}_s^{\alpha\beta}$ is the tensor $(\sigma_s^{\alpha\beta})^{k\mu}$ where k is a spatial coordinate index varying from 1 to 3 while μ is a surface coordinate index varying from 1 to 2. This convention has been used also by Moeckel (1975). Since there is no surface production of momentum, the averaged momentum jump condition takes the form:

$$\sum_\alpha \langle\rho\rangle_\alpha[e^\alpha(\rho\tilde{\mathbf{v}}) + e^\alpha(\rho)\bar{\mathbf{v}}^\alpha + \hat{\mathbf{T}}^\alpha] = \frac{1}{2}\sum_\alpha \nabla \cdot \underset{\sim}{\sigma}_s^\alpha \qquad [12]$$

where

$$\mathbf{N} \cdot \underset{\sim}{\sigma}_s^\alpha \equiv \sigma_s^\alpha \equiv \frac{1}{\delta A}\int_{C_\alpha} \nu'_{\alpha\beta} \cdot \underset{\sim}{\sigma}_s^{\alpha\beta}\, \mathrm{d}l.$$

Note $\underset{\sim}{\sigma}_s^\alpha$ is a macroscopic spatial stress tensor which arises due to local stresses at all interfaces which contact the α-phase.

Manipulation of the angular momentum interface condition along with [12] (see appendix B) will show that the sum of the macroscopic interfacial stress tensors is symmetric. That is,

$$\sum_\alpha \underset{\sim}{\sigma}_s^\alpha = \left(\sum_\alpha \underset{\sim}{\sigma}_s^\alpha\right)^T, \qquad [13]$$

although $\underset{\sim}{\sigma}_s^\alpha$ for each α has not been demonstrated to be symmetric. It should be observed that this result holds only for microscopically nonpolar materials.

In the averaging of the energy interfacial condition, it is convenient to define the

Table 1. Definition of local quantities

	ψ	$\mathbf{i}$	$\lambda_s^{\alpha\beta}$	$p_s^{\alpha\beta}$
Mass	1	0	0	0
Linear momentum	$\mathbf{v}$	$\underset{\sim}{t}$	$\underset{\sim}{\sigma}_s^{\alpha\beta}$	0
Angular momentum	$\mathbf{r} \times \mathbf{v}$	$\mathbf{r} \times \underset{\sim}{t}$	$\mathbf{r} \times \underset{\sim}{\sigma}_s^{\alpha\beta}$	0
Energy	$E + \frac{1}{2}v^2$	$\underset{\sim}{t} \cdot \mathbf{v} + \mathbf{q}$	$\underset{\sim}{\sigma}_s^{\alpha\beta} \cdot \mathbf{w} + \mathbf{k}_s^{\alpha\beta}$	0
Entropy	S	ϕ	$\eta_s^{\alpha\beta}$	Γ_s

following quantity:

$$\hat{k}_s^\alpha \equiv \hat{\mathbf{k}}_s^\alpha \cdot \mathbf{N} \equiv \frac{1}{\delta A} \int_{C_\alpha} \nu'_{\alpha\beta} \cdot (\underline{\sigma}_s^{\alpha\beta'} \cdot \hat{\mathbf{w}} + \mathbf{k}_s^{\alpha\beta'})\, \mathrm{d}l. \qquad [14a]$$

Here $\hat{\mathbf{w}}$ is a space vector defined as the difference between the interface and mass average velocities:

$$\hat{\mathbf{w}} = \mathbf{w} - \bar{\mathbf{v}}^\alpha.$$

$\hat{\mathbf{k}}_s^\alpha$ as defined above represents the heat flux due to intrainterfacial heat transfer along with the microscopic work performed by the interfacial stress. One possible physical interpretation of $\hat{\mathbf{k}}_s^\alpha$ is that it accounts for temperature discontinuities between adjacent phases. The averaged energy jump condition can now be written as:

$$\sum_\alpha \langle\rho\rangle_\alpha \left[e^\alpha(\rho) E^\alpha + e^\alpha(\rho\tilde{E}) + e^\alpha(\rho\tilde{\mathbf{v}}) \cdot \bar{\mathbf{v}}^\alpha + \frac{1}{2} \bar{v}^{\alpha^2} e^\alpha(\rho) + \hat{\mathbf{T}}^\alpha \cdot \bar{\mathbf{v}}^\alpha + \hat{Q}^\alpha \right] = \frac{1}{2} \sum_\alpha \nabla \cdot [\underline{\sigma}_s^\alpha \cdot \bar{\mathbf{v}}^\alpha + \hat{\mathbf{k}}_s^\alpha]. \qquad [14b]$$

The first term on the right-hand side of this equation represents the change in energy due to the macroscopic work performed by the interfacial stress.

Finally, the entropy interface condition may be given by:

$$\sum_\alpha \langle\rho\rangle_\alpha [\hat{\Phi}^\alpha + e^\alpha(\rho\tilde{S}) + e^\alpha(\rho) S^\alpha] \geq \frac{1}{2} \sum_\alpha \nabla \cdot \eta_s^\alpha. \qquad [15]$$

Here $\eta_s^\alpha \equiv \mathbf{N} \cdot \boldsymbol{\eta}_s^\alpha$ is a surface entropy flux. Note that the entropy production term has been omitted from [15]. Because this term is always non-negative (by the second law of thermodynamics), the balance condition is written as an inequality.

Much previous work in mixture theory (e.g. Bowen 1982; Passman *et al.* 1983) has made use of various forms of interfacial constraints. Rather than derive these constraints by the use of averaging principles, however, investigators have chosen to postulate their form. Such postulated constraint forms differ from those derived above in that their right hand sides are zero. In the next portion of this work, it will be shown that such a form can be consistent with an averaging theory approach if parameters are reinterpreted. Such reinterpretation, however, must necessarily be accounted for in any constitutive theory.

EXAMINATION OF THE ENTROPY INEQUALITY

The balance equations [10] along with the interfacial constraints [11–15] completely describe a multiphase system for which there is no macroscopic surface of discontinuity. Because they are no longer needed for clarification, all overbars and angle brackets will be dropped in the remaining portion of this paper. All variables which appear in subsequent equations are understood to represent macroscopic quantities. The remainder of this work will proceed under the common assumption that the entropy flux and external entropy supply terms are similarly proportional to the heat flux and external heat supply respectively such that

$$\phi^\alpha = \frac{1}{\theta^\alpha} \mathbf{q}^\alpha \quad \text{and} \quad b^\alpha = \frac{1}{\theta^\alpha} h^\alpha. \qquad [16]$$

The parameter of proportionality, θ^α, is called the temperature of the α phase.

Consider now the entropy balance equation [10e]. Equations [16] may be substituted into this equation and h^α eliminated by the use of the energy balance equation [10d] to achieve:

$$\begin{aligned}\rho^\alpha\epsilon_\alpha\Gamma^\alpha &= \rho^\alpha\epsilon_\alpha\frac{D^\alpha S^\alpha}{Dt} - \left(\frac{q_k^\alpha}{\theta^\alpha}\right)_{,k} \\ &- \frac{1}{\theta^\alpha}\left\{\rho^\alpha\epsilon_\alpha\frac{D^\alpha E^\alpha}{Dt} - t_{kl}^\alpha v_{l,k}^\alpha - q_{k,k}^\alpha - \rho^\alpha\epsilon_\alpha[\hat{Q}^\alpha + e^\alpha(\rho\tilde{E})]\right\} - \rho^\alpha\epsilon_\alpha[\hat{\Phi}^\alpha + e^\alpha(\rho\tilde{S})].\end{aligned} \tag{17a}$$

Here indicial notation has been employed (summation convention implied for indices k and l) and $\langle\rho\rangle_\alpha$ has been replaced by $\rho^\alpha\epsilon_\alpha$, where ρ^α is the intrinsic mass density of the α-phase and ϵ_α is the void fraction of the α-phase. If Helmholtz's free energy, A^α, is defined as:

$$A^\alpha = E^\alpha - \theta^\alpha S^\alpha$$

then [17a] may be rewritten as:

$$\begin{aligned}\rho^\alpha\epsilon_\alpha\Gamma^\alpha = \frac{1}{\theta^\alpha}\Bigg\{&-\rho^\alpha\epsilon_\alpha\left[S^\alpha\frac{D^\alpha\theta^\alpha}{Dt} + \frac{D^\alpha A^\alpha}{Dt}\right] \\ &+ t_{kl}^\alpha v_{l,k}^\alpha + \frac{q_k^\alpha}{\theta^\alpha}\theta_{,k}^\alpha + \rho^\alpha\epsilon_\alpha[\hat{Q}^\alpha + e^\alpha(\rho\tilde{E}) - \theta^\alpha[\hat{\Phi}^\alpha + e^\alpha(\rho\tilde{S})]]\Bigg\}.\end{aligned} \tag{17b}$$

Recalling the second law of thermodynamics which states that the net entropy production rate of a system must be non-negative, [17b] may be summed over all α phases to yield:

$$\begin{aligned}\sum_\alpha\frac{1}{\theta^\alpha}\left\{-\rho^\alpha\epsilon_\alpha\left[S^\alpha\frac{D^\alpha\theta^\alpha}{Dt} + \frac{D^\alpha A^\alpha}{Dt}\right] + t_{kl}^\alpha v_{l,k}^\alpha + \frac{q_k^\alpha}{\theta^\alpha}\theta_{,k}^\alpha\right\} \\ + \sum_\alpha\frac{\rho^\alpha\epsilon_\alpha}{\theta^\alpha}\{[\hat{Q}^\alpha + e^\alpha(\rho\tilde{E})] - \theta^\alpha[\hat{\Phi}^\alpha + e^\alpha(\rho\tilde{S})]\} \geq 0.\end{aligned} \tag{18}$$

The entropy equation [18] can now be expanded by incorporating the interfacial constraints derived in the preceeding section. For this expansion, it will be convenient to select one phase, r, as a "reference phase." Thus, temperatures and velocities of other phases may be expressed with respect to those parameters for the reference phase. Let

$$\begin{aligned}\theta^{\alpha r} &= \theta^\alpha - \theta^r \\ \mathbf{v}^{\alpha r} &= \mathbf{v}^\alpha - \mathbf{v}^r,\end{aligned} \tag{19}$$

then the operator D^α/Dt may be expanded as:

$$\frac{D^\alpha}{Dt}(\cdot) = \frac{D^r}{Dt}(\cdot) + v_k^{\alpha r}(\cdot)_{,k}. \tag{20}$$

Incorporation of [11–15] along with definitions [19], [20] into [18] results, after a great deal

of algebraic manipulation, in the following form:

$$\begin{aligned}
&\sum_\alpha \frac{1}{\theta^\alpha}\left\{-\rho^\alpha\epsilon_\alpha\left[\frac{D^r A^\alpha}{Dt} + S^\alpha\frac{D^r\theta^\alpha}{Dt} + v_k^{\alpha r}A^\alpha_{,k} + v_k^{\alpha r}S^\alpha\theta^\alpha_{,k}\right]\right.\\
&\quad\left. + v^\alpha_{l,k}\left[t^\alpha_{kl} + \frac{1}{2}\sigma^\alpha_{s_{kl}}\right] + \frac{1}{\theta^\alpha}\left[q^\alpha_k + \frac{1}{2}k^\alpha_{s_k}\right]\theta^\alpha_{,k}\right\}\\
&\quad - \sum_\alpha \frac{\rho^\alpha\epsilon_\alpha}{\theta^\alpha}A^\alpha e^\alpha(\rho) - \sum_\alpha \frac{\theta^{\alpha r}}{\theta^\alpha\theta^r}\left\{\rho^\alpha\epsilon_\alpha[\hat{Q}^\alpha + e^\alpha(\rho\tilde{E}) + E^\alpha e^\alpha(\rho)]\right.\\
&\quad\left. - \frac{1}{2}k^\alpha_{s_{k,k}} - \frac{1}{2}\sigma^\alpha_{kl}v^\alpha_{l,k}\right\} - \frac{1}{\theta^r}\sum_\alpha\left\{\rho^\alpha\epsilon_\alpha\left[\frac{1}{2}v_k^{\alpha r}v_k^{\alpha r}e^s(\rho) + v_k^{\alpha r}e^\alpha(\rho\tilde{v}_k)\right]\right.\\
&\quad\left. - v_k^{\alpha r}\left[\frac{1}{2}\sigma^\alpha_{s_{kl,l}} - \rho^\alpha\epsilon_\alpha\hat{T}^\alpha_k\right]\right\} + \frac{1}{2}\sum_\alpha\left\{\left(\frac{k^\alpha_{s_k}}{\theta^\alpha} - \eta^\alpha_{s_k}\right)_{,k}\right\} \geq 0.
\end{aligned} \tag{21}$$

The last term in [21] brings to mind the constitutive equations [16]. If it is assumed that the interfacial heat flux term is similarly proportional to the interfacial entropy flux, i.e.:

$$\eta^\alpha_{s_k} = \frac{k^\alpha_{s_k}}{\theta^\alpha}, \tag{22a}$$

then the last term in [21] will vanish. A less restrictive constitutive assumption, but one producing the same result might be:

$$\sum_\alpha \eta^\alpha_{s_k} = \sum_\alpha \frac{k^\alpha_{s_k}}{\theta^\alpha}. \tag{22b}$$

A close inspection of [21] will reveal that the interfacial terms always appear in conjunction with certain of the mixture parameters. The following definitions are proposed:

$$\bar{\bar{q}}^\alpha_k = q^\alpha_k + \tfrac{1}{2}k^\alpha_{s_k}, \tag{23a}$$

$$\bar{\bar{t}}^\alpha_{kl} = t^\alpha_{kl} + \tfrac{1}{2}\sigma^\alpha_{s_{kl}}, \tag{23b}$$

$$\rho^\alpha\epsilon_\alpha\bar{\bar{T}}^\alpha_k = \rho^\alpha\epsilon_\alpha\hat{T}^\alpha_k - \tfrac{1}{2}\sigma^\alpha_{s_{kl,l}}, \tag{23c}$$

$$\rho^\alpha\epsilon_\alpha\bar{\bar{Q}}^\alpha = \rho^\alpha\epsilon_\alpha\hat{Q}^\alpha - \tfrac{1}{2}k^\alpha_{s_{k,k}} - \tfrac{1}{2}\sigma^\alpha_{s_{kl}}v^\alpha_{l,k}. \tag{23d}$$

Here $\bar{\bar{q}}^\alpha_k$ represents some total heat flux due to both mixture and surface effects. Similarly, $\bar{\bar{t}}^\alpha_{kl}$ is some total stress tensor. The term $\rho^\alpha\epsilon_\alpha\bar{\bar{T}}^\alpha_k$ accounts for the exchange of momentum due to both mechanical interactions and surface tension. The exchange of energy due to mechancial interactions and interfacial effects is represented by $\rho^\alpha\epsilon_\alpha\bar{\bar{Q}}^\alpha$.

Incorporation of definitions [23] and [22a] into [21] yields a final form of the entropy inequality:

$$\begin{aligned}
&\sum_\alpha \frac{1}{\theta^\alpha}\left\{-\rho^\alpha\epsilon_\alpha\left[\frac{D^r A^\alpha}{Dt} + S^\alpha\frac{D^r\theta^\alpha}{Dt} + v_k^{\alpha r}A^\alpha_{,k} + v_k^{\alpha r}S^\alpha\theta^\alpha_{,k}\right]\right.\\
&\quad\left. + \bar{\bar{t}}^\alpha_{kl}v^\alpha_{l,k} + \frac{\bar{\bar{q}}^\alpha_k}{\theta^\alpha}\theta^\alpha_{,k}\right\} - \sum_\alpha \frac{\rho^\alpha\epsilon_\alpha}{\theta^\alpha}A^\alpha e^\alpha(\rho)\\
&\quad - \sum_\alpha \frac{\theta^{\alpha r}}{\theta^\alpha\theta^r}\rho^\alpha\epsilon_\alpha\{\bar{\bar{Q}}^\alpha + e^\alpha(\rho\tilde{E}) + E^\alpha e^\alpha(\rho)\}\\
&\quad - \frac{1}{\theta^r}\sum_\alpha\left[\rho^\alpha\epsilon_\alpha\left\{\frac{1}{2}v_k^{\alpha r}v_k^{\alpha r}e^\alpha(\rho) + v_k^{\alpha r}e^\alpha(\rho\tilde{v}_k) + v_k^{\alpha r}\bar{\bar{T}}^\alpha_k\right\}\right] \geq 0.
\end{aligned} \tag{24}$$

If this equation is compared to that developed for a multiphase system without surface effects (Gray 1983), the two equations are found to be identical in form though different in the way that terms must be interpreted.

In view of the definitions [23], the equations [10] and constraints [11–15] may also be rewritten as:

Mass

$$\frac{\partial}{\partial t}(\rho^\alpha \epsilon_\alpha) + (\rho^\alpha \epsilon_\alpha v_k^\alpha)_{,k} - \rho^\alpha \epsilon_\alpha e^\alpha(\rho) = 0. \qquad [25a]$$

Linear Momentum

$$\rho^\alpha \epsilon_\alpha \frac{D^\alpha v_l^\alpha}{Dt} - \bar{\bar{t}}_{kl,k}^\alpha - \rho^\alpha \epsilon_\alpha g_l^\alpha - \rho^\alpha \epsilon_\alpha \bar{\bar{T}}_l^\alpha - \rho^\alpha \epsilon_\alpha e^\alpha(\rho \tilde{v}_l) = 0. \qquad [25b]$$

Angular Momentum

$$\sum_\alpha \bar{\bar{t}}_{kl}^\alpha = \sum_\alpha \bar{\bar{t}}_{lk}^\alpha. \qquad [25c]$$

Energy

$$\rho^\alpha \epsilon_\alpha \frac{D^\alpha E^\alpha}{Dt} - \bar{\bar{t}}_{kl}^\alpha v_{l,k}^\alpha - \bar{\bar{q}}_{k,k}^\alpha - \rho^\alpha \epsilon_\alpha h^\alpha - \rho^\alpha \epsilon_\alpha \bar{\bar{Q}}^\alpha - \rho^\alpha \epsilon_\alpha e^\alpha(\rho \tilde{E}) = 0. \qquad [25d]$$

subject to:

$$\sum_\alpha \rho^\alpha \epsilon_\alpha e^\alpha(\rho) = 0, \qquad [26a]$$

$$\sum_\alpha \rho^\alpha \epsilon_\alpha (e^\alpha(\rho) v_l^\alpha + e^\alpha(\rho \tilde{v}_l) + \bar{\bar{T}}_l^\alpha) = 0, \qquad [26b]$$

$$\sum_\alpha \rho^\alpha \epsilon_\alpha \left(\frac{1}{2} v_l^\alpha v_l^\alpha e^\alpha(\rho) + v_l^\alpha e^\alpha(\rho \tilde{v}_l) + e^\alpha(\rho) E^\alpha + e^\alpha(\rho \tilde{E}) + v_l^\alpha \bar{\bar{T}}_l^\alpha + \bar{\bar{Q}}^\alpha\right) = 0. \qquad [26c]$$

Here explicit incorporation of interfacial properties into the balance equations has led to the interesting result that the macroscopic fluid stress tensor, $\bar{\bar{t}}^\alpha$, defined in [23b] is not necessarily symmetric. As stated by [25c], only the sum of these tensors has been shown to be symmetric for mixtures in which surface tension is of importance. With the exception of [25c], however, the system of equations [25] and [26] is found to be identical in form to those equations and constraints presented by Hassanizadeh & Gray (1979b).

Thus, it has been demonstrated that there exists a transformation, (definitions [23]) of the flux terms for the macroscopic multiphase balance equations whereby these equations can maintain the same structure as those balance equations which govern a system not influenced by interfacial effects. The system [25] and [26] is entirely consistent with that postulated by Bowen (1982) for multiphase mixtures. It should be pointed out that although the form of the equations is unchanged by the inclusion of surface effects, the additional effects must be accounted for in the constitutive theory.

DISCUSSION

The importance of incorporating surface effects in the mixture balance laws can be illustrated by the following simple example. Consider a three-phase air (g), water (w), and

solid (r) system which is in capillary equilibrium (i.e. there is no movement of fluids nor mass exchange between phases). For simplicity, suppose that the medium is laterally homogeneous such that the saturation profile is essentially one dimensional and that soil porosity does not vary in space. For this system, the linear momentum constraint [12] becomes:

$$\sum_{\alpha} \langle \rho \rangle_{\alpha} \hat{\mathbf{T}}^{\alpha} = \sum_{\alpha} \frac{1}{\delta V} \sum_{\beta \neq \alpha} \int_{\delta A_{\alpha\beta}} \mathbf{n}^{\alpha\beta} \cdot \underset{\sim}{t} \, \mathrm{d}a = \frac{1}{2} \sum_{\alpha} \nabla \cdot \underset{\sim}{q}_s^{\alpha}. \qquad [27]$$

It can be shown by the use of various averaging theorems (e.g. Gray 1975) that:

$$-\frac{1}{\delta V} \sum_{\beta \neq \alpha} \int_{\delta A_{\alpha\beta}} \mathbf{n}^{\alpha\beta} \, \mathrm{d}a = \nabla \epsilon_{\alpha}. \qquad [28]$$

Since there is no flow in the system, $\underset{\sim}{t}$ is an equilibrium stress which varies linearly in space. By use of this fact and identity [28], constraint [27] may be rewritten as:

$$-\sum_{\alpha} \nabla \epsilon_{\alpha} \cdot \underset{\sim}{t}^{\alpha} \big|_{e} = \frac{1}{2} \sum_{\alpha} \nabla \cdot \underset{\sim}{q}_s^{\alpha}, \qquad [29a]$$

where the subscript e refers to some equilibrium value. Equation [29a] may be expanded as:

$$-\nabla \epsilon_g \cdot \underset{\sim}{t}^{g} \big|_{e} + \nabla \epsilon_g \cdot \underset{\sim}{t}^{w} \big|_{e} = \frac{1}{2} \sum_{\alpha} \nabla \cdot \underset{\sim}{q}_s^{\alpha}. \qquad [29b]$$

Here, use has been made of the fact that $\nabla \epsilon_r = 0$ for the system under consideration and that $\Sigma_{\alpha} \epsilon_{\alpha} = 1$ by the definition of void fraction. Let the equilibrium stress be replaced by the relation:

$$\underset{\sim}{t}^{\alpha} \big|_{e} = -P_{\alpha} \underset{\sim}{I}, \qquad [30]$$

where P_{α} is the pressure of the α phase. Incorporation of [30] into [29b] then yields:

$$-(P_w - P_g) \nabla \epsilon_g = \frac{1}{2} \sum_{\alpha} \nabla \cdot \underset{\sim}{q}_s^{\alpha}. \qquad [31]$$

For the system under consideration, the vertical saturation profile will not be uniform ($\nabla \epsilon_g \neq 0$). If the right-hand side of [31] were set to zero (as, for example, it was implicity in the work of Hassanizadeh & Gray (1979a, b)), this would imply that $P_w = P_g$ (i.e. that the capillary pressure between the two fluids is zero). Only by incorporation of surface tension effects can one obtain the correct result that $P_w \neq P_g$.

Recall that, if one chooses to use constraints of the form [26], surface effects can still be incorporated into the mixture theory if certain parameters are redefined as in equations [28]. One must then be cautious, however, in the development of a constitutive theory for the system.

The principle of phase separation (Drew & Segel 1971) is commonly applied in mixture theory to reduce the general dependency of constitutive relations. This principle is the assumption that the internal state of one phase is unrelated to the internal state of another. Examination of the expressions [23a, b] for fluid stress and heat flux, reveals that these variables will have an interphase dependence due to the surface terms $\underset{\sim}{q}_s^{\alpha}$ and $\mathbf{k}_s^{\alpha}$. Thus, it should be recognized that the inclusion of surface effects is not compatible with the principle of phase separation for these variables.

CONCLUSIONS

In this paper, surface properties have been explicitly incorporated into a system of macroscopic balance laws for a mixture by the averaging of local interface conditions. A transformation has been presented whereby this system can be rewritten in a form identical to that which has been described previously in the literature for a multiphase system not influenced by interfacial effects. By this transformation, the effective stress tensor and heat flux vector for each phase are defined and shown to depend on interfacial properties. Phase interaction terms $\overline{\overline{T}}{}^{\alpha}_{k}$ and $\overline{\overline{Q}}{}^{\alpha}$ are also shown to exhibit an interfacial dependence.

The importance of the inclusion of surface effects for the description of multiphase mixtures was illustrated by a simple example for an unsaturated porous medium in equilibrium. It was demonstrated that, for this system, one cannot account for capillary pressure without incorporation of these surface terms.

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NOTATION

Special Notation/Definitions

$\frac{D^{\alpha}}{Dt}(\psi) = \frac{\partial}{\partial t}(\psi) + \bar{\mathbf{v}}^{\alpha} \cdot \nabla(\psi)$ material derivative

$e^{\alpha}(\rho\psi) = \frac{1}{\langle\rho\rangle_{\alpha}\,\delta V}\sum_{\beta\neq\alpha}\int_{\delta A_{\alpha\beta}} \rho\psi\,(\mathbf{w}-\mathbf{v})\cdot\mathbf{n}^{\alpha\beta}\,\mathrm{d}a$ density function for the exchange of ψ due to phase change

$\hat{I}^{\alpha} = \frac{1}{\langle\rho\rangle_{\alpha}\,\delta V}\sum_{\beta\neq\alpha}\int_{\delta A_{\alpha\beta}} \mathbf{n}^{\alpha\beta}\cdot\mathbf{i}\,\mathrm{d}a$ production of property ψ due to mechanical interaction

$\langle\psi\rangle_{\alpha}(\mathbf{x},t) = \frac{1}{\delta V}\int_{\delta V}\psi(\mathbf{x}+\xi,t)\,\gamma_{\alpha}(\mathbf{x}+\xi,t)\,\mathrm{d}V$ phase volume average

$\bar{\psi}^{\alpha}(\mathbf{x},t) = \langle\rho\psi\rangle_{\alpha}/\langle\rho\rangle_{\alpha}$ mass average

$=$ term is modified to account for surface effects

∇' two-dimensional surface gradient operator [$\nabla'\cdot\mathbf{f}' = (f^{\mu})_{,\mu}$ where μ is a surface coordinate index]
[$\nabla'\cdot\underline{f}' = (f^{k\mu})_{,\mu}$ where μ is a surface coordinate index and k is a spatial coordinate index.]

∇ spatial gradient operator

$\sum_{\alpha}$ summation over all phases

$'$ denotes surface (two-dimensional) vector

$\sum_{\beta\neq\alpha}$ summation over all N phases except the αth

$\tilde{\psi}^{\alpha} = \psi - \bar{\psi}^{\alpha}$ deviation term

$|_{e}$ equilibrium value

Roman letters

A surface area of V

A^{α} Helmholtz free energy

b external supply of entropy

C_α curve formed by intersection of all α interfaces with δA (see figure A)
E internal energy density function
E^α macroscopic internal energy density function $\equiv \overline{E}^\alpha + \frac{1}{2}\overline{\tilde{v}^2}^\alpha$
f external supply of ψ
G net rate of production of ψ
$\mathbf{g}$ external supply of momentum
h external supply of energy
$\mathbf{i}$ general flux vector for property ψ
k spatial index for indicial notation
$\hat{\mathbf{k}}_s^\alpha$ macroscopic interfacial heat flux (defined in [14a])
l spatial index for indicial notation
$\mathbf{n}^{\alpha\beta}$ unit vector normal to $\alpha\beta$-interface pointing away from the α-phase
p_α thermodynamic pressure
$p_s^{\alpha\beta}$ general surface production term
$\hat{p}_s^\alpha$ macroscopic quantity defined in eqn [7]
$\mathbf{q}^\alpha$ macroscopic heat flux vector
$\mathbf{r} = \mathbf{x} + \xi$
S internal entropy density function
t time
$\underset{\sim}{t}^\alpha$ macroscopic stress tensor
V volume of the macroscopic domain of interest
$\mathbf{v}$ velocity vector
$\mathbf{v}^{\alpha r}$ relative velocity defined in [19]
$\mathbf{w}$ interface velocity
$\hat{\mathbf{w}}$ $\equiv \mathbf{w} - \overline{\mathbf{v}}^\alpha$
$\mathbf{x}$ macroscopic spatial coordinate

Greek letters

α refers to α phase
β refers to β phase
Γ entropy production
γ_α phase distribution function $= \begin{cases} 1 \text{ in } \alpha \text{ phase} \\ 0 \text{ not in } \alpha \text{ phase} \end{cases}$
δA infinitesimal element of averaging area
$\delta A_{\alpha\beta}$ area of all α–β interfaces within REV
δV averaging volume
ϵ_α volume fraction of αth phase
η_s^α surface entropy flux defined by [15]
θ thermodynamic temperature
$\theta^{\alpha r}$ relative temperature defined in [19]
$\lambda_s^{\alpha\beta}$ general surface flux
μ surface coordinate index
$\nu'_{\alpha\beta}$ surface coordinate unit vector shown in figure A with components $(\nu'_{\alpha\beta})^\mu$
ξ position in space with respect to macroscopic coordinate
ρ mass density
$\underset{\sim}{\sigma}_s^\alpha$ macroscopic surface stress tensor defined by [12] with spatial components $(\sigma_s^\alpha)^{ij}$
$\underset{\sim}{\sigma}_s^{\alpha\beta}$ microscopic surface stress tensor defined prior to eqn [12]
ϕ entropy flux
ψ typical intrinsic thermomechanical property

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APPENDIX A

Application of Green's Theorem to Interfacial Flux Term

Green's theorem in a surface may be stated as (Aris 1962):

$$\int_S \nabla' \cdot \mathbf{f}' \, da = \oint_C \boldsymbol{\nu}' \cdot \mathbf{f}' \, dl \qquad [A.1]$$

for a given surface S and its bounding curve C. Here $\boldsymbol{\nu}'$ is a surface coordinate unit vector lying in S and normal to C. A corollary of [A.1] is that for any closed surface, $\hat{S}$:

$$\int_{\hat{S}} \nabla' \cdot \mathbf{f}' \, da = 0. \qquad [A.2]$$

Identity [A.2] holds as long as $\mathbf{f}'$ is continuous across any curve in $\hat{S}$. This corollary may be easily derived from [A.1] by splitting the surface $\hat{S}$ into two parts with some curve $\hat{C}$ and then summing the resultant integrals.

Now consider a surface integral over all α–β interfaces ($A_{\alpha\beta}$) in a volume V (see figure A]:

$$\int_{A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}a. \qquad [A.3]$$

If the volume V is divided into m subvolumes (δV_i) [A.3] can be expanded as a sum of integrals over the interfacial areas in each subregion ($\delta A_{\alpha\beta_i}$):

$$\int_{A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}a = \sum_{i=1}^{m} \left\{ \sum_{\alpha} \sum_{\beta \neq \alpha} \int_{\delta A_{\alpha\beta_i}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}a \right\}. \qquad [A.4]$$

The aforementioned division into subvolumes is arbitrary so that if M different divisions are considered [A.4] could be rewritten as:

$$\int_{A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}a = \sum_{j=1}^{M} \sum_{i=1}^{m_j} \frac{1}{\delta V_{ij}} \left[\sum_{\alpha} \sum_{\beta \neq \alpha} \int_{\delta A_{\alpha\beta_{ij}}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}a \right] \frac{\delta V_{ij}}{M}. \qquad [A.5]$$

Here δV_{ij} is the ith subvolume in the jth set. Since [A.5] is summed over all sets, division by M is necessary to preserve the equality. If the requirement is imposed that no two subvolumes have the same centroid (Hassanizadeh & Gray (1979a)), [A.5] becomes in the limit as $M \to \infty$:

$$\int_{A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}a = \int_{V} \sum_{\alpha} \sum_{\beta \neq \alpha} \frac{1}{\delta V} \int_{\delta A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}a \, \mathrm{d}V. \qquad [A.6]$$

In view of corollary [A.2], only those interfacial areas which do not form closed surfaces within V will contribute to the integral [A.3]. The only surfaces ($\delta A_{\alpha\beta}$) which are not closed in V are those which intersect A, the boundary of V. Let A be subdivided into m subareas (δA_i). Then, by the use of Green's theorem [A.1], integral [A.3] can be expanded as:

$$\int_{A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}a = \sum_{i=1}^{m} \left\{ \sum_{\alpha} \int_{C_{\alpha_i}} \nu'_{\alpha\beta} \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}l \right\}. \qquad [A.7]$$

Here C_{α_i} is the curve formed by the intersection of all interfaces which contact that α phase with the subarea δA_i and $\nu'_{\alpha\beta}$ is a two-dimensional unit vector lying inside the α–β interface and normal to C_{α_i}. As in the development of [A.5], different subdivisions of A are possible and [A.7] can be rewritten:

$$\int_{A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}a = \sum_{j=1}^{M} \sum_{i=1}^{m_j} \frac{1}{\delta A_{ij}} \left[\sum_{\alpha} \int_{C_{\alpha_{ij}}} \nu'_{\alpha\beta} \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}l \right] \frac{\delta A_{ij}}{M}. \qquad [A.8]$$

Taking the limit of [A.8] as $M \to \infty$ yields:

$$\int_{A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}a = \int_{A} \sum_{\alpha} \frac{1}{\delta A} \int_{C_\alpha} \nu'_{\alpha\beta} \cdot \lambda_s^{\alpha\beta'} \, \mathrm{d}l \, \mathrm{d}A. \qquad [A.9]$$

Comparison of [A.6] and [A.9] produces the final result:

$$\int_V \sum_\alpha \sum_{\beta\neq\alpha} \frac{1}{\delta V} \int_{\delta A_{\alpha\beta}} \nabla' \cdot \lambda_s^{\alpha\beta'} \, da \, dV = \int_A \sum_\alpha \frac{1}{\delta A} \int_{C_\alpha} \nu'_{\alpha\beta} \cdot \lambda_s^{\alpha\beta'} \, dl \, dA. \qquad [A.10]$$

It should be noted that the averaged integrals over $\delta A_{\alpha\beta}$ and C_α which appear in equation [A.10] are dependent upon the characteristic length of the representative elementary volume and area but not upon the shape of the elements.

APPENDIX B

Examination of the Symmetry of $\underset{\sim}{\sigma}_s^\alpha$

In this appendix, the linear and angular momentum jump conditions are manipulated to gain information about the interfacial stress tensor, $\underset{\sim}{\sigma}_s^\alpha$. The following development is a condensation of a more complete discussion of this subject which appears in Hassanizadeh (1979).

With reference to table 1, the interface constraint [9] for angular momentum may be written as:

$$\sum_\alpha \left\{ \frac{1}{\delta V} \sum_{\beta\neq\alpha} \int_{\delta A_{\alpha\beta}} \rho(\mathbf{r} \times \mathbf{v}) \cdot (\mathbf{w} - \mathbf{v}) \cdot \mathbf{n}^{\alpha\beta} \, da + \frac{1}{\delta V} \sum_{\beta\neq\alpha} \int_{\delta A_{\alpha\beta}} \mathbf{n}^{\alpha\beta} \cdot (\mathbf{r} \times \underset{\sim}{t}) \, da \right\} = \frac{1}{2} \sum_\alpha \nabla \cdot \left[\frac{1}{\delta A} \int_{C_\alpha} \nu'_{\alpha\beta} \cdot (\mathbf{r} \times \underset{\sim}{\sigma}_s^{\alpha\beta'}) \, dl \right]. \qquad [B.1]$$

Recalling that $\mathbf{r} = \mathbf{x} + \xi$, [B.1] can be rearranged to yield:

$$\sum_\alpha \{\mathbf{x} \times [\langle\rho\rangle_\alpha e^\alpha(\rho\bar{\mathbf{v}}) + \langle\rho\rangle_\alpha e^\alpha(\rho)\,\bar{\mathbf{v}}^\alpha + \langle\rho\rangle_\alpha \hat{\mathbf{T}}^\alpha] + \langle\rho\rangle_\alpha [e^\alpha(\rho\xi \times \mathbf{v}) + {}_a\hat{\mathbf{M}}^\alpha]\} = \frac{1}{2} \sum_\alpha \nabla \cdot (\mathbf{x} \times \underset{\sim}{\sigma}_s^\alpha) + \nabla \cdot {}_a\underset{\sim}{m}_s^\alpha, \qquad [B.2]$$

where

$${}_a\hat{\mathbf{M}}^\alpha = \frac{1}{\langle\rho\rangle_\alpha \delta V} \sum_{\beta\neq\alpha} \int_{\delta A_{\alpha\beta}} \xi \times \underset{\sim}{t} \cdot \mathbf{n}^{\alpha\beta} \, da$$

is a supply of angular momentum due to mechanical interactions.

and

$$\mathbf{N} \cdot {}_a\mathbf{m}_s^\alpha = {}_a\mathbf{m}_s^\alpha = \frac{1}{\delta A} \int_{C_\alpha} \nu'_{\alpha\beta} \cdot (\xi \times \underset{\sim}{\sigma}_s^{\alpha\beta'}) \, dl$$

is an apparent macroscopic stress couple vector due to interfacial stress.

Constraint [B.2] may be further simplified by incorporating the linear momentum constraint [12] and using the identity $\nabla\mathbf{x} = \underset{\sim}{I}$:

$$\sum_\alpha \langle\rho\rangle_\alpha [e^\alpha(\rho\xi \times \mathbf{v}) + {}_a\hat{\mathbf{M}}^\alpha] = \frac{1}{2} \sum_\alpha \{\underset{\sim}{I} \times \cdot \underset{\sim}{\sigma}_s^\alpha + \nabla \cdot {}_a\underset{\sim}{m}_s^\alpha\}. \qquad [B.3]$$

A macroscopic interface condition for local spin can also be derived by taking the cross

product of ξ with the microscopic linear momentum jump condition [2]:

$$(\rho\xi \times \mathbf{v}(\mathbf{w} - \mathbf{v}) + \xi \times \underset{\sim}{t})\,|_{\alpha} \cdot \mathbf{n}^{\alpha\beta} + (\rho\xi \times \mathbf{v}(\mathbf{w} - \mathbf{v}) + \xi \times \underset{\sim}{t})\,|_{\beta} \cdot \mathbf{n}^{\beta\alpha} = \nabla' \cdot (\xi \times \underset{\sim}{\sigma}_s^{\alpha\beta\prime}), \qquad [B.4]$$

and then averaging this equation over an REV to achieve:

$$\sum_{\alpha} \langle \rho \rangle_{\alpha} (e^{\alpha}(\rho\xi \times \mathbf{v}) + {}_{a}\hat{\mathbf{M}}^{\alpha}) = \frac{1}{2} \sum_{\alpha} \nabla \cdot {}_{a}\underset{\sim}{m}_s^{\alpha}. \qquad [B.5]$$

Constraint [B.5] is valid for microscopically nonpolar materials. Comparison of [B.3] and [B.5] yields the result

$$\underset{\sim}{I} \times \cdot \sum_{\alpha} \underset{\sim}{\sigma}_s^{\alpha} = 0$$

or

$$\sum_{\alpha} \sigma_{s_{ij}}^{\alpha} = \sum_{\alpha} \sigma_{s_{ji}}^{\alpha} \qquad [B.6]$$