

# Derivation of basic equations of mass transport in porous media, Part 1. Macroscopic balance laws

S. Majid Hassanizadeh

National Institute of Public Health and Environmental Hygiene (RIVM), PO Box 150,  
2260 AD Leidschendam, The Netherlands

This paper is the first part of a series of two papers on the development of a general thermodynamic basis for the study of transport phenomena in a porous medium composed of a multi-component fluid flowing through a porous rock skeleton. Fluid components are miscible and homogenous thermodynamic interactions among them take place at the molecular level. Heterogeneous thermodynamic interactions occur between fluid components and the rock at solid-fluid interfaces. In the microscopic description of the medium, balance laws of continuum theories of mixtures are employed as the governing equations at points within the fluid phase. At points within the rock aggregates, classical balance equations of continuum mechanics are employed. Interfacial jump conditions are given to account for interactions between fluid species and the rock. By averaging of these three sets of equations, we arrive at macroscopic equations of balance of mass, momentum, energy and entropy for the rock and for individual fluid species, as well as restrictions on interaction terms. Also, a macroscopic formulation of the second law of thermodynamics for the medium is provided. Macroscopic balance laws will have to be supplemented by appropriate constitutive relations to obtain a complete thermodynamic theory of transport processes in porous media. This approach, both in concept and methodology, is the same as that developed by Hassanizadeh and Gray<sup>14-16</sup>. It makes it possible to take into account coupling of thermodynamic effects. Among the final results, we shall provide a generalization of Fick's Law and Darcy's for transport of concentrated brine in porous media.

**Key Words:** species transport, multi-component fluid, porous media flow, mixtures, macroscopic balance laws, second law of thermodynamics.

## INTRODUCTION

Almost all existing models of mass transport in porous media are based on originally empirical relations such as Darcy's law and Fick's first law. During the past two decades, the study of physical foundations of such relations has been the subject of many theoretical investigations, using different models and various approaches. As a result, it seems that there is now a much deeper understanding of the physical basis of generalized Darcy's law in the form applicable to the single-phase flow in porous media. However, the same cannot be said about the extended form of Fick's law describing solute transport in porous media. In a critical review of theories of solute transport, Sposito *et al.*<sup>1</sup> pointed out that: 'Although much research has gone into the technology of mass transport during the past twenty five years, the physical basis of the currently applied quantitative theories remain incomplete'. In agreement with this inference, we point out that in continuum mechanics, Fick's first law for species of a multi-component fluid is derived from the equations of motion of individual species<sup>2,3</sup>. Thus, the thermodynamic basis of Fick's law is well understood there. Whereas, to the knowledge of the author, such a connection is not yet established between

the extended form of Fick's first law (as adopted for describing dispersion in porous media) and macroscopic equations of motion of fluid species.

It is not the purpose of this paper to review earlier works on fundamental derivations of equations of mass transport in porous media. However, few points of interest are briefly mentioned. The common feature of most works presented so far is that macroscopic equations of mass transport are solely based on the (microscopic or macroscopic) equation of mass conservation. Thus, the connection of relations such as extended Fick's law with the equation of motion of individual species cannot be explored. Furthermore, many theoretical derivations of (macroscopic) Fick's law<sup>4-8</sup>, assume *a priori* the validity of Fick's first law in the microscopic (pore) level, and then use an averaging procedure to arrive at more or less the same form, this time as the macroscopic equation. Such an approach does not provide the necessary theoretical framework within which one can fully investigate the restrictions and limitations of Fick's law and find possible ways of further generalizations.

Some authors are able to show that the dispersive (-diffusive) flux vector obeys a Fickian-type law by following other approaches, such as employing kinematic and geometric arguments<sup>9</sup>, using molecular theories<sup>10</sup>,

Accepted May 1986. Discussion closes February 1987.

0309-1708/86/040196-11\$2.00

© 1986 Computational Mechanics Publications

applying a cumulant expansion to the equation of mass balance<sup>11,12</sup>, and constructing a (macroscopic) constitutive relationship for the flux term<sup>13</sup>. These efforts, have all contributed to the increased understanding of basic assumptions underlying Darcy's and Fick's laws.

In almost all earlier treatments of the problem, an implicit (or sometimes explicit<sup>10-12</sup>) assumption has been the diluteness of the solution. The main consequence of this assumption is the decoupling of motion of fluid phase as a whole, from the motion of its components. This is evident from Fick's law and Darcy's law which are typically written in the following forms.

$$\mathbf{J}^\alpha = -\rho^f \mathbf{D} \cdot \nabla C^\alpha \quad (1)$$

$$\mathbf{v}^{fr} = -\mathbf{K} \cdot (\nabla p^f - \rho^f \mathbf{g}) \quad (2)$$

where  $\mathbf{J}^\alpha$  is the mass flux vector of component  $\alpha$ ,  $C^\alpha$  is its mass fraction,  $\rho^f$  is the fluid mass density,  $p^f$  is its pressure,  $\mathbf{v}^{fr}$  is the velocity of fluid with respect to the rock,  $\mathbf{K}$  is the permeability tensor, and  $\mathbf{D}$  is the dispersivity tensor.

According to these relations, concentration gradients of components do not act as a force in the motion of fluid phase and conversely the pressure gradient imposed on the medium does not affect the motion of components. Such conclusions are perhaps agreeable only if species exist at low concentrations. At high concentrations, however, one would expect the mean motion of the fluid phase to be affected by diffusive-dispersive forces. The situation becomes even more complicated where temperature gradients are of importance or ionic forces need to be accounted for. The study of such coupling effects, specially in the case of high concentrations, can be made possible only if more general formulations of mass, momentum, and energy conservation equations are provided. This work is an attempt in that direction.

The main feature of the present approach is that equations of mass transport are derived as part of the process of developing appropriate equations of macroscopic momentum and energy transfer for species as well as for the fluid phase and the solid phase. In contrast to other works on theoretical derivations of Fick's law, expressions for the dispersive mass flux terms are naturally obtained from equations of motion of species. This makes it possible to develop a general theory in the sense that all kinds of mass, momentum and energy transfer phenomena are brought into considerations and, thus, cross-coupling effects are properly accounted for. An important result of the development is the derivation of generalized Fick's law and Darcy's law which are valid for situations where high solute concentrations exist.

This work is a continuation and extension of the previous works<sup>14-17</sup>, hereby applied to a miscible mixture of fluids (alternatively called a multi-component fluid) flowing through a porous solid. The paper is presented in two parts. In the first part, macroscopic balance laws for mass, momentum, energy, and entropy of solid phase and individual species of the fluid phase are developed starting from a microscopic description of the porous medium. Furthermore, a macroscopic statement of the second law of thermodynamics for the system is provided. Then in the second part, we shall develop constitutive relations for certain thermodynamic properties of the fluid phase, the solid phase, and fluid species. Finally, combining balance laws and constitutive relations and adopting various assumptions in a number of steps, a hierarchy of

generalizations of Darcy's law and Fick's law is developed. Extension of results of Part 1 to the case of multi-phase flow of a number of multi-component fluids in a porous medium is quite straight forward. This extension has been discussed in Appendix A where appropriate (macroscopic) balance equations are also provided.

## MICROSCOPIC DESCRIPTION OF THE SYSTEM

Consider a body  $B$  occupying part of the space denoted by  $V$  and bounded by the surface  $A$ . The body  $B$  is a heterogeneous medium composed of two different phases: a fluid phase and a solid phase. The solid phase exists in the form of rock aggregates which together form a self-supporting matrix also called the rock phase. That portion of  $V$  that is occupied by the rock phase is denoted by  $V_r$ . The remaining portion, which is filled by the fluid phase, is denoted by  $V_f$  and called the void space. Throughout this work, indices 'f' and 'r' shall refer to the fluid and the rock, respectively. The boundary of the void space (or equally the boundaries of rock aggregates), called solid-fluid interfaces, are assumed to be singular surfaces across which material properties and thermodynamic quantities may undergo step discontinuities. No thermo-mechanical properties are attributed to these interfaces. This assumption, however, by no means excludes the possibility of exchange of mass, momentum, or energy between the solid and the fluid. Furthermore, surface properties pertinent to sorption and solution processes can be still taken into account whenever necessary.

For almost all practical situations, one can safely assume that the characteristic length of the pore space and rock aggregates are much larger than the mean free path of fluid and solid molecules. Thus, according to the fundamental assumption of continuum mechanics<sup>18</sup>, the fluid phase and the solid phase may be treated as a continuum over  $V_f$  and  $V_r$ , respectively. Therefore, classical balance laws of continuum mechanics can be employed at points lying within the pore space or rock aggregates. We now like to extend these ideas to the case where the fluid phase is a multi-component material composed of  $N$  different species. In this case, we treat the fluid phase as a continuum in the sense of modern theories of mixtures<sup>19</sup>. We assume that species composing the fluid phase are mixed in the molecular level so that in a continuum view (yet in the scale of the medium voids), their totality is regarded as a mixture of  $N$  miscible fluids. Thus, we view each species as a continuous matter which has its own motion continuously defined throughout the void space. It may undergo processes involving chemical reaction, momentum exchange and energy exchange with other species. Once again, we are allowed to adopt this point of view so long as the characteristic size of the porous medium voids are much larger than the mean free path of molecules of any of the species. Then, balance laws governing thermodynamic processes for a given species  $\alpha$  ( $\alpha = 1$  to  $N$ ), at a spatial point  $\mathbf{r}$  within the fluid phase, are provided by continuum theories of mixtures of fluids. The balance equation for a typical thermodynamic property  $\psi^\alpha$ , having a flux vector  $\mathbf{i}^\alpha$ , an external supply  $f^\alpha$ , and an internal supply  $G^\alpha$ , takes up the following form<sup>3</sup>:

$$\frac{\partial}{\partial t}(\rho^\alpha \psi^\alpha) + \nabla \cdot (\rho^\alpha \psi^\alpha \mathbf{v}^\alpha) - \nabla \cdot \mathbf{i}^\alpha - \rho^\alpha f^\alpha = \rho^\alpha G^\alpha \quad (3)$$

Table 1.

Quantity	$\psi^\alpha$	$\mathbf{i}^\alpha$	$f^\alpha$	$G^\alpha$
Mass	1	0	0	$\hat{r}^\alpha$
Momentum	$\mathbf{v}^\alpha$	$\boldsymbol{\sigma}^\alpha$	$\mathbf{g}^\alpha$	$\hat{r}^\alpha \mathbf{v}^\alpha + \hat{\mathbf{i}}^\alpha$
Energy	$E^\alpha + \frac{1}{2}(\mathbf{v}^\alpha)^2$	$\boldsymbol{\sigma}^\alpha \cdot \bar{\mathbf{v}}^\alpha + \mathbf{q}^\alpha$	$\mathbf{g}^\alpha \cdot \mathbf{v}^\alpha + h^\alpha$	$\hat{r}^\alpha (E^\alpha + \frac{1}{2}(\mathbf{v}^\alpha)^2) + \hat{\mathbf{i}}^\alpha \cdot \mathbf{v}^\alpha + \hat{q}^\alpha$
Entropy	$S^\alpha$	$\boldsymbol{\phi}^\alpha$	$b^\alpha$	$\hat{r}^\alpha S^\alpha + \hat{\phi}^\alpha + \Gamma^\alpha$

where  $\rho^\alpha$  is the mass of species  $\alpha$  per unit volume of the fluid phase,  $\mathbf{v}^\alpha$  is the mass-weighted mean velocity of molecules of species  $\alpha$ , and  $\nabla$  designates the gradient (or divergence) operator. Throughout Part 1, direct tensorial notation will be used. Individual balance laws for mass, momentum, energy, and entropy may be obtained by selecting appropriate variables from Table 1.

In Table 1,  $\hat{r}^\alpha$  is the rate of net production of mass of species  $\alpha$  as a result of (homogeneous) chemical reactions with other species and also due to decay/production processes, and  $\boldsymbol{\sigma}^\alpha$  is the microscopic 'partial stress' tensor for the species  $\alpha$  exterior to a diaphragm, on the species  $\alpha$  interior to that diaphragm, through the surface of the diaphragm. One can relate this quantity to a generalized definition of chemical potential for species  $\alpha$ <sup>19,20</sup>. Further in Table 1,  $\hat{\mathbf{i}}^\alpha$  is the internal body force exerted upon the species  $\alpha$  by all other species coexisting with  $\alpha$  within a diaphragm;  $\mathbf{g}^\alpha$  is the external body force (e.g., due to gravity or ionic attractions);  $E^\alpha$  and  $S^\alpha$  are internal energy and internal entropy density functions, respectively;  $\mathbf{q}^\alpha$  and  $\boldsymbol{\phi}^\alpha$  are surface fluxes of heat and entropy within the species- $\alpha$  continuum, respectively;  $h^\alpha$  and  $b^\alpha$  are external supplies of energy and entropy, respectively;  $\hat{q}^\alpha$  and  $\hat{\phi}^\alpha$  account for exchanges of energy and entropy, respectively, between species  $\alpha$  and all other species; and finally  $\Gamma^\alpha$  is the rate of net production of entropy of the species  $\alpha$ . A rather comprehensive list of symbols is given at the end of the paper. In writing the balance laws in the form suggested by equation (3) and Table 1, we have assumed that all species are microscopically non-polar so that all partial stress tensors are symmetric.

The exchanges of mass, momentum, energy, and entropy which take place among the species are all internal to the fluid phase. That is, they are actions and counteractions and, thus, do not give rise to a net production or decay of corresponding properties of the fluid phase. Therefore, they must satisfy the following restrictions<sup>3</sup>.

$$\sum_{\alpha} \rho^\alpha \hat{r}^\alpha = 0 \tag{4a}$$

$$\sum_{\alpha} \rho^\alpha (\hat{r}^\alpha \mathbf{v}^\alpha + \hat{\mathbf{i}}^\alpha) = 0 \tag{4b}$$

$$\sum_{\alpha} \rho^\alpha \left( \hat{r}^\alpha \left( E^\alpha + \frac{1}{2} \mathbf{v}^{\alpha^2} \right) + \hat{\mathbf{i}}^\alpha \cdot \mathbf{v}^\alpha + \hat{q}^\alpha \right) = 0 \tag{4c}$$

$$\sum_{\alpha} \rho^\alpha (\hat{r}^\alpha S^\alpha + \hat{\phi}^\alpha) = 0 \tag{4d}$$

Throughout this work,  $\sum_{\alpha}$  denotes a summation over all species (i.e.,  $\sum_{\alpha=1}^N$ ), and  $\alpha$  (or other Greek indices)

always range from 1 to  $N$  unless otherwise specified. Note that repetition of Greek indices does not imply a summation. Recognizing restrictions (4) and giving appropriate definitions for fluid bulk properties in terms of mean values of species properties, one can easily arrive at the balance laws for the fluid-phase continuum<sup>3</sup>. The resulting equations, however, do not constitute additional constraints on the system; they may be considered only as alternatives to restrictions (4). Additional balance laws, however, have to be provided for the rock aggregates. Thus, we employ classical balance equations of continuum mechanics at a spatial point  $\mathbf{r}$  lying within a rock aggregate. For a typical thermodynamic property  $\psi$ , they have the following general form:

$$\frac{\partial}{\partial t}(\rho\psi) + \nabla \cdot (\rho\mathbf{v}\psi) - \nabla \cdot \mathbf{i} - \rho f = \rho G \tag{5}$$

where appropriate variables for individual balance laws should be selected from Table 2.

It should be noted that one could also consider each rock aggregate as a multi-component continuum and follow the same approach that was employed for the fluid phase. Then, one has to give balance laws for individual components of the solid phase as well. Possibly, some of the solid phase components are also found in the fluid phase. However, in this work, we shall assume that diffusion of species within and among rock aggregates is not important and can be neglected. This means that in our view, components of the rock aggregates stay together throughout the course of thermodynamic processes, except possibly at the aggregates surfaces where exchange of mass of some species (extant to the rock) with the fluid phase may occur. Therefore, we do not need to employ separate balance laws for the solid phase components except for the mass of some species.

We now turn our attention to processes which occur at the solid-fluid interfaces. As mentioned earlier, all kinds of chemical and thermodynamical interactions may take place there. Processes such as adsorption/desorption, dissolution/precipitation, heat exchange, and exertion of viscous drag between rock aggregates and fluid species, are some of the possible mechanisms of interfacial interactions. Microscopic equations governing these interactions are provided by jump conditions of continuum mechanics valid at a surface of discontinuity. Clearly, because we treat the solid phase as a whole, and not in terms of its individual components, we can give only overall balance equations for interfacial exchange processes. They have the following general form for mass, momentum, and energy:

$$\sum_{\alpha} (\rho^\alpha \psi^\alpha (\mathbf{w} - \mathbf{v}^\alpha) + \mathbf{i}^\alpha) \cdot \mathbf{n}^{fr} = -(\rho\psi(\mathbf{w} - \mathbf{v}) + \mathbf{i}) \cdot \mathbf{n}^r \tag{6a}$$

Table 2.

Quantity	$\psi$	$\mathbf{i}$	$f$	$G$
Mass	1	0	0	0
Momentum	$\mathbf{v}$	$\boldsymbol{\sigma}$	$\mathbf{g}$	0
Energy	$E + \frac{1}{2} \mathbf{v}^2$	$\boldsymbol{\sigma} \cdot \mathbf{v} + \mathbf{q}$	$\mathbf{g} \cdot \mathbf{v} + h$	0
Entropy	$S$	$\boldsymbol{\phi}$	$b$	$\Gamma$

where appropriate quantities must be selected from Tables 1 and 2. The balance of entropy, however, is written in the following form.

$$\sum_a (\rho^a S^a(\mathbf{w} - \mathbf{v}^a) + \phi^a) \big|_f \cdot \mathbf{n}^{fr} \geq -(\rho S(\mathbf{w} - \mathbf{v}) + \phi) \big|_r \cdot \mathbf{n}^{rf} \quad (6b)$$

In these equations,  $\mathbf{w}$  is the velocity of the interface,  $\mathbf{n}^{fr}$  is the unit normal vector pointing into the rock aggregate, and  $\big|_{f(\text{or } r)}$  indicates the limit of the preceding terms as the interface is approached from the fluid- (or the solid-) phase side. Note that the inequality sign in equation (6b) allows for a possible increase of entropy as a result of interfacial phenomena.

This completes the microscopic description of the system under consideration. In the following section we describe the macroscopization process and provide the averaged (or macroscopic) balance laws.

### MACROSCOPIC BALANCE LAWS

Averaging of equations (3) to (6) over a representative elementary volume (REV) will lead to a set of macroscopic balance laws for the rock and the fluid species. A thorough discussion of properties of REV is provided elsewhere<sup>14</sup>. In defining macroscopic quantities, the following averaging operators will be used.

*volume average operator*

$$\langle \psi \rangle^a(\mathbf{x}, t) = \frac{1}{\varepsilon^a \delta V} \int_{\delta V} \psi(\mathbf{r}, t) \gamma_a(\mathbf{r}, t) dv \quad (7)$$

*mass average operator for a phase*

$$\bar{\psi}^a(\mathbf{x}, t) = \frac{1}{\varepsilon^a \langle \rho \rangle \delta V} \int_{\delta V} \rho(\mathbf{r}, t) \psi(\mathbf{r}, t) \gamma_a(\mathbf{r}, t) dv \quad (8)$$

*mass average operator for fluid species*

$$\bar{\psi}^a(\mathbf{x}, t) = \frac{1}{\varepsilon^f \langle \rho^a \rangle \delta V} \int_{\delta V} \rho^a(\mathbf{r}, t) \psi^a(\mathbf{r}, t) \gamma^a(\mathbf{r}, t) dv \quad (9)$$

where

- $\delta V$  is the averaging volume,
- $\delta A$  is the averaging area,
- $dv$  is the microscopic differential element of volume,
- $da$  is the microscopic differential element of area,
- $\mathbf{x}$  is the position vector of the centroid of the averaging region with respect to an inertial frame of reference,
- $\mathbf{r}$  is the position vector of points inside the averaging region,
- $a$  will be either 'f' (for fluid) or 'r' (for rock).
- $\gamma_a$  is the phase distribution function of phase 'a' defined by<sup>21</sup>:

$$\gamma_a(\mathbf{r}, t) = \begin{cases} 1 & \text{if } \mathbf{r} \text{ lies within phase 'a'} \\ 0 & \text{otherwise} \end{cases} \quad (10)$$

$\varepsilon^a$  is the volume fraction of phase 'a' within the averaging volume defined by

$$\varepsilon^a(\mathbf{x}, t) = \frac{1}{\delta V} \int_{\delta V} \gamma_a(\mathbf{r}, t) dv \quad (11)$$

The fluid phase volume fraction,  $\varepsilon^f$ , is called porosity and denoted by  $n$ . Then, the rock volume fraction will be simply  $\varepsilon^r = 1 - n$ . Note that fluid species have the same volume fraction as the fluid phase, i.e.,  $\varepsilon^a = n$ . In addition to operators (7) to (9), other averaging operators, defined later, will also be used.

In passing from microscopic balance laws to macroscopic equations, a number of mathematical and physical constraints must be fulfilled. Such constraints have been fully discussed by Hassanizadeh and Gray<sup>14</sup> and Nguyen *et al.*<sup>13</sup> and we will not repeat them here for the sake of brevity. However, they are all observed in the averaging process that will be followed to raise equations (3) to (6) to the macroscopic level.

The averaging process, in brief, is as follows. First, equations (3) and (4) are multiplied by the fluid phase distribution function  $\gamma_f$  and then integrated over the averaging volume. Next, resulting equations are integrated over all averaging volumes which encompass the space of interest  $V$ . Finally, the equations are localized to obtain macroscopic point equations for fluid species. The same procedure is repeated for equations (5), this time however, first multiplied by the rock distribution function  $\gamma_r$ . As a result, we shall obtain macroscopic point equations for the rock phase. Finally, interfacial relations (6) are integrated over  $\delta A^{fr}$ , which denotes the surface of aggregates within an REV. Resulting equations are then integrated over all REV's encompassing  $V$  and localized to obtain macroscopic restrictions on interfacial exchange terms. In the averaging process, various definitions of macroscopic quantities in terms of microscopic properties should be adopted in order to satisfy mathematical and physical requirements mentioned above. Also, various theorems which relate the derivative of an integral to the integral of the derivative will have to be employed. Details of such definitions, theorems, and the averaging procedure closely follow those given in the works of Hassanizadeh and Gray<sup>14-15</sup>, and thus, for the most part, will not be given here. The final form of macroscopic point equations for fluid species will read as follows.

*Mass*

$$\frac{\partial}{\partial t} (n \langle \rho^a \rangle^f) + \nabla \cdot (n \langle \rho^a \rangle^f \bar{\mathbf{v}}^a) = n \langle \rho^a \rangle^f (\bar{\dot{\mathbf{r}}} + \bar{\dot{\rho}}^a) = n \langle \rho^a \rangle^f \hat{R}^a \quad (12a)$$

*Momentum*

$$\begin{aligned} \frac{\partial}{\partial t} (n \langle \rho^a \rangle^f \bar{\mathbf{v}}^a) + \nabla \cdot (n \langle \rho^a \rangle^f \bar{\mathbf{v}}^a \bar{\mathbf{v}}^a) - \nabla \cdot \bar{\bar{\sigma}}^a - n \langle \rho^a \rangle^f \bar{\mathbf{g}}^a \\ = n \langle \rho^a \rangle^f (\bar{\dot{\mathbf{r}}} \bar{\mathbf{v}}^a + \bar{\mathbf{t}}^a + \bar{\dot{\rho}}^a \bar{\mathbf{v}}^a + \bar{\mathbf{m}}^a) = n \langle \rho^a \rangle^f (\hat{R}^a \bar{\mathbf{v}}^a + \hat{T}^a) \end{aligned} \quad (12b)$$

*Angular Momentum*

$$\bar{\bar{\sigma}}^a = (\bar{\bar{\sigma}}^a)^T \quad (12c)$$

## Energy

$$\begin{aligned} & \frac{\partial}{\partial t} \left( n \langle \rho^\alpha \rangle^f \left( \bar{E}^\alpha + \frac{1}{2} (\bar{v}^\alpha)^2 \right) \right) + \nabla \cdot (n \langle \rho^\alpha \rangle^f \bar{\mathbf{v}}^\alpha \left( \bar{E}^\alpha + \frac{1}{2} (\bar{v}^\alpha)^2 \right)) \\ & - \nabla \cdot (\bar{\boldsymbol{\sigma}}^\alpha \cdot \bar{\mathbf{v}}^\alpha + \bar{\mathbf{q}}^\alpha) - n \langle \rho^\alpha \rangle^f (\bar{\mathbf{g}}^\alpha \cdot \bar{\mathbf{v}}^\alpha + \bar{h}^\alpha) \\ & = n \langle \rho^\alpha \rangle^f [\bar{\mathbf{r}}^\alpha (\bar{E}^\alpha + \frac{1}{2} (\bar{v}^\alpha)^2) + \bar{\mathbf{t}}^\alpha \cdot \bar{\mathbf{v}}^\alpha + \bar{\mathbf{q}}^\alpha + \bar{\rho}^\alpha (\bar{E}^\alpha + \frac{1}{2} (\bar{v}^\alpha)^2) \\ & + \bar{\mathbf{m}}^\alpha \cdot \bar{\mathbf{v}}^\alpha + \bar{e}^\alpha] = n \langle \rho^\alpha \rangle^f \left[ \hat{R}^\alpha \left( \bar{E}^\alpha + \frac{1}{2} (\bar{v}^\alpha)^2 \right) + \hat{\mathbf{T}}^\alpha \cdot \bar{\mathbf{v}}^\alpha + \hat{\mathbf{Q}}^\alpha \right] \end{aligned} \quad (12d)$$

## Entropy

$$\begin{aligned} & \frac{\partial}{\partial t} (n \langle \rho^\alpha \rangle^f \bar{S}^\alpha) + \nabla \cdot (n \langle \rho^\alpha \rangle^f \bar{\mathbf{v}}^\alpha \bar{S}^\alpha) - \nabla \cdot \bar{\boldsymbol{\phi}}^\alpha - n \langle \rho^\alpha \rangle^f \bar{b}^\alpha \\ & = n \langle \rho^\alpha \rangle^f (\bar{\mathbf{r}}^\alpha \bar{S}^\alpha + \bar{\boldsymbol{\phi}}^\alpha + \bar{\rho}^\alpha \bar{S}^\alpha + \bar{\eta}^\alpha) + n \langle \rho^\alpha \rangle^f \bar{\Gamma}^\alpha \\ & = n \langle \rho^\alpha \rangle^f (\hat{R}^\alpha \bar{S}^\alpha + \hat{\boldsymbol{\phi}}^\alpha) + n \langle \rho^\alpha \rangle^f \bar{\Gamma}^\alpha \end{aligned} \quad (12e)$$

In these equations,  $\langle \rho^\alpha \rangle^f$  is defined by the averaging operator (7) and  $\bar{\mathbf{v}}^\alpha$ ,  $\bar{\mathbf{r}}^\alpha$ ,  $\bar{\mathbf{g}}^\alpha$ ,  $\bar{S}^\alpha$ ,  $\bar{b}^\alpha$ , and  $\bar{\Gamma}^\alpha$  are defined by the averaging operator (9). However, remaining quantities in above equations, which all carry the symbol ' $\bar{\cdot}$ ' over them, have various definitions that are specified hereunder.

$\bar{\boldsymbol{\sigma}}^\alpha$  is the macroscopic partial stress tensor of the species  $\alpha$ , and is defined such that:

$$\bar{\boldsymbol{\sigma}}^\alpha \cdot \mathbf{N} = \frac{1}{\delta A} \int_{\delta A} \gamma_f (\boldsymbol{\sigma}^\alpha - \rho^\alpha \bar{\mathbf{v}}^\alpha \bar{\mathbf{v}}^\alpha) \cdot \mathbf{n} \, da \quad (13)$$

where  $\mathbf{N}$  is the normal unit vector of the REA (representative elementary area), and  $\bar{\mathbf{v}}^\alpha$  is:

$$\bar{\mathbf{v}}^\alpha = \bar{\mathbf{v}}^\alpha(\mathbf{r}, t) = \mathbf{v}^\alpha(\mathbf{r}, t) - \bar{\mathbf{v}}^\alpha(\mathbf{x}, t) \quad (14)$$

Note that an interpretation similar to what was given for  $\boldsymbol{\sigma}^\alpha$  applies here to  $\bar{\boldsymbol{\sigma}}^\alpha$  as well, however, at a higher scale of observation.

$\bar{E}^\alpha$  is the macroscopic internal energy of species  $\alpha$  defined by:

$$\bar{E}^\alpha = \bar{E}^\alpha + \frac{1}{2} (\bar{v}^\alpha)^2 \quad (15)$$

$\bar{h}^\alpha$  is the macroscopic supply of energy defined by:

$$\bar{h}^\alpha = \bar{h}^\alpha + \bar{\mathbf{g}}^\alpha \cdot \bar{\mathbf{v}}^\alpha \quad (16)$$

$\bar{\mathbf{q}}^\alpha$  is the macroscopic heat vector defined such that:

$$\bar{\mathbf{q}}^\alpha \cdot \mathbf{N} = \frac{1}{\delta A} \int_{\delta A} \gamma_f \left( \mathbf{q}^\alpha + \boldsymbol{\sigma}^\alpha \cdot \bar{\mathbf{v}}^\alpha - \rho^\alpha \left( E^\alpha + \frac{1}{2} (\bar{v}^\alpha)^2 \right) \bar{\mathbf{v}}^\alpha \right) \cdot \mathbf{n} \, da \quad (17)$$

$\bar{\boldsymbol{\phi}}^\alpha$  is the macroscopic entropy flux vector defined such that:

$$\bar{\boldsymbol{\phi}}^\alpha \cdot \mathbf{N} = \frac{1}{\delta A} \int_{\delta A} \gamma_f (\boldsymbol{\phi}^\alpha - \rho^\alpha \bar{S}^\alpha \bar{\mathbf{v}}^\alpha) \cdot \mathbf{n} \, da \quad (18)$$

$\bar{\rho}^\alpha$  is the rate of net production of mass of species  $\alpha$  as a result of sorption and/or solution processes occurring at the surface of rock aggregates. It is defined by:

$$\bar{\rho}^\alpha = \frac{1}{n \langle \rho^\alpha \rangle^f \delta V} \int_{\delta A^f} \rho^\alpha (\mathbf{w} - \mathbf{v}^\alpha) \cdot \mathbf{n}^{fr} \, da \quad (19)$$

$\bar{\mathbf{t}}^\alpha$  is the macroscopic effect of molecular exchange of momentum between species  $\alpha$  and all other species. It is defined by:

$$\bar{\mathbf{t}}^\alpha = \bar{\mathbf{t}}^{\alpha\alpha} + \bar{\mathbf{r}}^{\alpha\alpha} \bar{\mathbf{v}}^{\alpha\alpha} \quad (20)$$

$\bar{\mathbf{m}}^\alpha$  accounts for the exchange of momentum between species  $\alpha$  and rock aggregates as a result of physio-chemical as well as mechanical interactions. It is defined by:

$$\bar{\mathbf{m}}^\alpha = \frac{1}{n \langle \rho^\alpha \rangle^f \delta V} \int_{\delta A^f} (\rho^\alpha \bar{\mathbf{v}}^\alpha (\mathbf{w} - \mathbf{v}^\alpha) + \boldsymbol{\sigma}^\alpha) \cdot \mathbf{n}^{fr} \, da \quad (21)$$

$\bar{q}^\alpha$  is the macroscopic effect of molecular exchange of energy between species  $\alpha$  and all other species. It is defined by:

$$\bar{q}^\alpha = \bar{q}^{\alpha\alpha} + \bar{\mathbf{t}}^\alpha \cdot \bar{\mathbf{v}}^{\alpha\alpha} + \bar{\mathbf{r}}^\alpha (\bar{E}^\alpha + \frac{1}{2} (\bar{v}^\alpha)^2)^\alpha \quad (22)$$

where,

$$\bar{E}^\alpha = E^\alpha - \bar{E}^\alpha \quad (23)$$

$\bar{e}^\alpha$  accounts for the exchange of energy between species  $\alpha$  and rock aggregates as a result of physio-chemical, mechanical, and thermal interactions. It is defined by:

$$\begin{aligned} \bar{e}^\alpha = \frac{1}{n \langle \rho^\alpha \rangle^f \delta V} \int_{\delta A^f} \left[ \rho^\alpha \left( \bar{E}^\alpha + \frac{1}{2} (\bar{v}^\alpha)^2 \right) (\mathbf{w} - \mathbf{v}^\alpha) \right. \\ \left. + \boldsymbol{\sigma}^\alpha \cdot \bar{\mathbf{v}}^\alpha + \mathbf{q}^\alpha \right] \cdot \mathbf{n}^{fr} \, da \end{aligned} \quad (24)$$

$\bar{\boldsymbol{\phi}}^\alpha$  is the macroscopic effect of molecular exchange of entropy between species  $\alpha$  and all other species, defined by:

$$\bar{\boldsymbol{\phi}}^\alpha = \bar{\boldsymbol{\phi}}^{\alpha\alpha} + \bar{\mathbf{r}}^{\alpha\alpha} \bar{S}^{\alpha\alpha} \quad (25)$$

where  $\bar{S}^\alpha$  is defined similar to  $\bar{E}^\alpha$ .

$\bar{\eta}^\alpha$  accounts for the supply of entropy to species  $\alpha$  as a result of thermodynamic interactions with rock aggregates. It is defined by:

$$\bar{\eta}^\alpha = \frac{1}{n \langle \rho^\alpha \rangle^f \delta V} \int_{\delta A^f} (\rho^\alpha \bar{S}^\alpha (\mathbf{w} - \mathbf{v}^\alpha) + \boldsymbol{\phi}^\alpha) \cdot \mathbf{n}^{fr} \, da \quad (26)$$

In the second parts of equations (14), quantities  $\hat{R}^\alpha$ ,  $\hat{\mathbf{T}}^\alpha$ ,  $\hat{\mathbf{Q}}^\alpha$ , and  $\hat{\boldsymbol{\phi}}^\alpha$  simply account for the combined effect of homogenous (molecular) and heterogeneous (occurring at interfaces) interactions. They are defined by:

$$\hat{R}^\alpha = \bar{\bar{r}}^\alpha + \bar{\bar{\rho}}^\alpha \quad (27a)$$

$$\hat{T}^\alpha = \bar{\bar{t}}^\alpha + \bar{\bar{m}}^\alpha \quad (27b)$$

$$\hat{Q}^\alpha = \bar{\bar{q}}^\alpha + \bar{\bar{e}}^\alpha \quad (27c)$$

$$\hat{\Phi}^\alpha = \bar{\bar{\phi}}^\alpha + \bar{\bar{\eta}}^\alpha \quad (27d)$$

Averaging of equations (4) provides the following restrictions on macroscopic terms accounting for exchange of properties among fluid species.

$$\sum_\alpha n \langle \rho^\alpha \rangle^f \bar{\bar{r}}^\alpha = 0 \quad (28a)$$

$$\sum_\alpha n \langle \rho^\alpha \rangle^f (\bar{\bar{r}}^\alpha \bar{\bar{v}}^\alpha + \bar{\bar{t}}^\alpha) = 0 \quad (28b)$$

$$\sum_\alpha n \langle \rho^\alpha \rangle^f \left( \bar{\bar{r}}^\alpha \left( \bar{\bar{E}}^\alpha + \frac{1}{2} (\bar{\bar{v}}^\alpha)^2 \right) + \bar{\bar{t}}^\alpha \cdot \bar{\bar{v}}^\alpha + \bar{\bar{q}}^\alpha \right) = 0 \quad (28c)$$

$$\sum_\alpha n \langle \rho^\alpha \rangle^f (\bar{\bar{r}}^\alpha \bar{\bar{S}}^\alpha + \bar{\bar{\phi}}^\alpha) = 0 \quad (28d)$$

The average of equations (5) results in the following balance laws for the rock phase.

Mass:

$$\frac{\partial}{\partial t} ((1-n) \langle \rho \rangle^r) + \nabla \cdot ((1-n) \langle \rho \rangle^r \bar{\bar{v}}^r) = (1-n) \langle \rho \rangle^r \hat{R}^r \quad (29a)$$

Momentum:

$$\frac{\partial}{\partial t} ((1-n) \langle \rho \rangle^r \bar{\bar{v}}^r) + \nabla \cdot ((1-n) \langle \rho \rangle^r \bar{\bar{v}}^r \bar{\bar{v}}^r) - \nabla \cdot \bar{\bar{\sigma}}^r - (1-n) \langle \rho \rangle^r \bar{\bar{g}}^r = (1-n) \langle \rho \rangle^r (\hat{R}^r \bar{\bar{v}}^r + \hat{T}^r) \quad (29b)$$

Angular Momentum:

$$\bar{\bar{\sigma}}^r = (\bar{\bar{\sigma}}^r)^T \quad (29c)$$

Energy:

$$\begin{aligned} & \frac{\partial}{\partial t} \left( (1-n) \langle \rho \rangle^r \left( \bar{\bar{E}}^r + \frac{1}{2} (\bar{\bar{v}}^r)^2 \right) \right) \\ & + \nabla \cdot \left( (1-n) \langle \rho \rangle^r \left( \bar{\bar{E}}^r + \frac{1}{2} (\bar{\bar{v}}^r)^2 \right) \bar{\bar{v}}^r \right) - \nabla \cdot (\bar{\bar{\sigma}}^r \cdot \bar{\bar{v}}^r + \bar{\bar{q}}^r) \\ & - (1-n) \langle \rho \rangle^r (\bar{\bar{g}}^r \cdot \bar{\bar{v}}^r + \bar{\bar{h}}^r) \\ & = (1-n) \langle \rho \rangle^r \left( \hat{R}^r \left( \bar{\bar{E}}^r + \frac{1}{2} (\bar{\bar{v}}^r)^2 \right) + \hat{T}^r \cdot \bar{\bar{v}}^r + \hat{Q}^r \right) \end{aligned} \quad (29d)$$

Entropy:

$$\begin{aligned} & \frac{\partial}{\partial t} ((1-n) \langle \rho \rangle^r \bar{\bar{S}}^r) \\ & + \nabla \cdot ((1-n) \langle \rho \rangle^r \bar{\bar{S}}^r \bar{\bar{v}}^r) - \nabla \cdot \bar{\bar{\phi}}^r - (1-n) \langle \rho \rangle^r \bar{\bar{b}}^r \\ & = (1-n) \langle \rho \rangle^r (\hat{R}^r \bar{\bar{S}}^r + \hat{\Phi}^r) + (1-n) \langle \rho \rangle^r \bar{\bar{\Gamma}}^r \end{aligned} \quad (29e)$$

Relationships between macroscopic and microscopic properties of the rock are quite similar to those given for fluid species. However, note that the exchange terms  $\hat{R}^r$ ,  $\hat{T}^r$ ,  $\hat{Q}^r$ , and  $\hat{\Phi}^r$  contain only the effects of interfacial interactions (i.e., they are equivalent to  $\bar{\bar{\rho}}^\alpha$ ,  $\bar{\bar{m}}^\alpha$ ,  $\bar{\bar{e}}^\alpha$ , and  $\bar{\bar{\eta}}^\alpha$ , respectively).

Finally, averaging of interfacial equations (6) results in the following restrictions on exchange terms.

$$n \sum_\alpha \langle \rho^\alpha \rangle^f \bar{\bar{\rho}}^\alpha = -(1-n) \langle \rho \rangle^r \hat{R}^r \quad (30a)$$

$$n \sum_\alpha \langle \rho^\alpha \rangle^f (\bar{\bar{\rho}}^\alpha \bar{\bar{v}}^\alpha + \bar{\bar{m}}^\alpha) = -(1-n) \langle \rho \rangle^r (\hat{R}^r \bar{\bar{v}}^r + \hat{T}^r) \quad (30b)$$

$$\begin{aligned} & n \sum_\alpha \langle \rho^\alpha \rangle^f \left( \bar{\bar{\rho}}^\alpha \left( \bar{\bar{E}}^\alpha + \frac{1}{2} (\bar{\bar{v}}^\alpha)^2 \right) + \bar{\bar{m}}^\alpha \cdot \bar{\bar{v}}^\alpha + \bar{\bar{e}}^\alpha \right) \\ & = -(1-n) \langle \rho \rangle^r \left( \hat{R}^r \left( \bar{\bar{E}}^r + \frac{1}{2} (\bar{\bar{v}}^r)^2 \right) + \hat{T}^r \cdot \bar{\bar{v}}^r + \hat{Q}^r \right) \end{aligned} \quad (30c)$$

$$n \sum_\alpha \langle \rho^\alpha \rangle^f (\bar{\bar{\rho}}^\alpha \bar{\bar{S}}^\alpha + \bar{\bar{\eta}}^\alpha) + (1-n) \langle \rho \rangle^r (\hat{R}^r \bar{\bar{S}}^r + \hat{\Phi}^r) \geq 0 \quad (30d)$$

Such restrictions must be expected because for the system as a whole, an internal net creation or destruction of total mass, momentum, and energy is not possible.

This completes derivation of macroscopic balance laws for the system under consideration. However, before closing this section, we like to derive balance laws which govern mean thermodynamic properties of the fluid phase. Such equations are readily obtained by summing of balance equations (12) over all species and using of appropriate definitions for bulk properties of the fluid. The procedure is straight forward and the results along with corresponding definitions are as follows.

$$\frac{\partial}{\partial t} (n \langle \rho \rangle^f) + \nabla \cdot (n \langle \rho \rangle^f \bar{\bar{v}}^f) = n \langle \rho \rangle^f \hat{R}^f \quad (31a)$$

$$\frac{\partial}{\partial t} (n \langle \rho \rangle^f \bar{\bar{v}}^f) + \nabla \cdot (n \langle \rho \rangle^f \bar{\bar{v}}^f \bar{\bar{v}}^f) - \nabla \cdot \bar{\bar{\sigma}}^f - n \sum_\alpha \langle \rho^\alpha \rangle^f \bar{\bar{g}}^\alpha = n \langle \rho \rangle^f (\hat{R}^f \bar{\bar{v}}^f + \hat{T}^f) \quad (31b)$$

$$\bar{\bar{\sigma}}^f = (\bar{\bar{\sigma}}^f)^T \quad (31c)$$

$$\begin{aligned} & \frac{\partial}{\partial t} \left( n \langle \rho \rangle^f \left( \bar{\bar{E}}^f + \frac{1}{2} (\bar{\bar{v}}^f)^2 \right) \right) + \nabla \cdot \left( n \langle \rho \rangle^f \left( \bar{\bar{E}}^f + \frac{1}{2} (\bar{\bar{v}}^f)^2 \right) \bar{\bar{v}}^f \right) \\ & - \nabla \cdot (\bar{\bar{\sigma}}^f \cdot \bar{\bar{v}}^f + \bar{\bar{q}}^f) - n \sum_\alpha \langle \rho^\alpha \rangle^f (\bar{\bar{g}}^\alpha \cdot \bar{\bar{v}}^\alpha + \bar{\bar{h}}^\alpha) \\ & = n \langle \rho \rangle^f \left( \hat{R}^f \left( \bar{\bar{E}}^f + \frac{1}{2} (\bar{\bar{v}}^f)^2 \right) + \hat{T}^f \cdot \bar{\bar{v}}^f + \hat{Q}^f \right) \end{aligned} \quad (31d)$$

$$\begin{aligned} & \frac{\partial}{\partial t} (n \langle \rho \rangle^f \bar{\bar{S}}^f) + \nabla \cdot (n \langle \rho \rangle^f \bar{\bar{S}}^f \bar{\bar{v}}^f) - \nabla \cdot \bar{\bar{\phi}}^f \\ & - n \sum_\alpha \langle \rho^\alpha \rangle^f \bar{\bar{b}}^\alpha = n \langle \rho \rangle^f (\hat{R}^f \bar{\bar{S}}^f + \hat{\Phi}^f) + n \langle \rho \rangle^f \bar{\bar{\Gamma}}^f \end{aligned} \quad (31e)$$

where,

$$\langle \rho \rangle^f = \sum_{\alpha} \langle \rho^{\alpha} \rangle^f \quad (32a)$$

$$\bar{\mathbf{v}}^f = \frac{1}{\langle \rho \rangle^f} \sum_{\alpha} \langle \rho^{\alpha} \rangle^f \bar{\mathbf{v}}^{\alpha} \quad (32b)$$

$$\bar{\bar{\sigma}}^f = \sum_{\alpha} (\bar{\bar{\sigma}}^{\alpha} - n \langle \rho^{\alpha} \rangle^f \mathbf{u}^{\alpha} \mathbf{u}^{\alpha}) \quad (32c)$$

$$\bar{\bar{E}}^f = \frac{1}{\langle \rho \rangle^f} \sum_{\alpha} \langle \rho^{\alpha} \rangle^f \left( \bar{\bar{E}}^{\alpha} + \frac{1}{2} (u^{\alpha})^2 \right) \quad (32d)$$

$$\bar{\bar{\mathbf{q}}}^f = \sum_{\alpha} \left( \bar{\bar{\mathbf{q}}}^{\alpha} + \bar{\bar{\sigma}}^{\alpha} \cdot \mathbf{u}^{\alpha} - n \langle \rho^{\alpha} \rangle^f \left( \bar{\bar{E}}^{\alpha} + \frac{1}{2} (u^{\alpha})^2 \right) \mathbf{u}^{\alpha} \right) \quad (32e)$$

$$\bar{\bar{S}}^f = \frac{1}{\langle \rho \rangle^f} \sum_{\alpha} \langle \rho^{\alpha} \rangle^f \bar{\bar{S}}^{\alpha} \quad (32f)$$

$$\bar{\bar{\phi}}^f = \sum_{\alpha} (\bar{\bar{\phi}}^{\alpha} - n \langle \rho^{\alpha} \rangle^f \bar{\bar{S}}^{\alpha} \mathbf{u}^{\alpha}) \quad (32g)$$

$$\bar{\Gamma}^f = \frac{1}{\langle \rho \rangle^f} \sum_{\alpha} \langle \rho^{\alpha} \rangle^f \bar{\Gamma}^{\alpha} \quad (32h)$$

$$n \langle \rho \rangle^f \hat{R}^f = n \sum_{\alpha} \langle \rho^{\alpha} \rangle^f \bar{\bar{\rho}}^{\alpha} = -(1-n) \langle \rho \rangle^f \hat{R}^r \quad (33a)$$

$$\hat{\mathbf{T}}^f = \frac{1}{\langle \rho \rangle^f} \sum_{\alpha} \langle \rho^{\alpha} \rangle^f (\bar{\bar{\mathbf{m}}}^{\alpha} + \bar{\bar{\rho}}^{\alpha} \mathbf{u}^{\alpha}) \quad (33b)$$

$$\hat{Q}^f = \frac{1}{\langle \rho \rangle^f} \sum_{\alpha} \langle \rho^{\alpha} \rangle^f \left[ \bar{\bar{e}}^{\alpha} + \bar{\bar{\mathbf{m}}}^{\alpha} \cdot \mathbf{u}^{\alpha} + \bar{\bar{\rho}}^{\alpha} \left( (\bar{\bar{E}}^{\alpha} - \bar{\bar{E}}^f) + \frac{1}{2} (u^{\alpha})^2 \right) \right] \quad (33c)$$

$$\hat{\Phi}^f = \frac{1}{\langle \rho \rangle^f} \sum_{\alpha} \langle \rho^{\alpha} \rangle^f (\bar{\bar{\eta}}^{\alpha} + \bar{\bar{\rho}}^{\alpha} (\bar{\bar{S}}^{\alpha} - \bar{\bar{S}}^f)) \quad (33d)$$

In these equations,  $\mathbf{u}^{\alpha}$  is the macroscopic diffusive-dispersive velocity of species  $\alpha$  defined by:

$$\mathbf{u}^{\alpha} = \bar{\mathbf{v}}^{\alpha} - \bar{\mathbf{v}}^f \quad (34)$$

and subject to:

$$\sum_{\alpha} \langle \rho^{\alpha} \rangle^f \mathbf{u}^{\alpha} = 0 \quad (35)$$

It should be noted that equations (31), so far as the  $N$  balance equations (12) are employed for all species, do not constitute an additional set of equations for the porous medium. In solute transport problems, however, often one set of the species balance equations (normally those of the pure fluid component) is discarded and replaced by equations (31) for the fluid phase bulk properties. This approach will be illustrated and exploited in the second part of this work.

## FORMULATION OF THE SECOND LAW OF THERMODYNAMICS

This law concerns itself with the sign of net entropy production rate terms  $\bar{\Gamma}^{\alpha}$ ,  $\bar{\Gamma}^r$ , and/or  $\bar{\Gamma}^f$ . The macroscopic form of second law of thermodynamics depends on how it is microscopically formulated. Two alternatives are possible. One is for the case that the second law can be admitted at any microscopic point within the fluid or the solid phase, i.e.:

$$\rho \Gamma|_{\mathbf{r} \in V_f} \geq 0 \quad (36a)$$

and

$$\sum_{\alpha} \rho^{\alpha} \Gamma^{\alpha}|_{\mathbf{r} \in V_f} \geq 0 \quad (36b)$$

The other alternative is that the second law can be admitted only for the whole medium occupying the domain  $V$ , i.e.:

$$\int_{V_f} \rho \Gamma \, dv + \int_{V_r} \sum_{\alpha} \rho^{\alpha} \Gamma^{\alpha} \, dv \geq 0 \quad (37)$$

The first alternative will result in an independent formulation of second law for the rock and the fluid in the macroscopic domain. That is, after applying the averaging procedure to equations (36) we get,

$$\langle \rho \rangle^f \bar{\Gamma}^f \geq 0 \quad (38a)$$

$$\langle \rho \rangle^f \bar{\Gamma}^f = \sum_{\alpha} \langle \rho^{\alpha} \rangle^f \bar{\Gamma}^{\alpha} \geq 0 \quad (38b)$$

However, the second alternative, after averaging and localization yields,

$$\bar{\Gamma}^m = (1-n) \langle \rho \rangle^r \bar{\Gamma}^r + n \sum_{\alpha} \langle \rho^{\alpha} \rangle^f \bar{\Gamma}^{\alpha} \geq 0 \quad (39)$$

Clearly, the second form is more general than the first one. In other words, it is possible to find certain materials for which the first formulation may not be admitted; while the second one is certainly admissible for all systems and processes. For further discussion in this regard, the interested reader may consult references 15, 22, and 23. In this work, we shall adopt equation (39) as the macroscopic statement of the second law of thermodynamics.

Finally, we need to introduce the temperature function for the fluid and the rock. One could arrive at these concepts by means of methods (such as the method of Lagrange multipliers<sup>24,25</sup>) involving balance laws and the second law of thermodynamics. Here, however, without going into such details, we simply define the rock and the fluid temperature functions, denoted by  $\theta^r$  and  $\theta^f$ , respectively, such that,

$$\bar{b}^r = \bar{h}/\theta^r \quad (40a)$$

$$\bar{b}^{\alpha} = \bar{h}^{\alpha}/\theta^f \quad (40b)$$

It is implicit in relation (40b) that fluid species, because miscible in the molecular level, attain a state of local thermal equilibrium such that they all have a common temperature function  $\theta^f$  at any given macroscopic point. Because of this important restriction on the behaviour of

Table 3.

Material	Quantity	$\bar{\Psi}^z$	$\bar{I}^z$	$\bar{F}^z$	$\bar{G}^z$
Components of fluid	Mass	$n\langle\rho^\alpha\rangle^f$	0	0	$n\langle\rho^\alpha\rangle^f\hat{R}^\alpha$
	Momentum	$n\langle\rho^\alpha\rangle^f\bar{\mathbf{v}}^\alpha$	$\bar{\boldsymbol{\sigma}}^\alpha$	$n\langle\rho^\alpha\rangle^f\bar{\mathbf{g}}^\alpha$	$n\langle\rho^\alpha\rangle^f(\hat{R}^\alpha\bar{\mathbf{v}}^\alpha + \hat{\mathbf{T}}^\alpha)$
Rock	Mass	$(1-n)\langle\rho\rangle^r$	0	0	$(1-n)\langle\rho\rangle^r\hat{R}^r$
	Momentum	$(1-n)\langle\rho\rangle^r\bar{\mathbf{v}}^r$	$\bar{\boldsymbol{\sigma}}^r$	$(1-n)\langle\rho\rangle^r\bar{\mathbf{g}}^r$	$(1-n)\langle\rho\rangle^r(\hat{R}^r\bar{\mathbf{v}}^r + \hat{\mathbf{T}}^r)$
	Energy	$(1-n)\langle\rho\rangle^r(\bar{E}^r + \frac{1}{2}(\bar{v}^r)^2)$	$\bar{\boldsymbol{\sigma}}^r \cdot \bar{\mathbf{v}}^r + \bar{\mathbf{q}}^r$	$(1-n)\langle\rho\rangle^r(\bar{\mathbf{g}}^r \cdot \bar{\mathbf{v}}^r + \bar{h}^r)$	$(1-n)\langle\rho\rangle^r[\hat{R}^r(\bar{E}^r + \frac{1}{2}(\bar{v}^r)^2) + \hat{\mathbf{T}}^r \cdot \bar{\mathbf{v}}^r + \hat{Q}^r]$
Fluid phase	Mass	$n\langle\rho\rangle^f$	0	0	$n\langle\rho\rangle^f\hat{R}^f$
	Momentum	$n\langle\rho\rangle^f\bar{\mathbf{v}}^f$	$\bar{\boldsymbol{\sigma}}^f$	$n\sum_\alpha\langle\rho^\alpha\rangle^f\bar{\mathbf{g}}^\alpha$	$n\langle\rho\rangle^f(\hat{R}^f\bar{\mathbf{v}}^f + \hat{\mathbf{T}}^f)$
	Energy	$n\langle\rho\rangle^f(\bar{E}^f + \frac{1}{2}(\bar{v}^f)^2)$	$\bar{\boldsymbol{\sigma}}^f \cdot \bar{\mathbf{v}}^f + \bar{\mathbf{q}}^f$	$n\sum_\alpha\langle\rho^\alpha\rangle^f(\bar{\mathbf{g}}^\alpha \cdot \bar{\mathbf{v}}^\alpha + \bar{h}^\alpha)$	$n\langle\rho\rangle^f[\hat{R}^f(\bar{E}^f + \frac{1}{2}(\bar{v}^f)^2) + \hat{\mathbf{T}}^f \cdot \bar{\mathbf{v}}^f + \hat{Q}^f]$

fluid components, we need to employ only one energy balance equation for all components. For practical reasons, this is commonly chosen to be the energy balance of fluid.

## SUMMARY OF RESULTS, DISCUSSION, AND CONCLUSION

The systematic averaging technique developed in earlier works<sup>14,15</sup> has been employed here to obtain a macroscopic description of a porous medium consisting of a multi-component fluid phase and a solid-phase rock matrix. Macroscopic properties for fluid species and rock aggregates, as well as for bulk properties of the fluid phase, are defined and the corresponding balance laws are obtained.

Macroscopic equations of balance can be put in the following general form:

$$\frac{\partial \bar{\Psi}^z}{\partial t} + \mathbf{V} \cdot (\bar{\mathbf{v}}^z \bar{\Psi}^z) - \mathbf{V} \cdot \bar{\mathbf{I}}^z - \bar{F}^z = \bar{G}^z \quad (41)$$

where  $z$  may take upon  $\alpha$ ,  $f$ , or  $r$ . Appropriate variables for equations of balance of mass, momentum, and energy must be selected from Table 3. The interaction terms  $\bar{G}^z$ 's are subject to the following restrictions:

$$\bar{G}^f = -\bar{G}^r = \sum_\alpha \bar{G}^\alpha \quad (42)$$

Note that although  $\bar{G}^\alpha$ 's for fluid species contain molecular as well as interfacial interactions,  $\sum_\alpha \bar{G}^\alpha$  contains only the latter effects. This is a consequence of definitions (27) and restrictions (28). Also, recall that the stress tensors  $\bar{\boldsymbol{\sigma}}^z$  are symmetric tensors. Furthermore, because of local thermal equilibrium among fluid components, only the energy equations for fluid and solid are given.

The second law of thermodynamics will be given in an expanded form. This is done with the help of equations (12), (29), and (40). The result, recognizing restriction (30d), will read as follows.

$$\begin{aligned} \Gamma^m = & \frac{1}{\theta^f} \sum_\alpha \left\{ -n\langle\rho^\alpha\rangle^f \left( \frac{D^\alpha A^\alpha}{Dt} + \bar{S}^\alpha \frac{D^\alpha \theta^f}{Dt} \right) + \theta^f \mathbf{V} \cdot \left( \frac{\bar{\mathbf{q}}^\alpha}{\theta^f} - \bar{\boldsymbol{\phi}}^\alpha \right) \right. \\ & \left. + \frac{1}{\theta^f} \bar{\mathbf{q}}^\alpha \cdot \mathbf{V} \theta^f + \bar{\boldsymbol{\sigma}}^\alpha : \mathbf{V} \bar{\mathbf{v}}^\alpha + n\langle\rho^\alpha\rangle^f \hat{Q}^\alpha \right\} \\ & + \frac{1}{\theta^r} \left\{ -(1-n)\langle\rho\rangle^r \left( \frac{D^r A^r}{Dt} + \bar{S}^r \frac{D^r \theta^r}{Dt} \right) + \theta^r \mathbf{V} \cdot \left( \frac{\bar{\mathbf{q}}^r}{\theta^r} - \bar{\boldsymbol{\phi}}^r \right) \right. \\ & \left. + \frac{1}{\theta^r} \bar{\mathbf{q}}^r \cdot \mathbf{V} \theta^r + \bar{\boldsymbol{\sigma}}^r : \mathbf{V} \bar{\mathbf{v}}^r + n\langle\rho\rangle^r \hat{Q}^r \right\} \\ & \geq \left( n \sum_\alpha \langle\rho^\alpha\rangle^f \hat{\phi}^\alpha + (1-n)\langle\rho\rangle^r \hat{\phi}^r \right) \geq 0 \end{aligned} \quad (43)$$

where  $A^z$  (or  $A^r$ ) is the Helmholtz free energy function and  $D^z/Dt$  is the material derivative of a function defined by:

$$A^z = E^z - \theta^z S^z \quad (44a)$$

$$\frac{D^z(\cdot)}{Dt} = \frac{\partial(\cdot)}{\partial t} + \bar{\mathbf{v}}^z \cdot \mathbf{V}(\cdot) \quad (44b)$$

Comparison of our results with those of other researchers is possible but only for the mass conservation equation. Our equations (12a), (28a), (29a), (30a), and (31a) are in full agreement with those obtained by other authors (compare e.g., with Marle<sup>26</sup>, Bear and Bachmat<sup>7</sup>, Nguyen *et al.*<sup>13</sup>, and Abriola<sup>27</sup>). For the rest, it is not possible to make a direct comparison, because derivations of equations of balance of momentum, energy, and entropy has not been sought by other authors. However, a clear consistency, both in form and in concept, is apparent between these balance laws and the mass conservation equation.

Also it is noted that macroscopic balance equations developed here for fluid species resemble, albeit only in form, the ones obtained for individual phases of a multi-phase system—compare equations (12) with equations of balance found in Hassanizadeh and Gray<sup>15</sup>. There are two main differences however. One is that fluid species have a common volume fraction equal to that of the fluid phase. The other important difference lies in the interpretation of exchange terms. Here, the exchange



terms ( $\hat{R}^\alpha$ ,  $\hat{T}^\alpha$ , and  $\hat{Q}^\alpha$ ) include the effect of molecular (or homogeneous) as well as interfacial (or heterogeneous) interactions. Whereas, the exchange terms for different fluid or solid phases in a multi-phase system account only for interfacial interactions.

The formalism of this paper and the results thereof provide the physical basis and rationale for proposing a continuum model of a porous solid containing a mixture of miscible fluids. Considering the fact that macroscopic thermodynamical properties for fluid species and rock aggregates along with governing balance equations are defined continuously throughout the space  $V$ , one can conceptually describe the porous medium as a superposition of  $N+1$  coexisting continua. Each continuum, while undergoing thermodynamic processes, interacts with other continua. Once again, major differences between such a model and a continuum model of immiscible phases lies in the two points discussed in the previous paragraph.

The approach followed here can be readily employed in order to obtain balance laws governing the multi-phase flow of a number of multi-component fluids in porous media. In Appendix A, macroscopic balance laws obtained here are directly generalized to include the case of multi-phase multi-component flow in porous media.

## ACKNOWLEDGEMENT

This research has been carried out while the author was working under the contract WAS-383-83-7 NL between the Commission of European Communities and the National Institute of Public Health and Environmental Hygiene (RIVM).

## NOMENCLATURE

Symbols used in the Introduction and Appendix A are not included here.

$A$	surface bounding the space occupied by the porous medium
$A'$	Helmholtz free energy function (also $A^\alpha$ )
$b$	external supply of entropy (also $b^\alpha$ )
$da$	microscopic differential element of area
$dv$	microscopic differential element of volume
$\bar{e}^\alpha$	interfacial exchange of energy defined in equation (24)
$E$	internal energy density function (also $E^\alpha$ )
$f$	external supply of thermodynamic property $\psi$ (also $f^\alpha$ )
$G$	molecular supply of thermodynamic property $\psi$ (also $G^\alpha$ )
$g$	external supply of momentum (also $g^\alpha$ )
$h$	external supply of energy (also $h^\alpha$ )
$i$	surface flux vector of thermodynamic property $\psi$ (also $i^\alpha$ )
$\bar{m}^\alpha$	interfacial exchange of momentum defined in equation (21)
$n$	porosity of the porous medium
$\mathbf{n}$	unit normal vector to a microscopic surface
$\mathbf{n}^{fr}$	unit normal vector to the solid-fluid interface
$N$	number of components of the fluid
$\mathbf{N}$	unit normal vector to a macroscopic surface
$\mathbf{q}$	surface flux vector of heat (also $\mathbf{q}^\alpha$ )
$\hat{q}^\alpha$	molecular supply of energy to species $\alpha$

$\hat{Q}^\alpha$	total supply of energy due to interactions (also $\hat{Q}^\alpha$ )
$\mathbf{r}$	position vector in the microscopic domain
$\hat{r}^\alpha$	molecular supply of mass to the species $\alpha$
$\hat{R}^\alpha$	total supply of mass due to interactions (also $\hat{R}^\alpha$ )
$REA$	representative elementary area
$REV$	representative elementary volume
$S$	internal entropy density function (also $S^\alpha$ )
$t$	time
$\hat{\mathbf{t}}^\alpha$	molecular supply of momentum to the species $\alpha$
$\hat{T}^\alpha$	total supply of momentum due to interactions (also $\hat{T}^\alpha$ )
$\mathbf{u}^\alpha$	diffusion-dispersion velocity of species $\alpha$
$\mathbf{v}$	velocity vector (also $\mathbf{v}^\alpha$ )
$V$	part of the space occupied by the porous medium
$V_f$	part of $V$ occupied by the fluid phase
$V_r$	part of $V$ occupied by the solid phase
$\mathbf{w}$	microscopic velocity of the solid-fluid interface
$\mathbf{x}$	position vector in the macroscopic domain

## Greek

$\gamma_a$	phase distribution function, defined in equation (10)
$\Gamma$	net rate of production of entropy (also $\Gamma^\alpha$ )
$\delta A$	area of $REA$
$\delta A^{fr}$	area of solid-fluid interfaces within $REV$
$\delta V$	volume of $REV$
$\bar{e}^a$	volume fraction of phase 'a'
$\bar{\eta}^\alpha$	interfacial exchange of entropy defined in equation (26)
$\theta^a$	temperature function of phase 'a'
$\rho$	mass density function (also $\rho^\alpha$ )
$\bar{\rho}^\alpha$	interfacial exchange of mass, defined in equation (19)
$\sigma$	stress tensor (also $\sigma^\alpha$ )
$\phi$	surface flux vector of entropy (also $\phi^\alpha$ )
$\hat{\phi}^\alpha$	molecular supply of entropy to species $\alpha$
$\hat{\Phi}^\alpha$	total supply of entropy (also $\hat{\Phi}^\alpha$ )
$\psi$	a typical thermodynamic property (also $\psi^\alpha$ )

## Subscripts and superscripts

$f$	fluid
$r$	rock (or solid)
$T$	transpose of tensor
$z$	can be either 'f', 'r', or 'a'
$\alpha$	a typical component of the fluid phase

## Averaging signs

$\langle \rangle^a$	volume-weighted average, defined in equation (7)
$-a$	mass-weighted average of rock or fluid phase (equation (8))
$-\alpha$	mass-weighted average of component $\alpha$ (equation (9))
$\sim \alpha$	difference between microscopic and macroscopic value of a variable
$= \alpha$	macroscopic properties of component $\alpha$ defined in equations (13)–(26) (also $=r$ )
$= f$	macroscopic properties of fluid phase defined in equations (32)

## Special notation

- $\nabla$  gradient or divergence operator  
 $\sum_{\alpha}$  summation over all  $\alpha$ 's, i.e.,  $\sum_{\alpha=1}^N$   
 $|_f$  limit of the preceding term at the fluid-phase side of a solid-fluid interface (also  $|_s$ )  
 $D/Dt$  material derivative defined in equation (44b)

## REFERENCES

- Sposito, G., Gupta, V. K. and Bhattacharya, R. N. Foundation theories of solute transport in porous media: a critical review, *Adv. Water Resources* 1979, **2**, 59
- Truesdell, C. Mechanical basis of diffusion, *J. Chem. Phys.* 1962, **37**, 2336
- Bowen, R. M. Theory of mixtures, *Continuum Physics*, (Edited by A. C. Eringen), Vol. 3, Academic Press, New York, 1976
- Bear, J. *Dynamics of Fluids in Porous Media*, American Elsevier, New York, 1972
- Gray, W. G. A derivation of the equations for multiphase transport, *Chem. Eng. Sci.* 1975, **30**, 229
- Blake, T. R. and Garg, S. K. On the species transport equations for flow in porous media, *Water Resour. Res.* 1976, **12**, 798
- Bear, J. and Bachmat, Y. Transport phenomena in porous media. The basic equations in *Fundamentals of Transport Phenomena in Porous Media*, (Eds J. J. Bear and M. Y. Corraçcioglu), Martinus Nijhoff, Dordrecht, 1984
- Carbonell, R. G. and Whitaker, S. Heat and mass transfer in porous media in *Fundamentals of Transport Phenomena in Prous Media*, (Eds J. Bear and M. Y. Corraçcioglu), Martinus Nijhoff, Dordrecht, 1984
- Bachmat, Y. and Bear, J. The dispersive flux in transport phenomena in porous media, *Adv. Water Resources* 1983, **6**, 169
- Gupta, V. K., Bhattacharya, R. N. and Sposito, G. A molecular approach to the theory of solute transport in porous media, *J. Hydrol.* 1981, **50**, 355
- Chu, S.-Y. and Sposito, G. A derivation of the macroscopic solute transport equation for homogeneous, saturated, porous media, *Water Resour. Res.* 1980, **16**, 542
- Chu, S.-Y. and Sposito, G. A derivation of the macroscopic solute transport equation for homogeneous, saturated, porous media 2. Reactive solutes at low concentrations, *Water Resour. Res.* 1981, **17**, 333
- Nguyen, V. V., Gray, W. G., Pinder, G. F., Botha, J. F. and Crerar, A. D. A theoretical investigation on the transport of chemicals in reactive porous media, *Water Resour. Res.* 1982, **18**, 1149
- Hassanizadeh, M. and Gray, W. G. General conservation equations for multi phase systems: 1. Averaging procedure, *Adv. Water Resources* 1979, **2**, 131
- Hassanizadeh, M. and Gray, W. G. General conservation equations for multi phase systems: 2. Mass, energy, and entropy equations, *Adv. Water Resources* 1979, **2**, 191
- Hassanizadeh, M. and Gray, W. G. General conservation equations for multi phase systems: 3. Constitutive theory for porous media, *Adv. Water Resources* 1980, **3**, 25
- Gray, W. G. General conservation equations for multi-phase systems: 4. Constitutive theory including phase change, *Adv. Water Resources*, 1983, **6**, 130
- Long, R. L. *Mechanics of Solids and Fluids*, Prentice-Hall, Englewood Cliffs, NJ, 1971
- Truesdell, C. *Rational Thermodynamics*, 2nd edition, Springer-Verlag, New York, 1984, chapter 5
- Bowen, R. M. Diffusion models implied by the theory of mixtures, 1984 in Reference no. 2 above
- Gray, W. G. and Lee, P. C. Y. On the theorems for local volume averaging of multiphase systems, *Int. J. Multiphase Flow* 1977, **3**, 333
- Green, A. E. and Naghdi, P. M. Entropy inequalities for mixtures, *Quart. J. Mech. Appl. Math.* 1971, **24**, 473
- Müller, I. A thermodynamic theory of mixtures of fluids, *Arch. Rat. Mech. Anal.* 1968, **28**, 1
- Liu, I-Shih Method of Lagrange multipliers for exploitation of the entropy principle, *Arch. Rat. Mech. Anal.* 1972, **46**, 131
- Müller, I. Thermodynamic theory of mixtures, *J. de Méch.* 1975, **14**, 267

- Marle, C. M. On macroscopic equations governing multi-phase flow with diffusion and chemical reactions in porous media, *Int. J. Engng. Sci.* 1982, **20**, 643
- Abriola, L. M. *Multiphase Migration of Organic Compounds in a Porous Medium, A Mathematical Model*, Lecture Notes in Engineering, (Eds C. A. Brebbia and S. A. Orszag), 1984, no. 8, Appendix A

## APPENDIX A

## Macroscopic balance laws for multi-phase flow of multi-component fluids

Consider a situation where the void space is occupied by  $M$  immiscible fluid phases. Each fluid phase is composed of  $N$  different components which are miscible in the molecular level. Furthermore, rock aggregates are also considered to be composed of  $N$  components mixed at the molecular level. It should be noted that different phases may be composed of a different number of components. Here, we choose  $N$  equal to the total number of distinct components existing in the porous medium. Then, in certain phases, the mass density and thermodynamic properties of some of the  $N$  components may be zero at all times. Microscopically, adjacent phases are separated by singular interfaces which are devoid of thermodynamic properties but allow for interactions between the phases. Thermodynamic processes at a microscopic point within any of the phases are governed by balance laws presented in equation (3) and Table 1. However, at interfaces the following jump condition for individual components of adjacent phases can be given.

$$(\rho^{\alpha}\psi^{\alpha}(\mathbf{w}-\mathbf{v}^{\alpha})+\mathbf{i}^{\alpha})|_{ab}\cdot\mathbf{n}^{ab}=-\left(\rho^{\alpha}\psi^{\alpha}(\mathbf{w}-\mathbf{v}^{\alpha})+\mathbf{i}^{\alpha}\right)|_{ba}\cdot\mathbf{n}^{ba}$$

$$a,b=r \text{ or } 1 \text{ to } M; \quad \alpha=1 \text{ to } N \quad (\text{A1})$$

The approach followed in this work can be readily applied to this situation in order to obtain macroscopic balance laws for individual components of each phase. Resulting equations will take the following general form.

$$\frac{\partial}{\partial t}(\varepsilon^a\langle\rho^{\alpha}\rangle^a\bar{\psi}^{za})+\nabla\cdot(\varepsilon^a\langle\rho^{\alpha}\rangle^a\bar{\mathbf{v}}^{za}\bar{\phi}^{za})-\nabla\cdot\bar{\mathbf{i}}^{za}-\varepsilon^a\langle\rho^{\alpha}\rangle^a\bar{f}^{za}=\varepsilon^a\langle\rho^{\alpha}\rangle^a(\bar{G}^{za}+\sum_b\bar{I}^{zab}) \quad (\text{A2})$$

where

$$a,b=\begin{cases} 1 \text{ to } M & \text{for fluid phases} \\ r & \text{for the rock phase} \end{cases}$$

$$\sum_a\varepsilon^a=1 \quad \text{and} \quad \sum_{a=1}^M\varepsilon^a=n \quad (\text{A3})$$

$\bar{\psi}^{za}$ ,  $\bar{\mathbf{v}}^{za}$ ,  $\bar{f}^{za}$  and  $\bar{G}^{za}$  are defined by the mass average operator:

$$\bar{\psi}^{za}=\frac{1}{\varepsilon^a\langle\rho^{\alpha}\rangle^a\delta V}\int_{\delta V}\gamma_a\rho^{\alpha}\psi^{\alpha}dv \quad (\text{A4})$$

$\bar{\mathbf{i}}^{za}$  is defined such that,

$$\bar{\mathbf{i}}^{za}\cdot\mathbf{N}=\frac{1}{\delta A}\int_{\delta A}\gamma_a(\mathbf{i}^z-\rho^{\alpha}\bar{\mathbf{v}}^{za}\bar{\psi}^{za})\cdot\mathbf{n}da \quad (\text{A5})$$

$\bar{I}^{ab}$  is the interfacial interaction term defined by:

$$\bar{I}^{ab} = \frac{1}{\varepsilon^a \langle \rho^a \rangle^a \delta V} \int_{\delta A^{ab}} (\rho^a \psi^a (\mathbf{w} - \mathbf{v}^a) + \mathbf{i}^a) \cdot \mathbf{n}^{ab} da \quad (\text{A6})$$

Clearly,  $\delta A^{ab} = 0$  and therefore  $\bar{I}^{ab} = 0$  for  $a = b$ . The interaction terms are subject to the following restrictions.

$$\sum_a \langle \rho^a \rangle^a \bar{G}^{za} = 0 \quad (\text{A7})$$

$$\varepsilon^a \langle \rho^a \rangle^a \bar{I}^{ab} = \sum_b \varepsilon^b \langle \rho^b \rangle^b \bar{I}^{ba} \quad (\text{A8})$$

Individual balance laws may be obtained by choosing

appropriate variables for  $\bar{\psi}^{za}, \bar{\mathbf{i}}^{za}, \dots$  from Table 3, only that that porosity  $n$  must be replaced by  $\varepsilon^a$ , and indices ' $\alpha$ ' shall be all changed to ' $za$ '. Balance laws for bulk properties of individual fluid phases may be obtained by summing of equation (A2) over all  $\alpha$ 's of a given phase. They will have the same form as equations (31)–(33), only that indices ' $f$ ' and ' $\alpha$ ' must be replaced by ' $a$ ' and ' $za$ ', respectively. The interfacial interaction terms for fluid and rock phases,  $\bar{I}^a$ , will be defined as:

$$\bar{I}^a = \frac{1}{\langle \rho \rangle^a} \sum_a \sum_b \langle \rho^a \rangle^a \bar{I}^{ab} \quad (\text{A9})$$

and equation (A8) will yield,

$$\sum_a \varepsilon^a \langle \rho \rangle^a \bar{I}^a = 0 \quad (\text{A10})$$