Continuum description of thermodynamic processes in porous media: Fundamentals and applications

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This is a brief exposition of a systematic procedure based on the Coleman and Noll method, [4], of exploitation of the entropy inequality for developing basic equations governing thermodynamic processes in porous media. First the procedure for single-phase materials is described, balance laws are presented and basic axioms of constitutive theory are introduced. The procedure is illustrated by developing consitutive equations for elastic solids, viscous fluid and viscoelastic materials. Next, the constitutive theory is presented for flow and transport in porous media and it is shown how Darcy's law for flow of water and Fick's law for transport of solutes can be obtained.

Key words: *Continuum mechanics, thermodynamics of porous media, Coleman and Noll method, entropy inequality*

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1. Thermodynamics of single - phase materials

1.1. Introduction

Basic equations governing thermo-mechanical processes at the continuum scale compose of two sets of equations: conservations laws and constitutive relationships. Conservation laws are not specific to any material type and have a common form for solids, liquids, or gasses. In continuum mechanics, conservation laws are postulated as axioms of continuum theory. It is also possible to derive balance laws for single-phase materials by averaging a molecular description of materials (see e.g. Murdoch and Bedeaux, [15]). Conservation laws for multiphase systems have been also derived by means of averaging, either starting at the molecular level (see e.g. Murdoch and Kubik, [16]; Murdoch and Hassanizadeh, [17]), or at the pore scale (see e.g. Hassanizadeh, [6, 7]; Gray and Hassanizadeh, [12, 14]). Constitutive relationships are specific to a given material type. They describe material behavior such as elasticity, viscosity, heat conductivity, diffusion, etc. Constitutive relationships have been often proposed as empirical equations. But, in continuum mechanics, a systematic procedure has been developed for obtaining constitutive relationships. This procedure was developed by Coleman and Noll, [4]. It is based on the exploitation of the second law of thermodynamics.

In this article, we describe the basis of Coleman and Noll method of development of constitutive relationships for saturated porous media. Conservation laws for both single- and multiphase systems are considered as given. First, we illustrate the method of elastic solids and viscous fluids. Then, we give an account of obtaining constitutive equations for flow of a compressible fluid in a deformable solid and the dispersion of solutes in a porous medium.

1.2. Kinematics

1.2.1. Motion and deformation

Consider a body, composed of a single-phase material and occupying a volume
V. Associated with the body is a measure called mass. The mass of a
body is assumed to be non-negative, additive, and indestructible. A point
of departure of continuum mechanics from discrete mechanics is to assume
that *the mass is absolutely continuous in the space* occupied by the body.
Therefore, it is possible to define a mass density ρ:

$$\rho = \frac{dM}{dV} = \frac{dM_0}{dV_0} \quad 0 \leq \rho < \infty, \qquad (1.1a)$$

such that

$$M = \int_V \rho dv, \qquad (1.1b)$$

where M_0 is the initial mass of the body and M is the mass at a later time.
The indestructibility of mass requires that $M = M_0$.

Each and every mathematical point is occupied by a *material point*. A
material point is an infinitesimal element of volume at the scale of the
continuum. Each point is a large collection of molecules of the matter
constructing the body. A point has a mass and all other properties that
will be defined and assigned to the body itself.

The coordinate of a material point at time $t = 0$ is denoted by $\mathbf{X}$. The motion
of the body carries the material point to a new position with coordinate $\mathbf{x}$,
at a later time t. Because we assume that matter is continuous and remains
continuous during displacement, there must be a unique correspondence
between $\mathbf{x}$ and $\mathbf{X}$. That is, a material point occupying the reference position
$\mathbf{X}$ can not be found at two different positions at a later time. Also, no region
of positive finite volume of matter will deform into a zero or infinite volume.
Taking the parameter time into account, we can write:

$$\mathbf{x} = \mathbf{F}(\mathbf{X}, t) \qquad (1.2a)$$

This is called *motion* and the transformation $\mathbf{F}$ denotes the motion. One may
also define *inverse motion*:

$$\mathbf{X} = \mathbf{F}^{-1}(\mathbf{x}, t) \qquad (1.2b)$$

The union of all $\mathbf{X}$'s is called the "reference configuration" and the union of
all $\mathbf{x}$'s is called the "deformed configuration." The components of $\mathbf{x}$ and $\mathbf{X}$ are

denoted by x_k and X_k, respectively. Note that capital subscripts designate components of a tensor in the reference configuration, whereas small subscripts indicate components of a tensor in the deformed configuration.

Displacement is the new position of a point, $\mathbf{x}$, with respect to its old position, $\mathbf{X}$.

$$\mathbf{u} = \mathbf{u}(\mathbf{X}, t) = \mathbf{x} - \mathbf{X}, \tag{1.3}$$

where $\mathbf{u}$ is the displacement vector. If different points of a body undergo different displacements (or more generally different motions), we will have *deformation*. Displacement tensor is given by the gradient of motion and is denoted by F_{kK} or $x_{k,K}$:

$$x_{k,K} \equiv F_{kK} = \frac{\partial F_k}{\partial X_K} \equiv \frac{\partial x_k}{\partial X_K} = \text{GRAD}\mathbf{F} \tag{1.4}$$

where GRAD denotes the gradient of a function with respect to the material coordinate. Note that this tensor is not necessarily symmetric. Some other measures of deformation are:

$$C_{KL} = F_{kK} F_{kL} \qquad \text{Cauchy Deformation Tensor} \tag{1.5a}$$

$$E_{KL} = \frac{1}{2}(C_{KL} - \delta_{KL}) \qquad \text{Lagrangian Strain Tensor} \tag{1.5b}$$

These are obviously symmetric tensors. The determinant of the displacement tensor is called the jacobian of motion, j, defined as:

$$j = \det x_{k,K} = |x_{k,K}| \tag{1.6a}$$

If an initial material volume dV_0 is changed into dv as a result of motion, one will have, Eringen [5]:

$$dv = j dV_0 . \tag{1.6b}$$

1.2.2. Velocity and acceleration

Velocity of a material point is the rate of change of position of that point with time:

$$\mathbf{v} = \left.\frac{\partial \mathbf{x}(\mathbf{X}, t)}{\partial t}\right|_{\mathbf{X}} = \frac{D\mathbf{x}}{Dt} \equiv \left.\frac{\partial \mathbf{u}(\mathbf{X}, t)}{\partial t}\right|_{\mathbf{X}} \tag{1.7}$$

The second part of this equation follows from the definition of displacement vector $\mathbf{u}$ (equation 1.3), and the fact that $\mathbf{X}$ is independent of time. Next,

acceleration of a point is defined as the rate of change of its velocity with time:

$$\mathbf{a} = \left.\frac{\partial \mathbf{v}}{\partial t}\right|_{\mathbf{X}} = \frac{D\mathbf{v}}{Dt} \equiv \left.\frac{\partial^2 \mathbf{u}}{\partial t}\right|_{\mathbf{X}} \tag{1.8}$$

Note that the symbol $\dfrac{D}{Dt}$ denotes a *material time derivative*; i.e. it is the derivative of a material property of a point moving with the motion of that point (keeping $\mathbf{X}$ constant). For a material property ψ, it is defined as:

$$\frac{D\psi\left(\mathbf{X}, t\right)}{Dt} = \left.\frac{\partial \psi}{\partial t}\right|_{\mathbf{X}} \tag{1.9a}$$

If, however, ψ is expressed in terms of spatial position $\mathbf{x}$, then (1.9a) becomes:

$$\frac{D\psi(\mathbf{x}, t)}{Dt} = \left.\frac{\partial \psi}{\partial t}\right|_{\mathbf{x}} + \left.\frac{\partial \mathbf{x}}{\partial t}\right|_{\mathbf{X}} \cdot \frac{\partial \psi}{\partial \mathbf{x}} = \frac{\partial \psi}{\partial t} + \mathbf{v} \cdot \nabla \psi = \frac{\partial \psi}{\partial t} + v_k \frac{\partial \psi}{\partial x_k} \tag{1.9b}$$

Then, one can show that, Eringen, [5]:

$$\frac{Dj}{Dt} = j\, v_{k,k} \tag{1.10}$$

In addition to velocity and acceleration, we need to define a number of other basic properties. These are linear momentum, angular momentum, and kinetic energy:

(Linear) Momentum: $\rho \mathbf{v}$

Angular Momentum: $\rho \mathbf{x} \times \mathbf{v}$

Kinetic Energy: $\dfrac{1}{2}\rho \mathbf{v} \cdot \mathbf{v} = \dfrac{1}{2}\rho v^2$

1.3. Fundamental axioms of physics: conservation laws and law of entropy

The behavior of materials is described by a number of physical laws augmented by many (physically-motivated) assumptions. The most important set of laws are for mass, momentum and energy. These laws are valid for any type of material (solid, liquid, gas, or any mix of them).

1.3.1. Conservation of mass

Because mass is indestructible, the total mass of body defined in equation (1.1b) must be constant for all thermodynamic processes. Thus, one has:

$$\int_V \rho dv = M_o \rightarrow \frac{D}{Dt} \int_V \rho dv = 0 \ . \tag{1.11a}$$

Next, we employ relationship (1.6b) to write this integral in the material frame of reference such that the material derivative may be moved into the integral:

$$\frac{D}{Dt} \int_V \rho dv = \frac{D}{Dt} \int_{V_0} \rho j dv = \int_{V_0} \left[j \frac{D\rho}{Dt} + \rho \frac{Dj}{Dt} \right] dv = \int_{V_0} \left[j \frac{D\rho}{Dt} + \rho j v_{k,k} \right] dv = 0 \ , \tag{1.11b}$$

where equation (1.10) has been used to obtain the last term. Now, equation (1.9b) is used again to transform this integral to the deformed frame of reference:

$$\frac{D}{Dt} \int_V \rho dv = \int_V \left[\frac{D\rho}{Dt} + \rho v_{k,k} \right] dv = \int_V \left[\frac{\partial \rho}{\partial t} + (\rho v_k)_{,k} \right] dv = 0 \ . \tag{1.11c}$$

We can now write this equation in a local form:

$$\frac{\partial \rho}{\partial t} + (\rho v_k)_{,k} = r \ , \tag{1.12a}$$

which must be subject to the condition that:

$$\int_V r dv = 0 \tag{1.12b}$$

Often we assume that $r = 0$ identically everywhere and all times such that:

$$\frac{\partial \rho}{\partial t} + (\rho v_k)_{,k} = 0 \ . \tag{1.13a}$$

Theories based on this assumption are called 'local theories'. For nonlocal theories one must use equations (1.12a) and (1.12b).

An alternative form of mass balance equation may be obtained from the definition (1.1a) of mass density which yields: $\rho dv = \rho_0 dv_0$. Using equation (1.6b), this expression becomes:

$$\rho j = \rho_0 \tag{1.13b}$$

1.3.2. General form of conservation equations

Equations of conservation of mass, momentum, energy and entropy can be written in a general form as given below for a generic thermodynamic property ψ:

$$\frac{\partial \rho\psi}{\partial t} + (\rho\psi v_\ell)_{,\ell} - i_{\ell,\ell} - \rho f = \rho G , \tag{1.14}$$

where i_l is the non-convective (or the conductive) flux of ψ, f is its external supply, and G is the rate of net production of ψ. Specific choices for ψ, i_l, f, and G will yield various conservation equations:

For mass : $\quad \psi \equiv 1; \ i_\ell \equiv 0; \ f \equiv 0; \ G \equiv 0$

For momentum : $\quad \psi \equiv v_k; \ i_\ell \equiv t_{k\ell}; \ f \equiv g_k; \ G \equiv 0$

For energy : $\quad \psi \equiv E + \frac{1}{2}v_k v_k; \ i_\ell \equiv q_\ell + t_{k\ell}v_k; \ f \equiv h + g_k v_k; \ G \equiv 0$

For entropy : $\quad \psi \equiv S; \ i_\ell \equiv \phi_\ell; \ f \equiv b; \ G \equiv \Gamma$

For angular momentum : $\quad \psi \equiv \varepsilon_{kmn}x_m v_n; i_\ell = \varepsilon_{kmn}x_n t_{n\ell}; f \equiv \varepsilon_{kmn}x_m g_n; G \equiv 0 ,$

where $t_{k\ell}$ is the stress tensor, g_k is the external supply of momentum (e.g. the gravity vector), E is the internal energy density, q_ℓ is the heat vector, h is the external supply of energy (e.g. through radiation), S is the internal entropy density, ϕ_ℓ is the entropy flux vector, b is the external supply of entropy, Γ is the rate of net production of entropy, and ε_{kmn} is the permutation tensor.

1.3.3. Second law of thermodynamics

It is evident from the above that the rates of net production of mass, momenta, and energy are zero; as these quantities are known to be conservative. Entropy of the system, however, is not conservative. The second law of thermodynamics requires that the rate of net production of entropy, Γ, must be non-negative for all possible thermodynamic states. The mathematical expression of this law is given as:

$$\rho\Gamma = \rho\frac{\partial S}{\partial t} + \rho v_k S_{,k} - \phi_{k,k} - \rho b \geq 0 \tag{1.15}$$

This is an extremely important restriction and it will be shown that this requirement plays an important role in developing constitutive relationships.

1.4. Constitutive theory; general axioms

1.4.1. Philosophy

In proposing conservation laws, no reference was made to the constitution of the matter. Thus, it is not surprising that conservation equations, supplemented by boundary and initial conditions are inadequate to fully determine the thermodynamic state of various systems, except possibly for non-conducting rigid materials (mechanics of rigid bodies). Therefore, constitutive equations are needed to describe the behavior of materials to be studied.

The "general behavior" of a medium (or system) is the response of that medium to internal and/or external changes. Thus, in the formulation of constitutive equations, one should have an *a priori* (even though crude) knowledge of the range of phenomena to be studied and the expected behavior of the material.

In continuum mechanics, materials are identified with their constitutive equations. Conversely, a given set of constitutive equations is a **model** that characterizes certain materials. Nothing but experience and experiments can verify whether a constitutive model can properly describe a particular material within a range of thermodynamic states of interest.

These remarks must not imply that the constitutive theory is arbitrary and unsystematic. On the contrary, there are certain mathematical and physical principles which must be satisfied. These are commonly presented as axioms of constitutive theory. In this section, these axioms are briefly described. For a detailed treatise of the constitutive theory see, for example, the work of Eringen, [5].

1.4.2. Axioms of causality and determinism

Axiom of causality states that certain properties of the system may be chosen as self-evident observable effects in every thermomechanical behavior of the body. The remaining system properties and quantities (other than those directly derivable from the observable effects) are considered to be causes. The causes are postulated to be dependent on the observable effects (axiom of determinism).

For our constitutive equations, we identify the observable effects **motion** and

temperature, $\mathbf{x}(\mathbf{X}, t)$ and $\theta(\mathbf{X}, t)$, as the *independent* constitutive variables. Then, other properties, namely, stress, heat, energy, and entropy are chosen to be *dependent* constitutive variables.

The *axiom of determinism* states that the values of thermodynamic constitutive functions $(t_{k\ell}, q_k, E, S)$ at a given material point X and a given time t are determined by the history of the motion and temperature of *all material points* of V at *all past times*. Thus, a typical constitutive equation should read:

$$\psi\Big|_{\mathbf{X},t} = \psi\left[\mathbf{x}(\mathbf{X}', t'), \theta(\mathbf{X}', t'), \mathbf{X}, t\right] \quad X' \in V \text{ and } 0 \le t' \le t, \qquad (1.16)$$

where X' denotes all points of the body V and t' denotes all past times; thus not only the point $\mathbf{X}$ and the time t, at which ψ is determined.

1.4.3. Axioms of neighborhood and memory

For many thermodynamic processes, one can safely assume that the values of independent constitutive variables at distant material points (i.e. far from $\mathbf{X}$) and at distant past (compared to the present time t) do not affect appreciably the values of dependent constitutive variables at $\mathbf{X}$ and t. In order to be able to formalize this statement, let's expand $\boldsymbol{x}$ and θ in a Taylor series around the material point $\mathbf{X}$:

$$x_k\left(X_K', t'\right) = x_k\left(X_K, t'\right) + \frac{\partial x_k}{\partial X_K'}\Big|_{X_K' = X_K} [X_K' - X_K] + \dots \qquad (1.17a)$$

A similar equation can be given for $\theta\left(X_K', t'\right)$. Thus, a dependence on $\mathbf{x}\left(\mathbf{X}', t'\right), \theta\left(\mathbf{X}', t'\right)$ may be replaced by a dependence on $x_k\left(X_K, t'\right)$, $x_{k,K}\left(X_K, t'\right)$, $\theta(X_K, t')$, $\theta_{,K}(X_K, t')$ and higher order derivatives. Neglecting derivatives of higher than the first order in the constitutive equation, (1.16) may be replaced by:

$$\psi\Big|_{\mathbf{X},t} = \psi\left(x_k\left(X_K, t'\right), x_{k,K}\left(X_K, t'\right), \theta\left(X_K, t'\right), \theta_{,K}\left(X_K, t'\right), X_K, t\right)$$

$$(1.17b)$$

Similarly, we can expand $x_k\left(X_K, t'\right), x_{k,K}\left(X_K, t'\right)$, $\theta\left(X_K, t'\right)$, and $\theta_{,K}\left(X_K, t'\right)$ in a Taylor's series around time t and then neglect terms of

higher than first order. For example, we get:

$$x_k\left(K_K, t'\right) = x_k\left(X_K, t\right) + \left.\frac{\partial x_k}{\partial t'}\right|_{t'=t} \left[t' - t\right] + ...$$
$$= x_k\left(K_K, t\right) + v_k\left(X_K, t\right)\left[t' - t\right] + ... , \qquad (1.18\text{a})$$

$$x_{k,K}\left(K_K, t'\right) = x_{k,K}\left(X_K, t\right) + \frac{\partial x_{k,K}}{\partial t}|_{t'=t}\left[t' - t\right] + ...$$
$$= x_{k,K}\left(X_K, t\right) + v_{k,K}\left(X_K, t\right) + ... , \qquad (1.18\text{b})$$

where the definition of the velocity vector is used in getting the second parts of these equations. Thus, a dependence on $x_k\left(X_K, t'\right)$ may be replaced by a dependence on $x_k\left(X_K, t\right), v_k\left(X_K, t\right)$, and $x_{k,K}\left(X_K, t'\right)$ may be replaced by $x_{k,K}\left(X_K, t\right), v_{k,K}\left(X_K, t\right)$ and higher order derivatives. Once again, neglecting derivatives of higher than the first order in the constitutive equations will allow us to replace the general form (1.16) with the following simpler relationship:

$$\psi = \psi(x_k, x_{k,K}, v_k, v_{k,K}, \theta, \theta_{,K}, \dot{\theta}, \dot{\theta}_{,K}; X_K, t) , \qquad (1.19)$$

where an overdot denotes a material time derivative. By simplifying the general form (1.16) to this simpler relationship, we have already taken a number of important steps in restricting our constitutive model to be valid only for certain classes of materials. Materials described by such constitutive equations are called *simple materials*.

1.4.4. Axiom of objectivity

This axiom stems from the physical consideration that the behavior of a material cannot depend on the motion of the observer. If our frame of reference undergoes a rigid translation $\mathbf{b}(t)$, a rigid rotation $\mathbf{Q}(\hat{t})$, and if the time origin is shifted by a constant a, then, the position vector $\mathbf{x}$ in the new reference frame and the shifted time $\hat{t} = t - a$ will become:

$$\hat{\mathbf{x}}(\hat{t}) = \mathbf{Q}(\hat{t})\mathbf{x} + \mathbf{b}(t) \qquad (1.20)$$

subject to $\mathbf{Q}\mathbf{Q}^T = \mathbf{Q}^T\mathbf{Q} = \mathbf{I}$, where I is the unit tensor. A carret denotes a transformed variable. Now, according to the axiom of objectivity,

the constitutive functions must be form-invariant for all proper orthogonal transformations $\mathbf{Q}(t)$, all translations $\mathbf{b}(t)$, and any constant a. This means that all constitutive variables must be objective.

To illustrate these concepts, let's consider some of the variables in the constitutive relationship (1.19). First, we can show that $\mathbf{x}$ is not objective. This can be verified by choosing the following admissible transformations:

$$\mathbf{Q} = \mathbf{I}; \quad \mathbf{b} = -\mathbf{x}; \text{ and } a = 0$$

Then, (1.20) yields:

$$\hat{\mathbf{x}}(\hat{t}) = \mathbf{x} - \mathbf{x} = \mathbf{0}$$

which means that a dependence of constitutive functions on $\mathbf{x}$ is not permissible.

To investigate the consequences of the objectivity axiom, the transformation rule for velocity is needed. This can be obtained by taking the material time derivative of equation (1.20). Using the definition of velocity, we'll obtain:

$$\hat{\mathbf{v}}(\hat{t}) = \dot{\mathbf{Q}}\mathbf{x} + \mathbf{Q}\mathbf{v} + \dot{\mathbf{b}}$$

It is obvious that velocity is not an objective quantity. Therefore a dependence of constitutive function on velocity is not permitted. Further, it can be shown that $x_{k,K}$ should be replaced by Cauchy deformation tensor, C_{KL}, or Lagrangian strain tensor, E_{KL}, and $v_{k,K}$ should be replaced by $d_{k\ell}x_{k,K}x_{\ell,L}$ where $d_{k\ell}$ is called "deformation rate tensor" and is defined by:

$$d_{k\ell} = v_{(k,\ell)} = \frac{1}{2}\left(v_{k,\ell} + v_{\ell,k}\right) \tag{1.21}$$

Finally, it must be noted that a dependence of constitutive relationships on time t is not admissible. This is because if we impose a shift of time only (i.e. $\mathbf{Q} = \mathbf{I}$, $\mathbf{b} = \mathbf{0}$; and $a = t$), then the value of constitutive function will change only because of the choice of the origin of time. These considerations would require the relationship (1.19) to take the following form:

$$\psi = \psi\left(E_{KL}, d_{kl}, \theta, \theta_{,K}, \ddot{\theta}, \dot{\theta}_{,K}; X_K\right) \tag{1.22}$$

We should note that these consequences of objectivity axiom are valid for single-phase materials only where only one motion and one velocity field exist.

1.4.5. Axiom of admissibility

The constitutive equations must not violate conservation laws and the second law of thermodynamics. This axiom has some very important consequences for the form of constitutive equations. Those consequences will be illustrated for a number of simple materials in the following section.

1.5. Constitutive theories for some single - phase systems

1.5.1. Thermodynamics of deformable elastic solids

First, balance laws and the second law of thermodynamics are given:

$$\frac{D\rho}{Dt} + \rho v_{k,k} = 0 \quad \text{or} \quad \rho j = \rho_o , \tag{1.23}$$

$$\rho \frac{Dv_k}{Dt} - t_{k\ell,\ell} - \rho g_k = 0 , \tag{1.24a}$$

or

$$\rho \frac{D^2 u_k}{Dt^2} - t_{k\ell,\ell} - \rho g_k = 0 , \tag{1.24b}$$

$$t_{k\ell} = t_{\ell k} , \tag{1.25}$$

$$\rho \frac{DE}{Dt} - t_{k\ell} v_{\ell,k} - q_{k,k} - \rho h = 0 , \tag{1.26}$$

$$\rho \Gamma = \rho \frac{DS}{Dt} - \varphi_{k,k} - \rho b \geq 0 . \tag{1.27}$$

This form of the second law, (the entropy inequality (1.27) is obtained by multiplying continuity equation (1.23) by S and subtracting it from (1.15).

As a special constitutive relationship, it is normally assumed that the external supply of entropy is proportional to the external supply of energy, with the constant of proportionality being the inverse of temperature:

$$b = \frac{h}{\theta} \quad \theta > 0 . \tag{1.28}$$

Furthermore, it is helpful to use Helmholtz free energy in constitutive relationships:

$$A = E - \theta S \tag{1.29}$$

Multiplication of energy equation (1.26) by $\dfrac{1}{\theta}$ and subtraction of results from equation (1.27) yield:

$$\rho\Gamma = -\frac{\rho}{\theta}\left[\frac{DA}{Dt} + S\frac{D\theta}{Dt}\right] + \frac{1}{\theta}t_{k\ell}d_{k\ell} + \phi_{k,k} + \frac{1}{\theta^2}q_k\theta_{,k} \geq 0 \ . \tag{1.30a}$$

where

$$\phi_k = \frac{q_k}{\theta} - \varphi_k \tag{1.30b}$$

Commonly, in thermodynamics it is assumed that ϕ_k vanishes identically. Note that this is a constitutive assumption that may be relaxed if one wishes. Here, we follow suit and in the remainder of this presentation, we assume that ϕ_k may be identically set to zero. As a result, the entropy inequality takes the following form:

$$\rho\Gamma = -\frac{\rho}{\theta}\left[\frac{DA}{Dt} + S\frac{D\theta}{Dt}\right] + \frac{1}{\theta}t_{k\ell}d_{k\ell} + \frac{1}{\theta^2}q_k\theta_{,k} \geq 0 \tag{1.31}$$

Balance laws introduced above constitute five equations for 16 unknowns (ρ, v_k, $t_{k\ell}$, E, q_k, S, and θ). Therefore, we are short of 11 equations. These are provided by constitutive equations for $t_{k\ell}$, E(or A), q_k, S. The external body force and the external supply of energy are assumed to be due to gravity and radiation, respectively, which are both considered to be known.

Next, constitutive assumptions are introduced. By definition, an elastic material is such a material whose response functions do not depend on the rate of deformation. Also, the material behavior is considered to be independent of the time rate of change of temperature. Therefore, instead of equation (1.22), the following set of constitutive relations is proposed:

$$t_{k\ell} = t_{k\ell}\left(E_{KL}, \theta, \theta_{,k}, X_K\right) \ , \tag{1.32a}$$

$$q_k = q_k\left(E_{KL}, \theta, \theta_{,k}, X_K\right) \ , \tag{1.32b}$$

$$S = S\left(E_{KL}, \theta, \theta_{,k}, X_K\right) \ , \tag{1.32c}$$

$$A = A\left(E_{KL}, \theta, \theta_{,k}, X_K\right) . \tag{1.32d}$$

Note that ρ is not included in the list of independent variables because from (1.13b) and the definitions of E_{KL} and j (equations (1.5b) and (1.6a), respectively) one has:

$$j = \left(2\det E_{KL} + 1\right)^{\frac{1}{2}} \tag{1.33}$$

According to the axiom of admissibility, these constitutive equations must not violate balance laws and the second law of thermodynamics. Thus, we should substitute relations (1.32) into the entropy inequality (1.31) and determine necessary and sufficient conditions to ensure that the entropy production rate remains non-negative for all thermodynamic states. For the first term in the inequality, use the chain rule of differentiation to obtain:

$$\frac{DA}{Dt} = \frac{\partial A}{\partial E_{KL}} \frac{DE_{KL}}{Dt} + \frac{\partial A}{\partial \theta} \frac{D\theta}{Dt} + \frac{\partial A}{\partial X_K} \frac{DX_K}{Dt} + \frac{\partial A}{\partial \theta_{,k}} \frac{D\theta_{,k}}{Dt} \tag{1.34}$$

Note that DX_K/Dt is zero because X_K and t are independent of each other. Also, from definitions of E_{KL} and d_{kl}, we can show that:

$$\frac{DE_{KL}}{Dt} = \frac{1}{2}\frac{D}{Dt}\left(x_{k,K}x_{k,L}\right) = d_{k\ell}x_{k,K}x_{\ell,L} \tag{1.35}$$

Therefore, substituting from (1.34) and (1.35) into the entropy inequality (1.31) we obtain:

$$\rho\Gamma = -\rho\left[\frac{\partial A}{\partial \theta} + S\right]\frac{D\theta}{Dt} + \left[t_{k\ell} - \rho\frac{\partial A}{\partial E_{KL}}F_{kK}F_{\ell L}\right]d_{k\ell} + \frac{\partial A}{\partial \theta_{,k}}\frac{D\theta_{,k}}{Dt} + \frac{1}{\theta}q_k\theta_{,k} \geq 0 \tag{1.36}$$

This inequality has the following form:

$$\rho\Gamma = \lambda^1\frac{D\theta}{Dt} + \lambda^2_{k\ell}d_{k\ell} + \lambda^3_k\frac{D\theta_{,k}}{Dt} + \lambda^4 \geq 0 \tag{1.37}$$

where $\lambda^1, \lambda^2, \lambda^3$, and λ^4 are functions of E_{KL}, θ, $\theta_{,k}$, and X_K only. They are independent of $D\theta/Dt$, $d_{k\ell}$, and $D\theta_{,k}/Dt$ by virtue of our constitutive assumptions (1.32). This means that the net entropy production $\rho\Gamma$ is linear in $D\theta/Dt$, d_{kl}, and $D\theta_{,k}/Dt$. The necessary and sufficient conditions for

the inequality (1.37) to hold for all possible thermodynamic states (i.e. all possible values of E_{KL}, θ, $\theta_{,k}$, $D\theta/Dt$, d_{kl}, and $D\theta_{,k}/Dt$) are:

$$\lambda^1 = 0, \quad \lambda^2 = 0, \quad \lambda^3 = 0, \quad \lambda^4 \geq 0$$

Therefore, we obtain the following relations:

$$\frac{\partial A}{\partial \theta_{,k}} = 0 \tag{1.38}$$

$$S = -\frac{\partial A}{\partial \theta} , \tag{1.39}$$

$$t_{k\ell}(E_{KL}, \theta, X_K) = \rho \frac{\partial A}{\partial E_{KL}} F_{(k,K}F_{\ell),L} , \tag{1.40a}$$

where parentheses in the subscripts designate the symmetric part of the tensor, defined by

$$F_{(k,K}F_{\ell),L} = \frac{1}{2}(F_{kK}F_{\ell L} + F_{\ell K}F_{kL}) . \tag{1.40b}$$

The residual entropy inequality becomes:

$$\rho\Gamma = q_k\theta_{,k} \geq 0 \tag{1.41}$$

These results mean that Helmholtz free energy is a functional of E_{KL}, θ, and X_K only. The same holds for t_{kl}. Note that if $\theta_{,k}$ were excluded from the list of independent variables in equations (1.32), then we would have obtained $q_k = 0$ for all states. That is, a material whose thermodynamic state is not affected by the existence of temperature gradients must be a non-heat-conducting material.

Next, the entropy inequality and constitutive relationships are examined under equilibrium conditions. First, we define equilibrium to be the state for which we have:

$$\{\theta_{,k}\}\Big|_e = 0 \tag{1.42}$$

where $\big|_e$ denotes evaluation at equilibrium. From (1.41), it is evident that at equilibrium $\rho\Gamma$ will attain an absolute minimum value. The necessary and

sufficient conditions for $\rho\Gamma$ to be at absolute minimum are:

(a)
$$\left.\frac{\partial\Gamma}{\partial\theta_{,k}}\right|_e = 0 \tag{1.43}$$

(b) $\left.\dfrac{\partial^2\Gamma}{\partial\theta_{,k}\partial\theta_{,\ell}}\right|_e$ must be positive semi $-$ definite $\tag{1.44}$

Applying these conditions to (1.41), we obtain:

$$q_k\big|_e = 0 \tag{1.45}$$

$\left.\dfrac{\partial q_k}{\partial\theta_{,\ell}}\right|_e$ is positive semi $-$ definite. $\tag{1.46}$

Finally, a linear constitutive theory is developed. Let's expand A and q_k in a Taylor's series around E_{KL} and $\theta_{,k}$.

$$A = A_o + \left.\frac{\partial A}{\partial E_{KL}}\right|_o E_{KL} + \left.\frac{\partial^2 A}{\partial E_{KL}\partial E_{MN}}\right|_o E_{KL}E_{MN} + \dots \tag{1.47}$$

$$q_k = \left.\frac{\partial q_k}{\partial E_{KL}}\right|_o E_{KL} + \left.\frac{\partial q_k}{\partial\theta_{,\ell}}\right|_o \theta_{,\ell} + \dots \tag{1.48}$$

Substitution of (1.47) in (1.40a) yields

$$t_{k\ell} = \rho\left.\frac{\partial A}{\partial E_{KL}}\right|_o F_{kK}F_{\ell L} + \rho\left.\frac{\partial^2 A}{\partial E_{KL}\partial E_{MN}}\right|_o E_{MN}F_{kK}F_{\ell L} \tag{1.49a}$$

In the linear theory, one can replace E_{KL} with the finite strain tensor $e_{k\ell}$:

$$t_{k\ell} = \rho\left.\frac{\partial A}{\partial e_{k\ell}}\right|_o + \sigma_{k\ell mn}(\theta)\,e_{mn} = (t_{k\ell})_0 + \sigma_{k\ell mn}(\theta)\,e_{mn} \tag{1.49b}$$

Assuming that there exists a stress-free state, we can set $(t_{k\ell})_0$ to zero so that (1.49b) yields:

$$t_{k\ell} = \sigma_{k\ell mn}(\theta)\,e_{mn} \tag{1.49c}$$

This is an extension of the Hooke's law of elasticity (in fact thermoelasticity). For an isotropic solid, σ_{klmn} must be a fully isotropic tensor. The most general form of a fourth-order isotropic tensor is:

$$\sigma_{klmn} = \sigma_1 \delta_{kl}\delta_{mn} + \sigma_2 \delta_{km}\delta_{ln} + \sigma_3 \delta_{kn}\delta_{lm} \tag{1.50}$$

Upon substitution into (1.49c), we obtain Hooke's Law of linear elasticity:

$$t_{kl} = \nu e_{mm}\delta_{k\ell} + E e_{kl} , \tag{1.51}$$

where ν and E are elasticity moduli. Similarly, the linearized relationship (1.48) for q_k becomes:

$$q_k = L_{k\ell m} e_{\ell m} + \kappa_{k\ell}\theta_{,\ell} \tag{1.52}$$

For an isotropic solid, $L_{k\ell m}$ and $\kappa_{k\ell}$ must be isotropic. The most general form of isotropic third and second rank tensors are $L_{klm} \equiv 0$ and $\kappa_{k\ell} \equiv \kappa\delta_{k\ell}$. Therefore, the following relation for q_k in an isotropic solid is obtained:

$$q_k = \kappa\theta_{,\ell} \quad \text{where } \kappa > 0 \tag{1.53}$$

where the restriction on κ follows from the equilibrium condition (1.46). This is the Fourier's law of heat transfer.

1.5.2. Thermodynamics of a viscous fluid

Balance laws and the entropy inequality are the same as those given for a solid. However, what makes a fluid distinct from a solid is that it does not have a shape of its own. Any deformed configuration, leaving the density constant, can be thermodynamically the same as the reference configuration. Therefore, one cannot make a distinction between a reference state and a deformed state. That means that the distinction between material and spatial frame of reference disappears. Then, $x_{k,K}$ becomes $\delta_{k,K}$ and j becomes 1 and one cannot talk about Dj/Dt any more. Therefore, $x_{k,K}$ (or E_{KL}) disappears from the list of independent variables and one must use the density ρ as an independent variable. Furthermore, from experience we know that a viscous fluid behaviour is sensitive to the velocity gradient or the deformation rate tensor. Thus, one can suggest the following set of constitutive equations for a thermo-viscous fluid.

$$t_{k\ell} = t_{k\ell} (\rho, d_{k\ell}, \theta, \theta_{,k}) \tag{1.54a}$$

$$A = A\left(\rho, d_{k\ell}, \theta, \theta_{,k}\right) \tag{1.54b}$$

$$q_k = q_k\left(\rho, d_{k\ell}, \theta, \theta_{,k}\right) \tag{1.54c}$$

$$S = S\left(\rho, d_{k\ell}, \theta, \theta_{,k}\right) \tag{1.54d}$$

Once again, we substitute these relations into the entropy inequality (1.31). For the first term in the entropy inequality, we apply the chain rule of differentiation to obtain:

$$\frac{DA}{Dt} = \frac{\partial A}{\partial \rho}\frac{D\rho}{Dt} + \frac{\partial A}{\partial d_{kl}}\frac{Dd_{kl}}{Dt} + \frac{\partial A}{\partial \theta}\frac{D\theta}{Dt} + \frac{\partial A}{\partial \theta_{,k}}\frac{D\theta_{,k}}{Dt} \tag{1.55a}$$

The term $D\rho/Dt$ in this equation can be evaluated from mass balance equation (1.23):

$$\frac{D\rho}{Dt} = -\rho v_{k,k} = -\rho d_{kl}\delta_{kl} \tag{1.55b}$$

where the definition (1.21) of d_{kl} has been used. Substitution of (1.55b) in (1.55a) and the result in (1.31) will yield:

$$\rho\Gamma = -\quad \rho\left[\frac{\partial A}{\partial \theta} + S\right]\frac{D\theta}{Dt} + \left[t_{k\ell} + \rho^2\frac{\partial A}{\partial \rho}\delta_{k\ell}\right]d_{k\ell}$$
$$+\quad \rho\frac{\partial A}{\partial d_{k\ell}}\frac{Dd_{k\ell}}{Dt} + \rho\frac{\partial A}{\partial \theta_{,k}}\frac{D\theta_{,k}}{Dt} + \frac{1}{\theta}q_{,k}\theta_{,k} \geq 0 \tag{1.56}$$

Because of our constitutive assumptions (1.54), it is obvious that $\rho\Gamma$ is linear in $\frac{D\theta}{Dt}$, $\frac{Dd_{k\ell}}{Dt}$, and $\frac{D\theta_{,k}}{Dt}$. Therefore, coefficients of these terms must vanish identically and we obtain the following results:

$$A = A\left(\rho, \theta\right) \tag{1.57a}$$

$$S = -\frac{\partial A}{\partial \theta} \tag{1.57b}$$

and the residual entropy inequality becomes:

$$\rho\Gamma = \left[t_{k\ell} + \rho^2\frac{\partial A}{\partial \rho}\delta_{k\ell}\right]d_{k\ell} + \frac{1}{\theta}q_k\theta_{,k} \geq 0 \tag{1.57c}$$

Define the equilibrium states to be the ones for which we have:

$$\{d_{k\ell}, \theta_{,k}\}\big|_e = 0 \tag{1.58}$$

Equilibrium conditions (1.43) and (1.44) must apply here too. As a result of the first condition of equilibrium, we obtain:

$$t_{k\ell}\big|_e = -\rho^2 \frac{\partial A}{\partial \rho}\delta_{k\ell} = -p\delta_{k\ell} \tag{1.59a}$$

where $p = \rho^2 \dfrac{\partial A}{\partial \rho}$ is identified as the thermodynamic pressure. We also obtain:

$$q_k\big|_e = 0 \tag{1.59b}$$

which means there is no heat flux at equilibrium. If we define viscous stress tensor $\tau_{k\ell} = t_{k\ell} + p\delta_{kl}$, then, (1.59a) implies that $\tau_{k\ell}\big|_e = 0$; i.e. there is no viscous stress at equilibrium.

A linear theory of viscosity can be developed along the lines that were followed for an elastic solid. The results will be:

$$\tau_{k\ell} = \mu_{k\ell mn}d_{mn} + K_{k\ell m}\theta_{,m} \tag{1.60a}$$

$$q_k = \kappa_{k\ell}\theta_{,\ell} + L_{k\ell m}d_{\ell m} \tag{1.60b}$$

But a simple fluid is by nature isotropic. Therefore, $\mu_{k\ell mn}$ and other material properties in these equations must be isotropic tensors:

$$\kappa_{k\ell} = \kappa\delta_{k\ell} \tag{1.61}$$

$$\mu_{k\ell mn} = \mu_1\delta_{kl}\delta_{mn} + \mu_2\delta_{km}\delta_{\ell n} + \mu_3\delta_{kn}\delta_{\ell m} \tag{1.62}$$

$$K_{k\ell m} = L_{k\ell m} \equiv 0 \tag{1.63}$$

Therefore, equations (1.60) become:

$$t_{k\ell} = -p\delta_{k\ell} + \lambda d_{mm}\delta_{k\ell} + 2\mu d_{k\ell} \quad \text{with} \quad \mu \geq 0 \text{ and } 2\mu + 3\lambda \geq 0 \tag{1.64}$$

$$q_k = \kappa\theta_{,k} \quad \text{with} \quad \kappa \geq 0 \tag{1.65}$$

where λ and μ are coefficients of bulk and dynamic viscosity, respectively. The restrictions on λ, μ, and κ are consequences of the second condition of equilibrium (1.44).

1.5.3. Thermodynamics of a viscoelastic fluid

There are a number of models for various types of viscoelastic fluids. One possible model is defined by the following set of constitutive equations

$$t_{k\ell} = t_{k\ell}\left(E_{KL}, d_{k\ell}, \theta, X_K\right) \tag{1.66}$$

Similar relations may be written for A, S and q. Note that both strain tensor and deformation rate tensor are among the list of independent variables. Exploitation of the entropy inequality will give us:

$$S = -\frac{\partial A}{\partial \theta}\,, \tag{1.67}$$

$$q_k = 0\,, \tag{1.68}$$

$$t_{k\ell} = \rho \left[\frac{\partial A}{\partial E_{KL}}\right] F_{k,K} F_{\ell,L} + \tau_{k\ell}\,, \tag{1.69}$$

$$\tau_{k\ell} d_{k\ell} \geq 0\,. \tag{1.70}$$

Note that the stress tensor has an elastic part as well as a viscous part, as it should be for viscoelastic materials. Equilibrium conditions and a linear theory can be developed in the same way that was done for a fluid and a solid.

2. Thermodynamics of multiphase systems: porous media

2.1. Kinematics

Consider a porous medium composed of a deformable rock skeleton saturated with a compressible fluid. At the microscale, the scale of the pores and grains, the fluid and the solid are modeled as continua with thermodynamic phase properties defined continuously over the domain occupied by the phase. The fluid and the solid phases are considered to be separated at the microscale by sharp interfaces. The interfaces are assumed to be devoid of thermodynamic properties, such as mass, momentum, and energy.

In this work, indices f and s are employed to designate the fluid phase and the solid phase, respectively. At the macroscale, a two-phase system is modeled as a superposition of two continua: fluid and solid. At every spatial point and at any instant in time, macroscopic properties are defined for each of the two continua which interact and exchange properties. Throughout this work, any reference to a phase is actually made to a macroscopic phase continuum. Macroscopic quantities are defined at the scale of a representative elementary volume (REV) characterized by a length scale much greater than that of a pore but much less than that of the full system. All quantities introduced are macroscopic. A full description of a multiphase system has been developed by Hassanizadeh and Gray, [6, 7], when interfacial properties are absent, by Gray and Hassanizadeh, [12], for interfacial properties, and by Gray and Hassanizadeh, [14] when common line properties as well as interfacial properties are considered. Here, we simply employ the macroscopic quantities and balance laws that are defined and/or derived in Hassanizadeh and Gray, [7].

At the macroscale in a multiphase system, a body is actually a superposition of a number of sub-bodies (equal to the number of phases).

All basic notions introduced for a single-phase body, such as mass, distance, deformation, motion, velocity, acceleration, momentum, energy, etc., can be employed for each and everyone of these sub-bodies. However, we do not need to consider them as new definitions and postulates, because they can be derived from their microscopic counterparts. Ideas presented here can be extended to the case of multi-component multi-phase systems (see Hassanizadeh, [10]).

To account for the microstructure of the system at the macroscale, the volume fractions of the two phases (ε^f and ε^s) are defined. Thus, ε^f is the fraction of the REV occupied by the f-phase, which is also known as the medium porosity, ε. Then, the volume fraction of the solid phase, ε^s, is:

$$\varepsilon^s = 1 - \varepsilon^f = 1 - \varepsilon \qquad (2.1)$$

The two phase continua, fluid and solid, each undergo independent motions as a result of thermodynamic processes. The solid phase motion is defined as a transformation $\mathbf{F}^s(\mathbf{X}^s, t)$ that changes the reference configuration $\mathbf{X}^s$ of the solid at time $t = 0$ to a new configuration $\mathbf{x}$ at time t, such that:

$$\mathbf{x} = \mathbf{F}^s(\mathbf{X}^s, t) \qquad (2.2a)$$

The velocity of the solid phase is then defined to be:

$$\mathbf{v}^s = \left(\frac{\partial \mathbf{F}^s}{\partial t}\right)_{\mathbf{X}^s} = \mathbf{v}^s(\mathbf{x}, t) \qquad (2.2b)$$

In writing $\mathbf{v}^s$ as a function of $\mathbf{x}$ rather than $\mathbf{X}^s$, it is assumed that transformation (2.2a) is reversible; i.e., there is an inverse motion. This will be true if, and only if, the jacobian of the transformation, defined by $J^s = det(\text{GRAD}\mathbf{F}^s)$, is nonzero where GRAD denotes differentiation with respect to the reference frame $\mathbf{X}^s$. This is commonly assumed to hold in local theories of continuum mechanics (see, e.g. [3]).

To characterize the motion of a fluid phase, a different approach is taken. As explained earlier, a fluid does not have a reference configuration, certainly not at the macroscale where a fluid is treated as a continuum with properties defined as averages of many "packets of fluid". Therefore, we do not define a displacement for the fluid. Instead, the motion of the fluid phase is characterized by its velocity field $\mathbf{v}^f(\mathbf{x}, t)$.

2.2. Fundamental theorems of conservation

2.2.1. Conservation of mass

The differential balance of mass for a phase α becomes:

$$\frac{D^\alpha (\varepsilon^\alpha \rho^\alpha)}{D^\alpha t} + \varepsilon^\alpha \rho^\alpha v_{k,k}^\alpha = \hat{\rho}^\alpha \quad \alpha = f, s \tag{2.3a}$$

where

$$\frac{D^\alpha}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}^\alpha \cdot \mathbf{\nabla} \tag{2.3b}$$

and $\hat{\rho}^\alpha$ is the exchange of mass between fluid and solid phases and is subject to:

$$\hat{\rho}^f + \hat{\rho}^s = 0 \tag{2.3c}$$

2.2.2. General form of conservations laws

For the description of thermo-mechanical processes in a saturated porous medium, two sets of macroscopic conservation equations are necessary: one for solid and one for the fluid. Equations of conservation of mass, momentum, energy, and entropy may be cast in the following general form:

$$\frac{D^\alpha \varepsilon^\alpha \rho^\alpha \psi^\alpha}{Dt} + \varepsilon^\alpha \rho^\alpha v_k^\alpha \psi_{,k}^\alpha - i_{k,k}^\alpha - \varepsilon^\alpha \rho^\alpha f^\alpha - \hat{i}^\alpha - \varepsilon^\alpha \rho^\alpha G^\alpha = 0 \tag{2.4a}$$

subject to:

$$\hat{i}^f + \hat{i}^s = 0 \tag{2.4b}$$

where $\hat{i}^f$ is the transfer of property ψ from the solid phase to the fluid phase due to microscale processes. Other symbols are defined similarly to those for single - phase materials.

2.2.3. Second law of thermodynamics

Here, the question is which one of the following are correct:

$$\varepsilon^\alpha \rho^\alpha \Gamma^a \geq 0 \tag{2.5a}$$

or:

$$\varepsilon^f \rho^f \Gamma^f + \varepsilon^s \rho^s \Gamma^s = \rho \Gamma \geq 0 \tag{2.5b}$$

We work with the latter one. For a discussion of equations (2.5), see Hassanizadeh and Gray, [6]. As for single-phase materials, the entropy fluxes φ^f and φ^s are assumed to be solely due to heat input; and the entropy external source terms are assumed to be only due to external energy source terms. Thus, for each of the phases, the following relations hold:

$$\varphi^\alpha = q^\alpha/\theta^\alpha \tag{2.6a}$$

$$b^\alpha = h^\alpha/\theta^\alpha \tag{2.6b}$$

where θ^α is identified with the experimentally-measured temperature function. In developing the constitutive equations, it is convenient to employ the Helmholtz free energy function instead of the internal energy. The Helmholtz free energies are defined by

$$A^\alpha = E^\alpha - \theta^\alpha \eta^\alpha \tag{2.6c}$$

2.3. Constitutive theory for a porous medium

Balance equations presented in the previous section are not sufficient to fully characterize a multiphase system. These must be supplemented with equations which describe the constitutive behavior of individual phases, and interfaces. In developing these constitutive equations, certain mathematical principles and physical considerations must be observed. These principles are commonly formulated as axioms of constitutive theory. Eringen, [5], has proposed eight axioms, described in Section 1.4, to serve as the basis for the development of constitutive equations. Here, we adapt and extend these axioms for the case of two fluid phases in a porous medium. For a detailed description of those axioms, see Hasanizadeh and Gray, [9].

2.3.1. Axiom of causality

Independent variables in constitutive relationships for a saturated porous medium are considered to be the following self-evident observable effects: motions of fluid and solid phases, mass density of fluid and solid phases, temperatures of the two phases, and porosity of the porous medium, denoted by:

$$\mathbf{F}^s, \mathbf{v}^f, \rho^f, \rho^s, \theta^f, \theta^s, \varepsilon \tag{2.7a}$$

Note that in the constitutive theory for a solid phase, only the motion and temperature were considered to be independent quantities. Mass density was not considered to be an independent quantity because it was related to the solid phase motion through the mass balance equation. However, in the case of multiphase systems, because an exchange of mass between phases is possible, the motion of the solid phase and the continuity equation are not sufficient to determine its density. Additionally, in the case of saturated porous media, the porosity is believed to affect the state of the system and should be included in the list of self-evident observable quantities. All other thermomechanical quantities that appear in the entropy inequality, and are not derivable from the independent variable listed in (2.7a), are considered to be dependent constitutive variables. Constitutive equations are required for these quantities.

2.3.2. Axiom of determinism

Dependent variables of constitutive relationships are identified to be members of the following set:

$$\{S\} = \left\{ A^f, A^s, \eta^f, \eta^s, t^f, t^s, q^f, q^s, \widehat{T}^f, \widehat{e}^f, \widehat{e}, \widehat{Q}^f \right\} \tag{2.7b}$$

According to the axiom of determinism, each of the quantities in the list (2.7b) may be proposed to be a function of all quantities in the list (2.7a) at all points of the system and and at all past times. However, such a general dependence on independent variables is often too extensive and may not be necessary for all constitutive functions. Simplifications may be introduced guided by other axioms of the constitutive theory formulated below.

2.3.3. Axiom of restricted dependence

Based on the known and observed behavior of various components of a multiphase system, a restriction of the dependence of constitutive functions on independent variables is allowed.
This axiom allows us for utilization of information available from general experience with various elements of a multiphase system at an early stage of development of constitutive equations. A specific application of this axiom is to the dependence of free energy functions. Given the fact that various phases are actually separated at the microscale, the free energy of one phase is not expected to depend on the state variables (such as temperature,

density, volume fraction) of another phase. Furthermore, the dependence of free energies on certain independent variables may be limited based on past experience in the development of the constitutive theory. Note that these discriminations are always subject to experimental verification at a later stage. In particular, the following formulation of constitutive relationships for free energies are proposed:

$$A^s(\mathbf{X}^s, t) = A^s \left[\rho^s(\mathbf{x}', t'), \theta^s(\mathbf{x}', t'), \mathbf{F}^s(\mathbf{X}^{s\,'}, t'), \varepsilon(\mathbf{x}', t'), \mathbf{X}^s, t \right] \qquad (2.8a)$$

$$A^f(\mathbf{X}^s, t) = A^f \left[\rho^f(\mathbf{x}', t'), \theta^f(\mathbf{x}', t'), \varepsilon(\mathbf{x}', t'), \mathbf{X}^s, t \right] \qquad (2.8b)$$

Note that except for the solid phase motion, all other observable variables are written as functions of the spatial coordinate $\mathbf{x}'$. This is allowed because of the reversibility of the motion. The axiom of restricted dependence is in contrast to, and replaces, the axiom of equipresence (see [5]) employed in the constitutive theory of single-phase materials.

2.3.4. Axiom of objectivity

As explained in part I, according to the axiom of objectivity, the constitutive functions must be form-invariant for all proper orthogonal transformations $\mathbf{Q}(t)$, translations $\mathbf{b}(t)$, and any constant a. Thus, for example, for a typical constitutive function, we must have:

$$\hat{\psi} \left[\hat{\mathbf{F}}^s \left(\hat{\mathbf{X}}^{s\,'}, \hat{t}' \right), \hat{\theta}^s \left(\hat{\mathbf{x}}', \hat{t}' \right), \hat{\mathbf{X}}^s, \hat{t} \right] = \psi \left[\mathbf{F}^s \left(\mathbf{X}^{s\,'}, t' \right), \theta^s \left(\mathbf{x}', t' \right), \mathbf{X}^s, t \right] \quad (2.9)$$

where:

$$\hat{\mathbf{F}}^s \left(\hat{\mathbf{X}}^{s\,'}, \hat{t}' \right) = \mathbf{Q}(t') \mathbf{F}^s \left(\mathbf{X}^{s\,'}, t' \right) + \mathbf{b}(t') \qquad (2.10)$$

As a special transformation of the frame $\mathbf{x}$, consider the case that:

$$\mathbf{Q}(t') = \mathbf{I}, \ \mathbf{b}(t') = -\mathbf{F}^s(\mathbf{X}^s, t') \quad \text{and} \quad a = 0 \qquad (2.11)$$

Then, the following transformation rule for $\mathbf{F}^s \left(\mathbf{X}^{s\,'}, t' \right)$ is obtained:

$$\hat{\mathbf{F}}^s \left(\hat{\mathbf{X}}^{s\,'}, \hat{t}' \right) = \mathbf{F}^s \left(\mathbf{X}^{s\,'}, t' \right) - \mathbf{F}^s \left(\mathbf{X}^s, t' \right) \qquad (2.12)$$

It can be readily shown that (2.12) remains invariant for any transformation of the spatial frame of reference. Thus, the axiom of objectivity requires that the constitutive equations must depend on $\mathbf{F}^s\left(\mathbf{X}^{s\,\prime}, t'\right)$ in a special way, namely the combination on the right side of (2.12). Thus, for example, equation (2.8a) must be replaced with:

$$A^s\left(\mathbf{X}^s, t\right) = A^s\left[\rho^s\left(\mathbf{x}', t'\right), \theta^s\left(\mathbf{x}', t'\right), \mathbf{F}^s\left(\mathbf{X}^{s\,\prime}, t'\right) - \mathbf{F}^s\left(\mathbf{X}^s, t'\right), \varepsilon\left(\mathbf{x}', t'\right), \mathbf{X}^s, t\right]$$

(2.13)

To complete the development of a constitutive theory and then model a system, a frame of reference must be selected. Based on practical considerations and the fact that the solid phase provides the structure of the domain through which the flow takes place, the solid phase motion is chosen as the reference motion in this development.

To further investigate the consequences of the objectivity axiom, the transformation rule for velocity must also be investigated. This can be obtained by taking the time derivative of equation (2.10):

$$\hat{\mathbf{v}}^s\left(\hat{\mathbf{X}}^{s\,\prime}, \hat{t}'\right) = \overset{\bullet}{\mathbf{Q}}\left(t'\right)\mathbf{F}^s\left(\mathbf{X}^{s\,\prime}, t'\right) + \mathbf{Q}\left(t\right)\mathbf{v}^s\left(\mathbf{X}^{s\,\prime}, t'\right) + \overset{\bullet}{\mathbf{b}}\left(t'\right)$$

(2.14)

Also, for the fluid velocities, where no reference configuration is defined, the transformation rule is assumed to be given by a similar relationship:

$$\hat{\mathbf{v}}^f\left(\hat{\mathbf{X}}^{s\,\prime}, \hat{t}'\right) = \overset{\bullet}{\mathbf{Q}}\left(t'\right)\mathbf{F}^s\left(\mathbf{X}^{s\,\prime}, t'\right) + \mathbf{Q}\left(t\right)\mathbf{v}^f\left(\mathbf{X}^{s\,\prime}, t'\right) + \overset{\bullet}{\mathbf{b}}\left(t'\right)$$

(2.15)

It is obvious that neither $\hat{\mathbf{v}}^s\left(\hat{\mathbf{X}}^{s\,\prime}, \hat{t}'\right)$ nor $\hat{\mathbf{v}}^f\left(\hat{\mathbf{X}}^{s\,\prime}, \hat{t}'\right)$ is objective. However, their difference is, as we obtain:

$$\left\{\hat{\mathbf{v}}^f\left(\hat{\mathbf{X}}^{s\,\prime}, \hat{t}'\right) - \hat{\mathbf{v}}^s\left(\hat{\mathbf{X}}^{s\,\prime}, \hat{t}'\right)\right\} = \mathbf{Q}\left(t\right)\left\{\mathbf{v}^f\left(\mathbf{X}^{s\,\prime}, t'\right) - \mathbf{v}^s\left(\mathbf{X}^{s\,\prime}, t'\right)\right\}$$

(2.16)

Now, consider, for example, the momentum exchange term $\mathbf{T}^f$. This quantity may depend, among other variables, on the motions of the fluid and solid phases:

$$\mathbf{T}^f\left(\mathbf{X}^s, t\right) = \mathbf{T}^f\left(\mathbf{v}^f\left(\mathbf{x}', t'\right), \mathbf{v}^s\left(\mathbf{x}', t'\right), ..., \mathbf{X}^s, t\right)$$

(2.17a)

Here again, the velocity is written as a function of the spatial coordinate $\mathbf{x}'$. The axiom of objectivity requires (2.17a) to be replaced with:

$$\mathbf{T}^f\left(\mathbf{X}^s, t\right) = \mathbf{T}^f\left(\left\{\mathbf{v}^f\left(\mathbf{x}', t'\right) - \mathbf{v}^s\left(\mathbf{x}', t'\right)\right\}, ..., \mathbf{X}^s, t\right) \qquad (2.17\text{b})$$

Also, as showed in Part I, the axiom of objectivity leads to the result that constitutive equations must not be a function of time, t.

2.3.5. Axiom of smooth neighborhood

The values of independent constitutive variables at distant points do not affect appreciably on the values of constitutive functions at a given point of interest.

The general constitutive relationships allow the possibility that the values of state variables at distant points may affect the behavior of the system at point $\mathbf{x}$ (or $\mathbf{X}^s$). However, for many materials and in commonly-encountered thermodynamic processes, only points in the immediate neighborhood are found to appreciably affect the value of dependent constitutive variables at a point of interest. A hierarchy of higher-order theories may be developed depending on the degree of dependence on farther points. This may be formalized by expanding the independent constitutive functions around the point $\mathbf{x}$ (or $\mathbf{X}^s$). So, for example, the function $\mathbf{F}^s\left(\mathbf{X}^{s\,\prime}, t'\right)$ is expanded in a Taylor series around point $\mathbf{X}^s$ to obtain:

$$\mathbf{F}^s\left(\mathbf{X}^{s\,\prime}, t'\right) = \mathbf{F}\left(\mathbf{X}^s, t'\right) + \left(\mathbf{X}^{s\,\prime} - \mathbf{X}^s\right) \cdot \text{GRAD}\mathbf{F}^s\left(\mathbf{X}^s, t'\right) +$$
$$\frac{1}{2}\left[\left(\mathbf{X}^{s\,\prime} - \mathbf{X}^s\right)\left(\mathbf{X}^{s\,\prime} - \mathbf{X}^s\right)\right] : \text{GRAD GRAD}\mathbf{F}^s\left(\mathbf{X}^s, t'\right) + ... \quad (2.18)$$

where ":" denotes a double inner product between two tensors (in this case between $\left(\mathbf{X}^{s\,\prime} - \mathbf{X}^s\right)\left(\mathbf{X}^{s\,\prime} - \mathbf{X}^s\right)$ and GRAD GRAD). This formulation suggests that a dependence on $F^s\left(X^{s\,\prime}, t'\right)$ may be replaced by a dependence on $\mathbf{F}^s\left(\mathbf{X}^s, t'\right)$ and its gradients. The larger the number of higher order gradients included, the greater the influence of distant points on the behavior of the system at point $\mathbf{X}^s$. Similar arguments hold for a function such as $\theta\left(\mathbf{x}', t'\right)$, which may be replaced by $\theta\left(\mathbf{x}, t'\right)$ and its gradients. As an example, consider the application of this principle to equation (2.13). Substitute from (2.18) into (2.13) (note that $\mathbf{F}\left(\mathbf{X}^s, t'\right)$ cancels out), and keep first order

gradients of all terms only. Then the functional relationship for A^s takes the form:

$$A^s\left(\mathbf{X}^s, t\right) = A^s\left[\, \rho^s(\mathbf{x}, t'), \nabla\rho^s(\mathbf{x}, t'), \theta^s(\mathbf{x}, t'), \nabla\theta^s(\mathbf{x}, t'),\right.$$
$$\left. \mathrm{GRAD}\mathbf{F}^s(\mathbf{X}^s, t'), \varepsilon(\mathbf{x}, t'), \nabla\varepsilon(\mathbf{x}, t'), \mathbf{X}^s\,\right] \qquad (2.19)$$

Corresponding results are obtained for other constitutive functions that depend on the displacement vectors of the solid phase and/or the fluid-solid interfaces. As another example, consider the constitutive equation (2.17a). The application of the axiom of smooth neighborhood results in:

$$\mathbf{T}^f\left(\mathbf{X}^s, t\right) = \mathbf{T}^f\left(\left\{\mathbf{v}^f\left(\mathbf{x}, t'\right) - \mathbf{v}^s\left(\mathbf{x}, t'\right)\right\}, \nabla\mathbf{v}^f\left(\mathbf{x}, t'\right), ..., \mathbf{X}^s, t\right) \qquad (2.20)$$

where the gradients of $\mathbf{v}^s$ have not been included.

2.3.6. Axiom of smooth memory

The values of independent constitutive variables at the distant past do not affect appreciably the values of constitutive functions at the present time.
This axiom is the counterpart of the axiom of smooth neighborhood. It regards the influence of the past history of the system on its present behavior. To investigate the consequences of this axiom, the independent variables must be expanded in a Taylor series around time t. This is done with a fixed frame of reference, selected here to be fixed to the solid phase motion as mentioned earlier. Thus, for example in equation (2.19), the dependence on $\mathrm{GRAD}\mathbf{F}^s\left(\mathbf{X}^s, t'\right)$ may be replaced by a dependence on $\mathrm{GRAD}\mathbf{F}^s\left(\mathbf{X}^s, t\right)$, its time derivative, which is $\mathrm{GRAD}\mathbf{v}^s\left(\mathbf{X}^s, t\right)$ or $\nabla\mathbf{v}^s(\mathbf{x}, t)$, and higher order derivatives. The larger the number of higher order time derivatives included in constitutive relationships, the larger the influence of the distant past on the present behavior of the system. In a similar fashion, independent variables such as $\theta\left(\mathbf{x}, t'\right)$ will be replaced by $\theta\left(\mathbf{x}, t\right), \dot{\theta}\left(\mathbf{x}, t\right)$, etc., where the overdot denotes the time derivative. The application of the axiom of smooth memory to constitutive relationships (2.19) and (2.20), when dependence is limited to first derivatives, leads, respectively, to:

$$A^s\left(\mathbf{X}^s, t\right) = A^s\left[\rho^s\left(\mathbf{x}, t\right), \nabla\rho^s\left(\mathbf{x}, t\right), \dot{\rho^s}\left(\mathbf{x}, t\right), \theta^s\left(\mathbf{x}, t\right), \nabla\theta^s\left(\mathbf{x}, t'\right),\right.$$
$$\left. \dot{\theta^s}\left(\mathbf{x}, t\right), \mathrm{GRAD}\mathbf{F}^s\left(\mathbf{X}^s, t\right), \varepsilon\left(\mathbf{x}, t\right), \nabla\varepsilon\left(\mathbf{x}, t\right), \dot{\varepsilon}\left(\mathbf{x}, t\right), \mathbf{X}^s\right]$$
$$(2.21)$$

$$
\mathbf{T}^f\left(\mathbf{X}^s, t\right) = \mathbf{T}^f\left[\rho^f\left(\mathbf{x}, t\right), \nabla\rho^f\left(\mathbf{x}, t\right), \overset{\bullet}{\rho^f}\left(\mathbf{x}, t\right), \theta^f\left(\mathbf{x}, t\right), \nabla\theta^f\left(\mathbf{x}, t\right),\right.
$$

$$
\left. \overset{\bullet}{\theta^f}\left(\mathbf{x}, t\right), \mathbf{v}^{fs}\left(\mathbf{x}, t\right), \nabla\mathbf{v}^f\left(\mathbf{x}, t\right), \varepsilon\left(\mathbf{x}, t\right), \nabla\varepsilon\left(\mathbf{x}, t\right), \overset{\bullet}{\varepsilon}\left(\mathbf{x}, t\right), \mathbf{X}^s\right] \quad (2.22)
$$

where $\mathbf{v}^{fs}\left(\mathbf{x}, t\right)$ denotes the relative velocity of fluid with respect to the solid. Note that the dependence of $\mathbf{T}^f$ on other variables has been added. Similar relationships apply for other constitutive functions.

2.3.7. Axiom of admissibility

All constitutive relationships must be consistent with the principles of conservation of mass, momenta, and energy, and the second law of thermodynamics.

This axiom requires that in the formulation of constitutive equations, the basic laws of continuum mechanics must not be violated. For example, certain independent variables may be shown to be actually dependent on each other when conservation laws are examined, in which case one of the two variables should be eliminated from the list of independent variables. Also, restrictions on the allowable functional dependence of a variable such as in (2.21) or (2.22) on independent variables are obtained through imposition of inequality (2.7a), the second law of thermodynamics.

The consequences that this axiom may have on constitutive relations depend on the particular choice of the functional forms and entails lengthy algebraic manipulations (e.g. Ingram and Eringen, [5]; Bowen, [13]; Gray and Hassanizadeh, [13]).

2.3.8. Axiom of geometric closure

The decomposition of the densities of the phases, from mass per total volume to mass per geometric region introduces the variable ε into the formulation. Closure of the system of equations requires that a relationship for the porosity variable in terms of the other independent system variables be introduced.

In the mechanics of single-phase continua, one may consider the mass balance equation as an equation for the mass density, the linear momentum equation

as a relation for the deformation vector of a solid or the velocity vector of a fluid, and the energy equation as an equation for the temperature. In the case of multiphase systems, in passing from the microscale to macroscale a new set of primary variables related to the microscale geometry is introduced. Examples are porosity, saturation, and interfacial area density. However, no additional balance laws are obtained. Therefore, a deficit of primary equations exists. This is commonly referred to as the closure problem.

To resolve the closure problem, an additional constitutive equation is needed. This is proposed in the form of a relationship among intrinsic mass densities and porosity. Taking the axiom of restricted dependence into account, the following equation is proposed:

$$\Im \left[\rho^s \left(\mathbf{x'}, t' \right), \rho^f \left(\mathbf{x'}, t' \right), \theta^s \left(\mathbf{x'}, t' \right), \theta^f \left(\mathbf{x'}, t' \right), \varepsilon \left(\mathbf{x'}, t' \right), \mathbf{X}^s \right] = 0 \qquad (2.23)$$

This equation may be considered as a constitutive relationship for ε. Now, if axioms of objectivity, smooth neighborhood, and smooth memory are applied to this functional relationship, one obtains:

$$\Im \left\{ \rho^f \left(\mathbf{x}, t \right), \nabla \rho^f \left(\mathbf{x}, t \right), \overset{\bullet}{\rho^f} \left(\mathbf{x}, t \right), \theta^f \left(\mathbf{x}, t \right), \nabla \theta^f \left(\mathbf{x}, t \right), \overset{\bullet}{\theta^f} \left(\mathbf{x}, t \right), \rho^s \left(\mathbf{x}, t \right), \right.$$

$$\nabla \rho^s \left(\mathbf{x}, t \right), \overset{\bullet}{\rho^s} \left(\mathbf{x}, t \right), \theta^s \left(\mathbf{x}, t \right), \nabla \theta^s \left(\mathbf{x}, t' \right), \overset{\bullet}{\theta^s} \left(\mathbf{x}, t \right),$$

$$\left. \varepsilon \left(\mathbf{x}, t \right), \nabla \varepsilon \left(\mathbf{x}, t \right), \overset{\bullet}{\varepsilon} \left(\mathbf{x}, t \right), \mathbf{X}^s \right\} = 0 \qquad (2.24)$$

where only first-order derivatives have been kept. This equation can be solved to obtain a relationship for ε.

2.4. Single - phase flow in non - reacting rigid porous media

2.4.1. Balance laws

Consider a medium composed of an inert fluid phase and a rigid solid phase. Balance laws are given by equation (2.4a) except that there would be no mass exchange:

$$\frac{D^\alpha \varepsilon^\alpha \rho^\alpha}{Dt} + \varepsilon^\alpha \rho^\alpha d_{kk}^\alpha = 0 \qquad (2.25a)$$

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha v_k^\alpha}{Dt} - t_{k\ell,\ell}^\alpha - \varepsilon^\alpha \rho^\alpha g_k^\alpha - T_k^\alpha = 0 \tag{2.25b}$$

$$\varepsilon^\alpha \rho^\alpha \frac{D^\alpha E^\alpha}{Dt} - t_{k\ell}^\alpha d_{k\ell}^\alpha - q_{k,k}^\alpha - \varepsilon^\alpha \rho^\alpha h^\alpha - \hat{Q}^\alpha = 0 \tag{2.25c}$$

$$\varepsilon^\alpha \rho^\alpha \Gamma^\alpha = \varepsilon^\alpha \rho^\alpha \frac{D^\alpha S^\alpha}{Dt} - \varphi_{k,k}^\alpha - \varepsilon^\alpha \rho^\alpha b^\alpha - \hat{\phi}^\alpha \tag{2.25d}$$

subject to

$$\sum_\alpha^N \hat{T}_k^\alpha = 0 \tag{2.26a}$$

$$\sum_\alpha^N (\hat{T}_k^\alpha v_k^\alpha + \hat{Q}^\alpha) = 0 \tag{2.26b}$$

$$\sum_\alpha^N \hat{\phi}^\alpha \geq 0 \tag{2.26c}$$

We now assume that the solid and fluid are in local thermal equilibrium such that

$$\theta^f = \theta^s \equiv \theta(X, t) \tag{2.27}$$

Combining equations (2.6a) through (2.6c) and (2.25a) through (2.27) and substitution into the second law of thermodynamic, inequality (2.5b), we obtain the following inequality:

$$\begin{aligned}
\rho \theta \Gamma = - \quad & \varepsilon^f \rho^f \left[\frac{D^f A^f}{Dt} + S^f \frac{D^f \theta}{Dt} \right] - \varepsilon^s \rho^s \left[\frac{D^s A^s}{Dt} + S^s \frac{D^s \theta}{Dt} \right] \\
+ \quad & t_{k\ell}^f d_{k\ell}^f + t_{k\ell}^s d_{k\ell}^s - T_k^f v_k^{fs} + \frac{1}{\theta} \left(q_k^f \theta_{,k} + q_k^s \theta_{,k} \right) \geq 0 \tag{2.28}
\end{aligned}$$

2.4.2. Constitutive equations

Assuming the solid phase to be rigid means that ρ^s remains a constant and $d_{k\ell}^s = 0$. Then, from the solid's equation of mass balance, we obtain $\varepsilon^s \rho^s = $ constant, which means that $\varepsilon = (1 - \varepsilon^s)$ is also constant in time. That is, one does not need to include ε as an independent variable. Therefore, we employ the following set of constitutive equations:

$$A^\alpha = A^\alpha \left(\rho^f, \theta \right) \qquad \alpha = f, s \tag{2.29}$$

Note that we have left out any dependence on $\varepsilon, \rho_{,k}^f, E_{KL}^s, d_{k\ell}^f$ and $\theta_{,k}$. Therefore, we are considering the fluid to be nonviscous (no $d_{k\ell}^f$), the medium to be non-heat-conducting (no $\theta_{,k}$) and the solid is rigid (no E_{KL}^s). Substitution of equation (2.29) and the like in (2.28) yields:

$$
\begin{aligned}
\rho\Gamma = \ & - \left[\varepsilon\rho^f \left(\frac{\partial A^f}{\partial\theta} + S^f \right) + \varepsilon^s\rho^s \left(\frac{\partial A^s}{\partial\theta} + S^s \right) \right] \frac{D^s\theta}{Dt} \\
& + \left[t_{k\ell}^f + \varepsilon \left(\rho^f \right)^2 \frac{\partial A^f}{\partial\rho^f} \delta_{k\ell} \right] d_{k\ell}^f \\
& - \left[T_k^f - \left(\rho^f \right)^2 \frac{\partial A^f}{\partial\rho^f} \varepsilon_{,k} \right] v_k^{fs} \\
& + \left[\frac{1}{\theta} \left(q_k^f + q_k^s \right) - \varepsilon\rho^f \left(S^f + \frac{\partial A^f}{\partial\theta} \right) v_k^{fs} \right] \theta_{,k} \geq 0 \tag{2.30}
\end{aligned}
$$

Applying argument similar to the case of single-phase materials, about linearity of (2.30) in $\dot{\theta}, d_{k\ell}^f$, and $\theta_{,k}$, we obtain:

$$\left(\varepsilon\rho^f S^f + \varepsilon^s\rho^s S^s \right) = -\varepsilon\rho^f \frac{\partial A^f}{\partial\theta^f} - \varepsilon^s\rho^s \frac{\partial A^s}{\partial\theta^s} \tag{2.31a}$$

$$q_k = q_k^f + q_k^s = \varepsilon\rho^f \theta \left(S^f + \frac{\partial A^f}{\partial\theta} \right) v_k^{fs} \tag{2.31b}$$

$$p^f = \left(\rho^f \right)^2 \frac{\partial A^f}{\partial\rho^f} \tag{2.31c}$$

$$t_{k\ell}^f = -\varepsilon p^f \delta_{k\ell} \tag{2.31d}$$

and the residual entropy inequality becomes:

$$\rho\Gamma = -\left(\hat{T}_k^f - p^f \varepsilon_{,k}\right) v_k^{fs} \geq 0 \qquad (2.31\text{e})$$

Note that although $\varepsilon_{,k}$ is a constant of the medium, it may be nonzero if the medium is inhomogeneous. Define equilibrium to be the state for which

$$\left\{v_k^{fs}\right\} = 0$$

Therefore, at equilibrium we will have

$$T_k^f\Big|_e = p^f \varepsilon_{,k} \qquad (2.32\text{a})$$

Let's propose a linear relationship for $\hat{T}_k^f$ that would be valid near equilibrium:

$$T_k^f = T_k^f\Big|_e + \frac{T_k^f}{\partial v_\ell^{fs}}\Big|_e v_\ell^{fs} \qquad (2.32\text{b})$$

Because of (2.32a), we obtain:

$$T_k^f = p^f \varepsilon_{,k}^f - R_{k\ell} v_\ell^{fs} \qquad (2.32\text{c})$$

where $R_{k\ell} = -\dfrac{T_k^f}{\partial v_\ell^{fs}}\Big|_e$. Substitute this result in (2.31e) to get:

$$\rho\Gamma = R_{k\ell} v_k^{fs} v_\ell^{fs} \geq 0 \qquad (2.33)$$

Applying the second condition of equilibrium requires $\dfrac{\partial^2 \rho\Gamma}{\partial v_\ell^{fs} \partial v_\ell^{fs}} = R_{k\ell}$ to be positive semi-definite. From this, we also obtain the interesting result that $R_{k\ell}$, and therefore the permeability tensor, is symmetric. Now, substitute (2.31a) and (2.32c) in the equation of motion of the fluid to get:

$$\frac{D^f v_k^f}{Dt} + \varepsilon^f \left(p_{,k}^f - \rho^f g_k\right) + R_{k\ell} v_\ell^{fs} = 0 \qquad (2.34\text{a})$$

Neglect the acceleration term and denote the inverse of $R_{k\ell}$ by $K_{k\ell}$ to obtain Darcy's law:

$$v_\ell^{fs} = -\varepsilon^f K_{k\ell}(p_{,k}^f - \rho^f g_k) \qquad (2.34\text{b})$$

2.5. Single - phase flow of a viscous fluid in a heat - conducting deformable solid

In this case, because the solid is deformable, the volume fraction ε may also vary. However, ε is not needed to be included in the set of independent variables if $E_{k\ell}^s$ is already included. This is because the solid phase is nonreacting and, thus, the balance of mass of the solid becomes $\varepsilon^s \rho^s j^s = \varepsilon_0^s \rho_0^s$. Then because the jacobian j^s can be obtained from $E_{k\ell}^s$, knowing j^s and ρ^s, we can calculate ε. We select the following set of independent constitutive variables:

$$\left\{ \rho^f, \rho^s, \varepsilon_{,k}, E_{k\ell}^s, d_{k\ell}^f, v_k^{fs}, \theta, \theta_{,k} \right\} \tag{2.35}$$

Application of the second law of thermodynamics yields:

$$A^s = A^s \left(\rho^s, E_{KL}^s, \theta \right) \tag{2.36a}$$

$$A^f = A^f \left(\rho^f, \theta \right) \tag{2.36b}$$

$$\varepsilon \rho^f S^f + \varepsilon^s \rho^s S^s = - \left[\varepsilon \rho^f \frac{\partial A^f}{\partial \theta} + \varepsilon^s \rho^s \frac{\partial A^s}{\partial \theta} \right] \tag{2.36c}$$

$$t_{k\ell}^f = -\varepsilon p^f \delta_{k\ell} + \tau_{k\ell}^f \tag{2.36d}$$

$$t_{k\ell}^s = -\varepsilon^s p^f \delta_{k\ell} + \rho^s \frac{\partial A^s}{\partial E_{KL}^s} F_{kK}^s F_{\ell L}^s = -\varepsilon^s p^f \delta_{k\ell} + {}_E t_{k\ell}^s \tag{2.36e}$$

where

$$p^f = \left(\rho^f \right)^2 \frac{\partial A^f}{\partial \rho^f} \tag{2.37a}$$

$$T_k^f = p^f \varepsilon_{,k} + \hat{\tau}_k^f \tag{2.37b}$$

where ${}_E t_{k\ell}^s$ is the effective stress tensor of the solid phase.

Constitutive functions are subject to the residual entropy inequality:

$$\tau_{k\ell}^f d_{k\ell}^f - \hat{\tau}_k^f v_k^{fs} + \left(\frac{q_k}{\theta} - \varepsilon \rho^f \left(S^f + \frac{\partial A^f}{\partial \theta} \right) v_k^{fs} \right) \theta_{,k} \geq 0 \qquad (2.38)$$

Define the equilibrium state such that:

$$\left\{ d_{k\ell}^f, v_k^{fs}, \theta_{,k} \right\} \equiv 0 \qquad (2.39a)$$

Then, from the first condition of equilibrium we obtain:

$$\tau_{k\ell}^f \Big|_e = \hat{\tau}_k^f \Big|_e = q_k \Big|_e = 0 \qquad (2.39b)$$

A linear theory for $\hat{\tau}_k^f$ yields

$$\hat{\tau}_k^f = R_{k\ell} v_k^{fs} + \lambda_{k\ell} \theta_{,\ell} \qquad (2.40)$$

Substitution of equations (2.36d), (2.37b), and (2.40) into the equation of motion of fluid yields:

$$\varepsilon \rho^f \frac{D^f v_k^f}{Dt} - \left(-\varepsilon p^f \delta_{k\ell} + \tau_{k\ell}^f \right)_{,\ell} - \left(\hat{\tau}_k^f + p^f \varepsilon_{,k} \right) - \varepsilon \rho^f g_k = 0 \qquad (2.41)$$

Or after rearrangement:

$$\varepsilon \rho^f \frac{D^f v_k^f}{Dt} - \tau_{k\ell,\ell}^f + \varepsilon \left(p_{,k}^f - \rho^f g_k \right) = R_{k\ell} v_k^{fs} + \lambda_{k\ell} \theta_{,\ell} \qquad (2.42)$$

It is apparent that in order to obtain Darcy's law one has to neglect inertial terms, (macroscopic) viscous terms, and the effect of temperature gradients. It is also interesting to note that from equations (2.36d) and (2.36e), neglecting viscous stress, one has the following well-known equation for total stress in the porous medium:

$$t_{k\ell} = t_{k\ell}^f + t_{k\ell}^s = -p^f \delta_{k\ell} + {}_E t_{k\ell}^s \qquad (2.43)$$

This equation was first suggested by Terzaghi.

2.6. Transport of a dissolved solute in a porous medium

2.6.1. Balance laws

Consider a medium composed of one fluid phase and one solid phase. The fluid phase is made of two components: pure water (designated by superscript w) and a solute (designated by superscript i), which are miscible at the microscopic level. Assume that both the solid phase and the fluid components are non-reacting, are locally in thermal equilibrium, and do not conduct heat. Also, consider the solid phase to be rigid so that porosity is constant in time.

Balance laws are given for mass and momentum of pure water and solute components, and for energy of the fluid phase as a whole and the solid phase.

Water mass balance:

$$\varepsilon^f \frac{\partial \rho^w}{\partial t} + \varepsilon^f \left(\rho^w v_k^w \right)_{,k} = 0 \tag{2.44}$$

Solute mass balance:

$$\varepsilon^f \frac{\partial \rho^i}{\partial t} + \varepsilon^f \left(\rho^i v_k^i \right)_{,k} = 0 \tag{2.45}$$

Water momentum balance:

$$\varepsilon^f \rho^w \frac{D^w v_k^w}{Dt} - t_{k\ell,\ell}^w - \varepsilon^f \rho^w g_k^w - \hat{T}_k^w = 0 \tag{2.46}$$

Solute momentum balance:

$$\varepsilon^f \rho^i \frac{D^i v_k^i}{Dt} - t_{k\ell,\ell}^i - \varepsilon^f \rho^i g_k^i - \hat{T}_k^i = 0 \tag{2.47}$$

Fluid phase energy balance:

$$\varepsilon^f \rho^f \frac{\partial E^f}{\partial t} + \varepsilon^f \rho^f v_k^f E_{,k}^f - t_{k\ell}^f v_{\ell,k}^f - \varepsilon^f \rho^f h^f - \hat{Q}^f = 0 \tag{2.48}$$

Solid phase energy balance:

$$\varepsilon^s \rho^s \frac{\partial E^s}{\partial t} + \varepsilon^s \rho^s v_k^s E_{,k}^s - t_{k\ell}^s v_{k,\ell}^s - \varepsilon^s \rho^s h^s - \hat{Q}^s = 0 \tag{2.49}$$

Because we are commonly interested in the mean motion of fluid phase and the dispersive motion of the solute, we recast equations of conservation of mass and momentum accordingly and obtain the following equations:

Fluid Mass Balance:

$$\frac{D^f \rho^f}{Dt} + \rho^f v^f_{k,k} = 0 \tag{2.50a}$$

where

$$\rho^f = \rho^w + \rho^i \tag{2.50b}$$

$$\rho^f v^f_k = \rho^i v^i_k + \rho^w v^w_k \tag{2.50c}$$

Solute Mass Balance:

$$\varepsilon^f \rho^f \frac{D^f \omega^i}{Dt} + J^i_k = 0 \tag{2.51a}$$

where

$$\omega^i = \rho^i / \rho^f \tag{2.51b}$$

$$u^i_k = v^i_k - v^f_k \tag{2.51c}$$

$$J^i_k = \varepsilon^f \rho^f \omega^i u^i_k \tag{2.51d}$$

Fluid Momentum Balance:

$$\varepsilon^f \rho^f \frac{D^f v^f_k}{Dt} - t^f_{k\ell,\ell} - \varepsilon^f \rho^f g^f_k - \hat{T}^f_k = 0 \tag{2.52a}$$

Solute Momentum Balance:

$$\varepsilon^f \rho^f \omega^i \left(\frac{D^i v^i_k}{Dt} - \frac{D^w v^w_k}{Dt} \right) \quad - \quad \left(t^i_{k\ell,\ell} - \frac{\omega^i}{\omega^w} t^w_{k\ell,\ell} \right) - \varepsilon^f \rho^f \omega^i \left(g^i_k - g^w_k \right)$$
$$- \left(\hat{T}^i_k - \hat{T}^w_k \right) = 0 \tag{2.52b}$$

The expanded form of the entropy inequality will read:

$$\rho\theta\,\Gamma = -\varepsilon^f\rho^f\frac{D^fA^f}{Dt} + \left(t^f_{k\ell} + \varepsilon^f\rho^f\omega^iu^i_ku^i_\ell\right)d^f_{k\ell} - \varepsilon^s\rho^s\frac{D^sA^s}{Dt} - t^s_{k\ell}d^s_{k\ell}$$

$$-\hat{T}^f_kv^{fs}_k + \left[\left(t^i_{k\ell} - \frac{\omega^i}{\omega^w}t^w_{k\ell}\right) - \varepsilon^f\rho^f\omega^i\left(A^i - A^w\right)\delta_{k\ell}\right]u^i_{k,\ell}$$

$$-\left[(\hat{T}^i_k - \hat{T}^w_k) + \varepsilon^f\rho^f\omega^i\left(A^i - A^w\right)_{,k} + \left(A^i - A^w\right)\left(\varepsilon^f\rho^f\omega^i\right)_{,k} + t^w_{k\ell}\left(\frac{\omega^i}{\omega^w}\right)_{,\ell}\right]u^i_k$$

$$-(\varepsilon^f\rho^fS^f + \varepsilon^s\rho^sS^s)\frac{D^s\theta}{Dt} + \left(\frac{q^f_k + q^s_k}{\theta} - \varepsilon^f\rho^f\omega^iS^iv^{is}_k\right)\theta_{,k} \ge 0$$

$$(2.53)$$

2.6.2. Constitutive equations

We select the following sets of dependent and independent variables:

Dependent: $A^f, A^s, A^i - A^w, t^i_{k\ell}, q_k, S^f, S^s, \hat{T}^f_k, \hat{T}^i_k - \hat{T}^w_k$

Independent: $\rho^f, \omega^i, \omega^i_{,k}, \theta, u^i_k, v^{fs}_k$

Consequences of the axiom of admissibility will be ([11]):

$$A^f = A^f\left(\rho^f, \omega^i, \theta\right) \tag{2.54a}$$

$$A^s = A^s\left(\theta\right) \tag{2.54b}$$

$$A^i - A^w = \overset{*}{A}{}^i\left(\rho^f, \omega^i, \theta\right) \tag{2.54c}$$

$$\varepsilon^f\rho^fS^f + \varepsilon^s\rho^sS^s = -\left(\varepsilon^f\rho^f\frac{\partial A^f}{\partial\theta} + \varepsilon^s\rho^s\frac{\partial A^s}{\partial\theta}\right) \tag{2.54d}$$

$$t^f_{k\ell} = -\varepsilon^fp^f\delta_{k\ell} - \varepsilon^f\rho^f\omega^iu^i_ku^i_\ell \tag{2.54e}$$

where

$$p^f = \left(\rho^f\right)^2 \frac{\partial A^f}{\partial \rho^f} \tag{2.54f}$$

$$t^i_{k\ell} - \frac{\omega^i}{\omega^w} t^w_{k\ell} = -\varepsilon^f \rho^f \omega^i \left(\overset{*i}{\mu} - \overset{*i}{A}\right) \delta_{k\ell} \tag{2.54g}$$

where

$$\overset{*i}{\mu} = \mu^i - \mu^w = \frac{\partial A^f}{\partial \omega^i}; \text{ Thus}: \overset{*i}{\mu} = \overset{*i}{\mu}\left(\rho^f, \omega^i, \theta\right) \tag{2.54h}$$

$$\hat{T}^f_k = \hat{\tau}^f_k + p^f \varepsilon^f_{,k} \tag{2.54i}$$

$$\hat{T}^f_k - \hat{T}^w_k = \overset{*i}{\tau}_k + \left[\varepsilon^f \rho^f \omega^i \left(\overset{*i}{\mu} - \overset{*i}{A}\right)\right]_{,k} - \varepsilon^f \rho^f \omega^i \overset{*i}{\mu}_{,k} - t^w_{k\ell} \left(\omega^i/\omega^w\right)_{,\ell} \tag{2.54j}$$

The residual entropy inequality becomes:

$$-\hat{\tau}^f_k v^{fs}_k - \overset{*i}{\tau}_k u^i_k \geq 0 \tag{2.55}$$

Substitution of equations (2.54e), (2.54g), (2.54i), and (2.54j) in the equations of motion of the fluid and the solute yields

$$\varepsilon^f \rho^f \frac{D^f v^f_k}{Dt} + \varepsilon^f \left(p^f_{,k} - \rho^f g^f_k\right) - \hat{\tau}^f_k = 0 \tag{2.56a}$$

$$\left(\frac{D^i v^i_k}{Dt} - \frac{D^w v^w_k}{Dt}\right) - \left(g^i_k - g^w_k\right) + \overset{*i}{\mu}_{,k} = \frac{1}{\varepsilon^f \rho^f \omega^i} \overset{*i}{\tau}_k \tag{2.56b}$$

Neglect inertial terms and assume that the only body force present is the gravity, g_k. Then, these equations become:

$$\varepsilon^f \left(p^f_{,k} - \rho^f g^f_k\right) = \hat{\tau}^f_k \tag{2.57a}$$

$$\overset{*i}{\mu}_{,k} = \frac{1}{\varepsilon^f \rho^f \omega^i} \overset{*i}{\tau}_k \tag{2.57b}$$

From (2.55), we can say that at equilibrium we should have:

$$\hat{\tau}_k^f\bigg|_e = \overset{*i}{\tau}_k\bigg|_e = 0 \tag{2.58}$$

Recall that $\hat{\tau}_k^f$ and $\overset{*i}{\tau}_k$ are still general functions of $\rho^f, \omega^i, \omega_{,k}^i, v_k^{fs}, u_k^i$, and θ. Let's propose a linear relationship for $\hat{\tau}_k^f$ and $\overset{*i}{\tau}_k$:

$$\hat{\tau}_k^f = R_{k\ell}^f v_\ell^{fs} + B_{k\ell}^f u_\ell^f \tag{2.59}$$

$$\overset{*i}{\tau}_k = R_{k\ell}^i v_\ell^{fs} - B_{k\ell}^i u_\ell^i \tag{2.60}$$

Now, substitute these relations into equations (2.57a) and also expand $\overset{*i}{\mu}_{,k}$ using chain rule to obtain

$$\varepsilon^f \left(p_{,k}^f - \rho^f g_k \right) = -R_{k\ell}^f v_\ell^{fs} + B_{k\ell}^f u_\ell^i \tag{2.61}$$

$$\frac{\partial \overset{*i}{\mu}}{\partial \omega^i} \omega_{,k}^i + \frac{\partial \overset{*i}{\mu}}{\partial \rho^f} \rho_{,k}^f = \left(R_{k\ell}^i v_\ell^{fs} - B_{k\ell}^i u_\ell^i \right) / \varepsilon^f \rho^f \omega^i \tag{2.62}$$

Solve these equations for v_ℓ^{fs} and u_k^i to obtain:

$$v_k^{fs} = -K_{k\ell}^f \left(p_{,\ell}^f - \rho^f g_\ell \right) - B_{k\ell}^f \rho_{,\ell}^f - D_{k\ell}^f \omega_{,l}^i \tag{2.63}$$

$$\varepsilon^f \rho^f \omega^i u_k^i = J_k^i = -D_{k\ell}^i \omega_{,\ell}^i - B_{k\ell}^i \rho_{,\ell}^f - K_{k\ell}^i \left(p_{,\ell}^f - \rho^f g_\ell \right) \tag{2.64}$$

For low concentration situations, these equations reduce to the classical Darcy's law and Fick's, respectively:

$$v^{fs} = -K_{k\ell}^f \left(p_{,\ell}^f - \rho^f g_\ell \right) \tag{2.65}$$

$$J_k^i = -D_{k\ell}^i \omega_{,\ell}^i \tag{2.66}$$

2.7. Transport of a large concentration solute in a porous medium

This is the same as the previous example, only the solute is considered to be present at a high concentration at parts of the system. This means that large concentration (or mass fraction) gradients exist. In fact, balance laws and basic constitutive equations will be the same as those developed in Section 2.6 until equations (2.59) where $\hat{\tau}_k^f$ and $\overset{*i}{\tau}_k$ are assumed to be linear functions of v_k^{fs} and u_k^i. This is because large mass fraction gradients may lead to large dispersive fluxes u_k^i (or J_k^i). Therefore, the assumption of linearity for $\overset{*i}{\tau}_k$ does not hold when large mass fraction gradients are present. Instead, (2.60) should be replaced with:

$$\overset{*i}{\tau}_k = -R_{k\ell}^i u_\ell^i \left| u_\ell^i \right| - B_{k\ell}^i u_\ell^i \tag{2.67}$$

where the coupling with the fluid flow velocity is neglected. After substitution of this relation into equation (2.57b), expansion of $\overset{*i}{\mu}_{,k}$ using chain rule, and with simplifying assumption, we obtain an non-Fickian dispersion equation valid for large-concentration solutes:

$$\left(1 + \beta \left| J_k^i \right| \right) J_k^i = -D_{k\ell}^i \omega_{,\ell}^i \tag{2.68}$$

where β is the coefficient of nonlinear dispersion.

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