Thermodynamics of transport, phase changes, chemical reactions and heat conduction phenomena in stressed elastic porous materials

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Thermodynamics of transport, phase changes, chemical reactions and heat conduction phenomena in stressed elastic porous materials

Björn Johannesson
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Abstract

By using the mixture theory defined in continuum mechanics, together with constitutive theory it is possible to derive classical and generalized forms of, for example, Fick’s, Darcy’s and Fourier’s laws, and conditions for phase changes and chemical reactions. These conditions are very important in several engineering disciplines. The report includes the necessary definitions and axioms needed to derive the classical physical laws. The different mathematical steps performed to reach different results are in almost every case shown explicitly.

1. Introduction

A review of the paper Macroscale Thermodynamics and the Chemical Potential for Swelling Porous Media is performed in this article. The concepts described in the paper of Bowen, The Theory of Mixtures, is also included as an important background to the present work.

The presented material in this paper is stuff that the author has studied during preparation of a doctoral thesis. Since no ‘simple’ text book treats the combination of the explanation of basic definitions in mechanics and the more complicated mixture theory I thought that engineers with basic knowledge in mechanics might be interested in having all the needed essential information collected in one place. The drawback with having the goal that an ambitious student should be able to follow the content in this paper is that the many mathematical steps tends to destroy the
simplicity of most of the presented results. On the other hand if successfully coming through this paper the reader will obtain a solid understanding of the background to many common theories of interests to engineers and will, furthermore, most probably develop thoughts about how to apply them and how to develop them further.

The work is more or less identical to the paper *Macroscale Thermodynamics and the Chemical Potential for Swelling Porous Media*. The difference is that an extensive description of all essentials steps needed to receive the closed set of equations for the studied thermodynamical problem are explicitly included in the review to be presented. Furthermore, is the background leading to, for example, kinematic relations and different forms of balance principles included to make this article complete, in the sense that all significant information about the theory in question are included.

The paper consider, among different things, three different important issues

1. A novel definition of the macroscale chemical potential for a porous medium is introduced.

2. The properties of the novel macroscale chemical potential are derived by slightly expanding the usual Coleman and Noll approach of exploiting the entropy inequality to obtain near-equilibrium results.

3. A discussion of the applications of mixture theory to swelling porous media.

The modified approach using an appropriate definition of the chemical potential, one is able to derive properties of the chemical potential which corresponds exactly with the properties of the classical Gibbsian chemical potential. The motivation of the use of a new chemical potential is illustrated.

### 2. Kinematics and definitions

The *spatial position*, or the *place* \( x \), of a particle labeled \( X_a \) is given by a function \( x = X_a(X_a, t) \)

where \( X_a \) is the *material coordinates* of the particle \( X_a \) of the \( a \)th body or *constituent* in its fixed reference configuration. At time \( t \) the *spatial position* \( x \) will be occupied by the particle \( X_a \) labeled with its corresponding material coordinates \( X_a \). Assuming that an inverse to the deformation functions, i.e. \( X_a^{-1} \), exists for all continuous bodies \( 1, ..., \mathcal{R} \) the motion of the \( a \)th constituent could be described as

\[
X_a = X_{a}^{-1}(x, t)
\]

The velocity and acceleration of the particle \( X_a \) at time \( t \) are defined by

\[
x'_a = \frac{\partial X_a(X_a, t)}{\partial t}
\]

\[
x''_a = \frac{\partial^2 X_a(X_a, t)}{\partial t^2}
\]
respectively. That is, the velocity and the acceleration are regarded as functions of the particle \( X_0 \) having the material coordinates \( X_0 \) and the time \( t \). This is the so-called material description. Hence the prime affixed to a symbol with a subscript \( a \) will denote the material derivative following the motion of the \( a \)th constituent.

Given (2.2), the velocity and acceleration of \( X_0 \) can be regarded as given by functions of \((x,t)\), i.e.

\[
\begin{align*}
    x'_0 &= x'_0 (x,t) \\
    x''_0 &= x''_0 (x,t)
\end{align*}
\]  

(2.5) (2.6)

The velocity gradient for the \( a \)th constituent at \((x,t)\) is defined by

\[
L_a = \text{grad} x'_a (x,t); \quad L_{(a)ij} = \frac{\partial x'_a (x,t)}{\partial x_j}
\]

(2.7)

The velocity gradient can be decomposed as

\[
L_a = D_a + W_a
\]

(2.8)

where \( D_a \) is the symmetric part of \( L_a \) defined by

\[
D_a = \frac{1}{2} (L_a + L_a^T)
\]

(2.9)

and \( W_a \) the skew-symmetric defined by

\[
W_a = \frac{1}{2} (L_a - L_a^T)
\]

(2.10)

Here \( D_a \) is called the rate of strain tensor or stretching tensor and \( W_a \) is called the spin tensor.

For a mixture, the \( \mathbb{R} \) bodies \( 1, \ldots, \mathbb{R} \) are allowed to occupy common portions of physical space. Then each spatial position \( x \) in the mixture is occupied by \( \mathbb{R} \) particles, one from each constituent. Each constituent is assigned a density. The mass density for the \( a \)th constituent is denoted \( \rho_a \). The density is a function of \((x,t)\), i.e.

\[
\rho_a = \rho_a (x,t)
\]

(2.11)

The density of the mixture at \( x \) and time \( t \) is defined by

\[
\rho = \rho(x,t) = \sum_{a=1}^{\mathbb{R}} \rho_a (x,t)
\]

(2.12)

The mass concentration of the \( a \)th constituent at \((x,t)\) is

\[
c_a = c_a (x,t) = \frac{\rho_a}{\rho}
\]

(2.13)

Following (2.12) and (2.13), the mass concentrations are related by

\[
\sum_{a=1}^{\mathbb{R}} c_a = 1
\]

(2.14)
The mean velocity, or simply the velocity of the mixture, at \((x, t)\) is the mass-weighted average of the constituent velocities defined by

\[
\bar{\mathbf{x}} = \bar{\mathbf{x}}(x, t) = \frac{1}{\rho} \sum_{a=1}^{\mathcal{R}} \rho_a \mathbf{x}_a'(x, t)
\]

(2.15)

The diffusion velocity for the \(a\)th constituent at \((x, t)\) is defined by

\[
\mathbf{u}_a = \mathbf{u}_a(x, t) = \mathbf{x}_a'(x, t) - \bar{\mathbf{x}}(x, t)
\]

(2.16)

The diffusion velocity \(\mathbf{u}_a\) is the velocity for the \(a\)th constituent related to the mixture. It follows from (2.15), (2.16), and (2.12) that

\[
\sum_{a=1}^{\mathcal{R}} \rho_a \mathbf{u}_a = 0
\]

(2.17)

The velocity gradient for the mixture at \((x, t)\) is

\[
\mathbf{L} = \text{grad} \, \bar{\mathbf{x}}(x, t); \quad L_{ij} = \frac{\partial \bar{x}_i}{\partial x_j}
\]

(2.18)

The relation between \(\mathbf{L}\) and \(\mathbf{L}_a\) is obtained by considering the identity

\[
\text{grad} (\rho_a \mathbf{u}_a) = \mathbf{u}_a \otimes \text{grad} \rho_a + \rho_a \text{grad} \mathbf{u}_a
\]

(2.19)

where \(\otimes\) denotes the dyad product. From (2.17), it follows that

\[
\text{grad} \sum_{a=1}^{\mathcal{R}} \rho_a \mathbf{u}_a = 0
\]

(2.20)

which together with (2.19) give the relation

\[
\sum_{a=1}^{\mathcal{R}} \mathbf{u}_a \otimes \text{grad} \rho_a = \sum_{a=1}^{\mathcal{R}} \rho_a \text{grad} \mathbf{u}_a
\]

(2.21)

In addition, the expression

\[
\rho \mathbf{L} = \sum_{a=1}^{\mathcal{R}} \rho_a \mathbf{L}_a = \sum_{a=1}^{\mathcal{R}} \rho_a \text{grad} \, \bar{x} = \sum_{a=1}^{\mathcal{R}} \rho_a \text{grad} (\mathbf{x}_a' - \mathbf{u}_a)
\]

(2.22)

must be considered, in which (2.12) and (2.16) are used. The definition (2.7) together with the expressions (2.21) and (2.22) give the relation between \(\mathbf{L}\) and \(\mathbf{L}_a\) as

\[
\rho \mathbf{L} = \sum_{a=1}^{\mathcal{R}} (\rho_a \mathbf{L}_a + \mathbf{u}_a \otimes \text{grad} \rho_a)
\]

(2.23)

Any time-dependent vector fields, and in fact any time-dependent scalar, vector, or tensor field \(\Gamma_a\) associated with the \(a\)th constituent, can be regarded either as a function \(\Gamma_a(X_a, t)\) of the
particle $X_a$ (having the fixed material coordinates $X_a$) and the time $t$, or as a function $\Gamma_a(x, t)$ of the place $x$ and the time $t$, provided that a definite motion $x = X_a(X_a, t)$ is given. Again, the prime affixed to a symbol with a subscript $a$ will denote the material derivative following the motion of the $a$th constituent. The material time derivative of $\Gamma_a$ is defined by

$$\Gamma'_a = \frac{\partial \Gamma_a}{\partial t} [X_a(X_a, t), t]; \quad X_a = \text{const.} \quad (2.24)$$

If the inverse to the deformation function $X_a$ exists, the arbitrary function $\Gamma_a$ can be expressed by functions of $(x, t)$. The definition (2.24) and the chain rule for partial differentiation together produce

$$\Gamma'_a = \frac{\partial \Gamma}{\partial t} (x, t) + \text{grad} \Gamma (x, t) X'_a (x, t) \quad (2.25)$$

which is the relation between the material derivative $\Gamma'_a$ and the spatial derivative $\partial \Gamma / \partial t$.

The derivative of $\Gamma$ following the motion defined by the mixture, that is $\dot{x}$, is denoted by $\dot{\Gamma}$ and is defined, in the same manner, by

$$\dot{\Gamma} = \frac{\partial \Gamma}{\partial t} (x, t) + \text{grad} \Gamma (x, t) \dot{x} (x, t) \quad (2.26)$$

As an example, considering the one-dimensional case: $\Gamma = \Gamma(x_1, t)$. Differentiation yields, $d\Gamma = (\partial \Gamma / \partial x_1) dx_1 + (\partial \Gamma / \partial t) dt$, by dividing the whole expression with $dt$, one obtain: $d\Gamma / dt = (\partial \Gamma / \partial x_1) dx_1 / dt + (\partial \Gamma / \partial t) dt / dt$. By identifying that $\partial \Gamma / \partial t \equiv \Gamma$ and also that $dx_1 / dt = \dot{x}_1$ one obtain the one-dimensional version of (2.26) as: $\dot{\Gamma} = d\Gamma / dt + (\partial \Gamma / \partial x_1) \dot{x}_1$.

Sometimes the material derivative following the motion of the $\alpha$ component, i.e. $\dot{\Gamma}_\alpha$ is written as $D_\alpha (\Gamma) / Dt$ and the velocity, as defined in (2.3), as $v_\alpha$. That is a common way of expressing (2.26) is

$$D_\alpha (\Gamma) / Dt = \frac{\partial \Gamma}{\partial t} + \text{grad} \Gamma v_\alpha \quad (2.27)$$

For example, the material time derivative of the mass density $\rho'_a$ can be related to the spatial time derivative $\partial \rho_a / \partial t$ by identifying $\Gamma$ as $\rho_a$ to yield

$$\rho'_a = \frac{\partial \rho_a}{\partial t} + \text{grad} \rho_a \cdot x'_a \quad (2.28)$$

It follows directly from (2.16), (2.25), and (2.26) that

$$\Gamma'_a - \dot{\Gamma} = (\text{grad} \Gamma) u_a \quad (2.29)$$

$$\frac{D_\alpha (\Gamma)}{Dt} - \frac{D_\alpha (\Gamma_a)}{Dt} = (\text{grad} \Gamma_a) u_a$$

The deformation gradients for the $a$th constituent is defined by

$$F_a = \text{GRAD} X_a (X_a, t); \quad F_{(a)ik} = \frac{\partial x_i}{\partial X_{(a)k}} \quad (2.30)$$
where GRAD denote the gradient with respect to the material coordinates $X_0$. Note that $F_a^{-1}$ only exists if $\det F_a \neq 0$, which is the case because of the assumed invariability of $X_0$. The linear transformation inverse to $F_a$ is

$$F_a^{-1} = \text{grad } X_0^{-1}(x, t); \quad F_a^{-1}_{(a)kj} = \frac{\partial X_{(a)k}}{\partial x_j} \quad (2.31)$$

In accordance with (2.30) and (2.31) it is concluded that

$$F_a F_a^{-1} = F_a^{-1} F_a = I; \quad \frac{\partial x_i}{\partial X_{(a)k}} \frac{\partial X_{(a)k}}{\partial x_j} = \delta_{ij} \quad (2.32)$$

Using the chain rule together with the definition of the velocity gradient as

$$L_{(a)ij} = \frac{\partial x_{(a)i}}{\partial x_j} = \frac{\partial x_{(a)i}}{\partial X_{(a)k}} \frac{\partial X_{(a)k}}{\partial x_j} \quad (2.33)$$

and noting that $X_0$ is independent of the time $t$, it follows that

$$L_{(a)ij} = \left( \frac{\partial x_{(a)i}}{\partial X_{(a)k}} \right)' \frac{\partial X_{(a)k}}{\partial x_j} = F_{(a)ik} F_{(a)kj}^{-1} \quad (2.34)$$

i.e.

$$L_a = F_a' F_a^{-1} \quad (2.35)$$

which is the relation between the velocity gradient and the deformation gradient for the $a$th constituent.

Another property of the deformation gradient of the $a$th constituent will be examined, namely the relation between determinant of, i.e. $\det F_a$ denoted $J_{(a)}^F$ and deformation gradient $F_a$. Recall that the deformation gradient and the inverse to the deformation gradient can be written as

$$F_a = x_{k,K} = \frac{\partial x_k}{\partial X_{(a)k}}; \quad F_a^{-1} = X_{K,k} = \frac{\partial X_{(a)K}}{\partial x_k} \quad (2.36)$$

where indices after comma indicate partial differentiation with respect to $X_{(a)K}$ when they are majuscules, and with respect to $x_k$ when they are minuscules. The determinant of $F_a$ can be obtained by the permutation symbols $e_{KLM}$ and $e_{klm}$, as

$$J_{(a)}^F = |x_{k,K}| = \frac{1}{6} e_{KLM} e_{klm} x_{k,K} x_{L,M} \quad (2.37)$$

where $e_{KLM}$ and $e_{klm}$ are; (i) zero when at least two indices are equal; (ii) 1, if the sequence of numbers $k, l, m$ is the sequence 1, 2, 3 or an even permutation of the sequence; and (iii) -1, if the sequence of $k, l, m$ is and odd permutation of the sequence 1, 2, 3. Hence, $e_{123} = e_{312} = e_{312} = 1$, $e_{132} = e_{213} = e_{231} = -1$, all other $e_{klm} = 0$.

Each of the two sets of equations in (2.36) is a set of nine linear equations for the nine unknowns $x_{k,K}$ or $X_{K,k}$. A unique solution exists, since the Jacobian of the transformation is
assumed not to vanish. Using Cramer's rule of determinants, the solution for $X_{K,k}$ may be obtained in terms of $x_{k,K}$. Thus

$$X_{K,k} = \frac{\text{cofactor } x_{k,K}}{J_f^{(a)}} = \frac{1}{2J_f^{(a)}} e_{KLM} e_{klm} x_{l,L} x_{m,M}$$  \hspace{1cm} (2.38)

Differentiating (2.37), yields

$$\frac{\partial J_f^{(a)}}{\partial x_{k,K}} = \frac{1}{2} e_{KLM} e_{klm} x_{l,L} x_{m,M}$$  \hspace{1cm} (2.39)

that is, the important identity for the Jacobi is obtained by combining (2.38) and (2.39), which gives

$$\frac{\partial J_f^{(a)}}{\partial x_{k,K}} = \text{cofactor } x_{k,K} = J_f^{(a)} X_{K,k}$$  \hspace{1cm} (2.40)

or, equally

$$\frac{\partial J_f^{(a)}}{\partial F_a} = J_f^{(a)} F_a^{-1}$$  \hspace{1cm} (2.41)

For certain problems it is convenient to introduce the vector $w_a$ denoting the displacement of particle $X_a$ of the $a$th body from its place $X_a$ in the reference configuration to its place $x = X_a(X_a)$ in its deformed state:

$$w_a(X_a) = X_a(X_a) - X_a$$  \hspace{1cm} (2.42)

i.e.

$$w_a(X_a) = x(X_a) - X_a$$  \hspace{1cm} (2.43)

Differentiation yields

$$dx_i (X_a) = \frac{\partial x_i}{\partial X_a} dX_a = \left( \delta_{ij} + \frac{\partial w_a(i)}{\partial X_a(j)} \right) dX_a$$  \hspace{1cm} (2.44)

that is

$$\frac{\partial x_i}{\partial X_a} = \delta_{ij} + \frac{\partial w_a(i)}{\partial X_a(j)}$$  \hspace{1cm} (2.45)

The displacement gradient $H_a$ is also introduced as

$$H_a = \text{GRAD } w_a; \quad H_{(a)ij} = \frac{\partial w_a(i)}{\partial X_a(j)}$$  \hspace{1cm} (2.46)

This definition together with (2.45) and (2.30) give the relation between the deformation gradient $F_a$ and the displacement gradient $H_a$ as

$$F_a = I + H_a$$  \hspace{1cm} (2.47)

One of the strain measures is the Lagrangian strain defined as

$$E_a = \frac{1}{2} (F_a^T F_a - I)$$  \hspace{1cm} (2.48)
which may be expressed in terms of the displacement gradient \( H_a \) as

\[
E_a = \frac{1}{2} (F_a^T F_a - I) = \frac{1}{2} \left( (I + H_a)^T (I + H_a) - I \right) = \frac{1}{2} (H_a + H_a^T) + \frac{1}{2} H_a^T H_a
\]

(2.49)

where (2.47) was used. The Lagrangian strain measure has the benefit of giving zero contribution of strains during rigid body rotation. However, the linear strain measure

\[
e_a = \frac{1}{2} (H_a + H_a^T)
\]

(2.50)

is often adopted.

In solid mechanics one is often interested in calculating the displacement of a body from its initially undeformed state. In order to do this one must introduce the concept of strains (and stresses). The strain is a relative measure of the length change between two neighboring point with regard to its initial undeformed length.

The classical linear strain measure, i.e. \( e = \frac{1}{2} (H + H^T) \) where \( H \) is the displacement gradient, gives unphysical results when rigid body rotations occurs from the initial configuration and when large deformations is considered. Due to this fact one is interested to define a strain measure that gives zero contribution to strains during rigid body rotation and also a measure which makes it possible to study bodies with arbitrary large deformation.

Consider the relation between the current place \( x \) of a point in a body and the reference configuration \( X \) and the displacement \( w \), i.e. equation (2.43) repeated

\[
x(X) = X + w(X)
\]

(2.51)

The differential \( d \) will be used denoting, for example, a differentiation like

\[
d\frac{\partial x}{\partial X} = \frac{\partial x}{\partial X}
\]

(2.52)

i.e.

\[
d(x(X)) = \frac{\partial x}{\partial X} dX
\]

(2.53)

By inserting the expression for \( x \) in (2.51) into equation (2.53) gives

\[
d(x(X)) = \frac{\partial (X + w(X))}{\partial X} dX = \frac{\partial X}{\partial X} dX + \frac{\partial w(X)}{\partial X} dX = \left( I + \frac{\partial w(X)}{\partial X} \right) dX
\]

(2.54)

From (2.54) and (2.52) one obtain

\[
\frac{\partial x}{\partial X} = \left( I + \frac{\partial w}{\partial X} \right)
\]

(2.55)

Recall that the deformation gradient is defined as

\[
F = \text{GRAD}(x)
\]

(2.56)
where \( \text{GRAD} \) is used to symbolize that the differentiation is with respect to the initial configuration \( X \), i.e.

\[
F = \begin{bmatrix}
\frac{\partial w_1}{\partial X_1} & \frac{\partial w_1}{\partial X_2} & \frac{\partial w_1}{\partial X_3} \\
\frac{\partial w_2}{\partial X_1} & \frac{\partial w_2}{\partial X_2} & \frac{\partial w_2}{\partial X_3} \\
\frac{\partial w_3}{\partial X_1} & \frac{\partial w_3}{\partial X_2} & \frac{\partial w_3}{\partial X_3}
\end{bmatrix}
\]  

(2.57)

The displacement gradient \( H \) is defined as

\[
H^{G-L} = \text{GRAD} (w)
\]  

(2.58)

where the super-script denotes 'Green-Lagrange' which will be included to emphasize that the displacement is differentiated with respect to the initial configuration \( X \), i.e.

\[
H^{G-L} = \begin{bmatrix}
\frac{\partial w_1}{\partial X_1} & \frac{\partial w_1}{\partial X_2} & \frac{\partial w_1}{\partial X_3} \\
\frac{\partial w_2}{\partial X_1} & \frac{\partial w_2}{\partial X_2} & \frac{\partial w_2}{\partial X_3} \\
\frac{\partial w_3}{\partial X_1} & \frac{\partial w_3}{\partial X_2} & \frac{\partial w_3}{\partial X_3}
\end{bmatrix}
\]  

(2.59)

Hence, (2.55) can be written as

\[
F = (I + H^{G-L})
\]  

(2.60)

Consider two points in a undeformed body the vector located between these two points is the vector \( dX \) having the length \( ds \) in the same manner \( dx \) and \( ds \) are considered in the deformed state between the same points. The relation between \( dX \) and \( ds \) and also between \( dx \) and \( ds \), is

\[
|dx| = ds = \sqrt{dx \cdot dx}; \quad |dX| = dS = \sqrt{dX \cdot dX}
\]  

(2.61)

And the quadratic length in the deformed and undeformed state, therefore is

\[
(ds)^2 = dx \cdot dx; \quad (dS)^2 = dX \cdot dX
\]  

(2.62)

The 'Green-Lagrange' strain measure \( \epsilon_{G-L} \) defined in the direction defined by \( dX/dS \), i.e. in the initial undeformed direction, is

\[
\epsilon_{G-L} = \frac{(ds)^2 - (dS)^2}{2(dS)^2} = \frac{dx \cdot dx - dX \cdot dX}{2(dS)^2}
\]  

(2.63)

This can be compared to the linear strain measure \( \varepsilon \), i.e. \( \varepsilon = (ds - dS)/dS \). This means that the relative length change should be about 1.05-1.1 before any important differences between the linear strain measure and the 'Green-Lagrange' strain measure is obtained. The benefit of using the non-linear strain measure in (2.63) is, however, that this strain definition gives zero contributions during rigid body rotation. This will be shown later.

From the definition of the deformation gradient \( F \) and from (2.55) is concluded that

\[
dx = FdX = \left( I + H^{G-L} \right) dX
\]  

(2.64)
This means that the 'Green-Lagrange' strain measure $\varepsilon_{G-L}$ defined in (2.63) could be written as

$$\varepsilon_{G-L} = \frac{(ds)^2 - (dS)^2}{2(dS)^2} = \frac{\mathbf{F}d\mathbf{X} \cdot d\mathbf{X} - d\mathbf{X} \cdot d\mathbf{X}}{2(dS)^2} \tag{2.65}$$

Using the following two identities

$$\frac{1}{2} \frac{d\mathbf{X}}{dS} \cdot \frac{d\mathbf{X}}{dS} = \frac{1}{2} \frac{d\mathbf{X}}{dS} \cdot \left( \frac{d\mathbf{X}}{dS} \right) \tag{2.66}$$

$$\mathbf{F} \frac{d\mathbf{X}}{dS} \cdot \frac{1}{2} \mathbf{F} \frac{d\mathbf{X}}{dS} = \frac{d\mathbf{X}}{dS} \cdot \left( \frac{1}{2} \mathbf{F}^T \mathbf{F} \frac{d\mathbf{X}}{dS} \right) \tag{2.67}$$

it is concluded that (2.65) can be written as

$$\varepsilon_{G-L} = \frac{(ds)^2 - (dS)^2}{2(dS)^2} = \frac{d\mathbf{X}}{dS} \cdot \left( \frac{1}{2} \left( \mathbf{F}^T \mathbf{F} - \mathbf{I} \right) \right) \frac{d\mathbf{X}}{dS} \tag{2.68}$$

which shows that the strain measure $\varepsilon_{G-L}$ is defined in the direction given from the vector $d\mathbf{X}/dS$ in the undeformed configuration.

The 'Green-Lagrange' strain tensor $\mathbf{E}^{G-L}$ is introduced as

$$\mathbf{E}^{G-L} = \frac{1}{2} \left( \mathbf{F}^T \mathbf{F} - \mathbf{I} \right) \tag{2.69}$$

which is the term in the brackets of (2.65). This is a generalization of the strain measure $\varepsilon_{G-L}$, that is, $\mathbf{E}^{G-L}$ holds for all directions of interest.

The term $\mathbf{F}^T \mathbf{F}$ is often denoted $\mathbf{C}$ referred to as the right Cauchy-Green tensor, this tensor was used by Green in 1841. That is, $\mathbf{C}$ is defined as

$$\mathbf{C} = \mathbf{F}^T \mathbf{F} \quad \text{Cachy-Green tensor} \tag{2.70}$$

The 'Green-Lagrange' strain tensor $\mathbf{E}^{G-L}$ can be formulated solely in terms of the displacement gradient instead of with the deformation gradient. Using the expression (2.69) and (2.60) one can write

$$\mathbf{E}^{G-L} = \frac{1}{2} \left( \mathbf{F}^T \mathbf{F} - \mathbf{I} \right) = \frac{1}{2} \left( \left( \mathbf{I} + \mathbf{H}^{G-L} \right)^T \left( \mathbf{I} + \mathbf{H}^{G-L} \right) - \mathbf{I} \right)$$

$$= \frac{1}{2} \left( \mathbf{I} + \mathbf{H}^{G-L} + \mathbf{I} \left( \mathbf{H}^{G-L} \right)^T + \left( \mathbf{H}^{G-L} \right)^T \left( \mathbf{H}^{G-L} \right) - \mathbf{I} \right) \tag{2.71}$$

$$= \frac{1}{2} \left( \mathbf{H}^{G-L} + \left( \mathbf{H}^{G-L} \right)^T \right) + \frac{1}{2} \left( \mathbf{H}^{G-L} \right)^T \left( \mathbf{H}^{G-L} \right)$$

That is, the 'Green-Lagrange' strain tensor $\mathbf{E}^{G-L}$ is given by

$$\mathbf{E}^{G-L} = \frac{1}{2} \left( \mathbf{H}^{G-L} + \left( \mathbf{H}^{G-L} \right)^T \right) + \frac{1}{2} \left( \mathbf{H}^{G-L} \right)^T \left( \mathbf{H}^{G-L} \right) \tag{2.72}$$

where the last term on the right hand side is the non-linear contribution to the strains when using the 'Green-Lagrange' strain tensor. It should be observed that the displacement gradients are with respect to the undeformed configuration $\mathbf{X}$. 

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By simply ignoring the non-linear contribution in (2.72), one obtain the classical linear strain measure $e^{G-L}$, still with respect to the undeformed configuration $X$, i.e.

$$
e^{G-L} = \frac{1}{2} \left( (H^{G-L}) + (H^{G-L})^T \right)$$

\hspace{1in} (2.73)

**Example 1.** Consider a case where the motion is known in hand for a rigid body. The body will be subjected to a rotation in the $x_1 - x_2$ plane from its initial configuration $X$ to its deformed state $x$. Such an rotation can be described by a relation

$$x = QX$$

where the rotation matrix is $Q$

$$Q = \begin{bmatrix}
cos \varphi & -sin \varphi & 0 \\
sin \varphi & cos \varphi & 0 \\
0 & 0 & 1
\end{bmatrix}$$

where $\varphi$ denotes the angle, i.e. the magnitude of the rotation from its initial configuration. That is, the place $x$ can be related to the initial fixed configuration $X$ for a rigid body rotation, as

$$\begin{bmatrix}
x_1 \\
x_2 \\
x_3
\end{bmatrix} = \begin{bmatrix}
cos \varphi & -sin \varphi & 0 \\
sin \varphi & cos \varphi & 0 \\
0 & 0 & 1
\end{bmatrix} \begin{bmatrix}
X_1 \\
X_2 \\
X_3
\end{bmatrix}$$

i.e.

$$
x_1 = X_1 \cos \varphi - X_2 \sin \varphi \\
x_2 = X_1 \sin \varphi + X_2 \cos \varphi \\
x_3 = X_3
$$

Recall that the deformation gradient is defined as $F = \text{GRAD}(x)$, i.e. $F_{ij} = \partial x_i / \partial X_j$. The terms of interest is therefore: $\partial x_1 / \partial X_1 = \cos \varphi$, $\partial x_1 / \partial X_2 = -\sin \varphi$, $\partial x_2 / \partial X_1 = \sin \varphi$ and $\partial x_2 / \partial X_2 = \cos \varphi$. This means that the deformation gradient for a rigid body rotation takes the form

$$F = \begin{bmatrix}
cos \varphi & -sin \varphi & 0 \\
sin \varphi & cos \varphi & 0 \\
0 & 0 & 1
\end{bmatrix}$$

Using the definition of the 'Green-Lagrange' strain tensor, i.e. $E^{G-L} = \frac{1}{2} (F^T F - I)$ one obtain

$$E^{G-L} = \frac{1}{2} \begin{bmatrix}
\cos \varphi & -\sin \varphi & 0 \\
\sin \varphi & \cos \varphi & 0 \\
0 & 0 & 1
\end{bmatrix} \begin{bmatrix}
\cos \varphi & \sin \varphi & 0 \\
-\sin \varphi & \cos \varphi & 0 \\
0 & 0 & 1
\end{bmatrix} - \frac{1}{2} \begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}$$
This means that the 'Green-Lagrange' strain tensor gives the correct response during rigid body rotation since no strains develops in this case.

For the linear strain measure i.e.

\[
e^{G-L} = \frac{1}{2} \left( (H^{G-L}) + (H^{G-L})^T \right) = \frac{1}{2} \left( (F - I) + (F - I)^T \right)
\]

one obtain

\[
e^{G-L} = \frac{1}{2} \begin{bmatrix}
\cos \varphi - 1 & -\sin \varphi & 0 \\
\sin \varphi & \cos \varphi - 1 & 0 \\
0 & 0 & 0
\end{bmatrix} + \frac{1}{2} \begin{bmatrix}
\cos \varphi - 1 & \sin \varphi & 0 \\
-\sin \varphi & \cos \varphi - 1 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

i.e.

\[
e^{G-L} = \begin{bmatrix}
\cos \varphi - 1 & 0 & 0 \\
0 & \cos \varphi - 1 & 0 \\
0 & 0 & 0
\end{bmatrix}
\]

This means that important errors is introduced when using the linear strain measure when the rigid body rotation significant deviates from zero.

2.1. Euler-Cauchy strain tensor

In this section the a strain measure which is related to an evaluation of the strain at the current place will be derived. In the previous section the 'Green-Lagrange' strain tensor was discussed which relates the strain state to its initial undeformed state. The 'Euler-Cauchy' strain tensor to be derived here the current place is used as reference when calculating the strain. The derivation follows the same concepts as in the previous section.

Consider the relation between the current place \(x\) of a point in a body and the reference configuration \(X\) and the displacement \(w\), i.e. equation (2.43) repeated

\[
x(X) = X + w(x)
\]  
(2.74)

i.e.

\[
X = x(X) - w(x)
\]  
(2.75)

a differentiation expressed as

\[
dX = \frac{\partial X}{\partial x} dx
\]  
(2.76)

will be performed by inserting the expression for \(X\) in (2.75) into (2.76), as

\[
dX = \frac{\partial (x(X) - w(x))}{\partial x} dx = \frac{\partial x}{\partial x} dx - \frac{\partial w(x)}{\partial x} dx = \left( I - \frac{\partial w(x)}{\partial x} \right) dx
\]  
(2.77)

From (2.77) one obtain
\[
\frac{\partial \mathbf{x}}{\partial x} = \left( I - \frac{\partial \mathbf{w}}{\partial x} \right)
\]  
(2.78)

Recall that the inverse of the deformation gradient is

\[
\mathbf{F}^{-1} = \text{grad} \, (\mathbf{x})
\]
(2.79)
i.e.

\[
\mathbf{F}^{-1} = \begin{bmatrix}
\frac{\partial x_1}{\partial x_1} & \frac{\partial x_1}{\partial x_2} & \frac{\partial x_1}{\partial x_3} \\
\frac{\partial x_2}{\partial x_1} & \frac{\partial x_2}{\partial x_2} & \frac{\partial x_2}{\partial x_3} \\
\frac{\partial x_3}{\partial x_1} & \frac{\partial x_3}{\partial x_2} & \frac{\partial x_3}{\partial x_3}
\end{bmatrix}
\]  
(2.80)
The displacement gradient \( \mathbf{H}^{E-C} \) will be defined as

\[
\mathbf{H}^{E-C} = \text{grad} \, (\mathbf{w})
\]
(2.81)
i.e.

\[
\mathbf{H}^{E-C} = \begin{bmatrix}
\frac{\partial w_1}{\partial x_1} & \frac{\partial w_1}{\partial x_2} & \frac{\partial w_1}{\partial x_3} \\
\frac{\partial w_2}{\partial x_1} & \frac{\partial w_2}{\partial x_2} & \frac{\partial w_2}{\partial x_3} \\
\frac{\partial w_3}{\partial x_1} & \frac{\partial w_3}{\partial x_2} & \frac{\partial w_3}{\partial x_3}
\end{bmatrix}
\]  
(2.82)
where the difference between \( \mathbf{H}^{E-C} \) compared to \( \mathbf{H}^{G-L} \) should be clear.

Hence, equation (2.78) can be written as

\[
\mathbf{F}^{-1} = \left( I - \mathbf{H}^{E-C} \right)
\]
(2.83)
Consider, again, two points in an undeformed body, the vector located between these two points is the vector \( d\mathbf{x} \) having the length \( dS \) in the same manner \( dx \) and \( ds \) are considered in the deformed state between the same points. The relation between \( d\mathbf{x} \) and \( dS \) and also between \( dx \) and \( ds \), is

\[
|dx| = ds = \sqrt{dx \cdot dx}; \quad |d\mathbf{x}| = dS = \sqrt{d\mathbf{x} \cdot d\mathbf{x}}
\]
(2.84)
i.e.

\[
(ds)^2 = dx \cdot dx; \quad (dS)^2 = d\mathbf{x} \cdot d\mathbf{x}
\]
(2.85)
The 'Euler-Cauchy' strain \( \varepsilon_{E-C} \) is defined as

\[
\varepsilon_{E-C} = \frac{(ds)^2 - (dS)^2}{2(ds)^2} = \frac{dx \cdot dx - d\mathbf{x} \cdot d\mathbf{x}}{2(ds)^2}
\]
(2.86)
in the direction defined by \( dx/ds \). Using

\[
d\mathbf{x} = \mathbf{F}^{-1} dx = \left( I - \mathbf{H}^{E-C} \right) dx
\]
(2.87)
to rewrite (2.86) by replacing \( d\mathbf{x} \) by \( \mathbf{F}^{-1} dx \), as

\[
\varepsilon_{E-C} = \frac{(ds)^2 - (dS)^2}{2(ds)^2} = \frac{dx \cdot dx - \mathbf{F}^{-1} dx \cdot \mathbf{F}^{-1} dx}{2(ds)^2}
\]
(2.88)
This can be brought to the form
\[ \varepsilon_{E-C} = \frac{(ds)^2 - (dS)^2}{2(ds)^2} = \frac{dx}{ds} \cdot \left( \frac{1}{2} \left( \mathbf{I} - (\mathbf{F}^{-1})^T \mathbf{F}^{-1} \right) \frac{dx}{ds} \right) \] (2.89)
if the following two identities is used.
\[ \frac{1}{2} \frac{dx}{ds} \frac{dx}{ds} = \frac{1}{2} \frac{dx}{ds} \cdot \left( \mathbf{I} \frac{dx}{ds} \right) \] (2.90)
\[ \mathbf{F}^{-1} \frac{dx}{ds} \cdot \frac{1}{2} \mathbf{F}^{-1} \frac{dx}{ds} = \frac{dx}{ds} \cdot \left( \frac{1}{2} (\mathbf{F}^{-1})^T \mathbf{F}^{-1} \frac{dx}{ds} \right) \] (2.91)
In the same manner as the 'Green-Lagrange' strain tensor was introduced the 'Euler-Cauchy' strain tensor \( \mathbf{E}^{E-C} \) is defined as the terms in the brackets of (2.89), i.e.
\[ \mathbf{E}^{E-C} = \frac{1}{2} \left( \mathbf{I} - (\mathbf{F}^{-1})^T \mathbf{F}^{-1} \right) \] (2.92)
where the inverse to the deformation gradient is \( \mathbf{F}^{-1} = \left( \mathbf{I} + \mathbf{H}^{E-C} \right) \). The term \( (\mathbf{F}^{-1})^T \mathbf{F}^{-1} \) is often denoted \( \mathbf{B}^{-1} \) where \( \mathbf{B} \) is referred to as the left Cauchy-Green tensor, introduced by Cauchy in 1827.

Since the inverse to the deformation gradient is \( \mathbf{F}^{-1} = \left( \mathbf{I} + \mathbf{H}^{E-C} \right) \), the 'Euler-Cauchy' strain tensor \( \mathbf{E}^{E-C} \) can be formulated as
\[
\mathbf{E}^{E-C} = \frac{1}{2} \left( \mathbf{I} - (\mathbf{F}^{-1})^T \mathbf{F}^{-1} \right) = \frac{1}{2} \left( \mathbf{I} - (\mathbf{I} - \mathbf{H}^{E-C})^T (\mathbf{I} - \mathbf{H}^{E-C}) \right) \\
= \frac{1}{2} \left( \mathbf{I} - \left( \mathbf{I} - \mathbf{H}^{E-C} \right)^T \mathbf{I} + (\mathbf{H}^{E-C})^T (\mathbf{H}^{E-C}) \right) \\
= \frac{1}{2} \left( \mathbf{H}^{E-C} + (\mathbf{H}^{E-C})^T \right) - \frac{1}{2} \left( \mathbf{H}^{E-C} \right)^T (\mathbf{H}^{E-C}) \] (2.93)
i.e.
\[ \mathbf{E}^{E-C} = \frac{1}{2} \left( \mathbf{H}^{E-C} + (\mathbf{H}^{E-C})^T \right) - \frac{1}{2} \left( \mathbf{H}^{E-C} \right)^T (\mathbf{H}^{E-C}) \] (2.94)
where the displacement gradient \( \mathbf{H}^{E-C} \) is with respect to the current deformed place \( x \).

One possibility, is to use this type of strain measure together with updating of the material coordinates in every calculation step. It should be noted that calculations which involves non-linear strain measures, e.g. \( \mathbf{E}^{E-C} \) or \( \mathbf{E}^{E-F} \) must be solved numerically with equilibrium iterations in every computation step in order to search for equilibrium.

2.2. Strain rate

Often one is interested in developing equations in a so-called rate form, for example, the stress rate can be a (constitutive) function of the strain rate. These type of relations are often adopted in a step by step calculation in non-linear problems.

It will be shown later that some problems is related to the rate form of the strains. This problem steams from the fact that an observer recording the strain rates, for example between
two points in a body, will record different strain rate depending on which frame (or coordinate system) this observer happens to relate the measured strain rates to. This is in general an unacceptably effect. Physical properties which is independent of the (observers) coordinate system chosen is said to be frame-indifferent. In continuum mechanics one only use to relate physical properties to each other if the can be shown to behave frame-indifferent, which seems reasonable. Frame-indifference will be discussed in more detail later.

Furthermore, it is of interest to compare the choice of kinematic definitions and the constitutive relations introduced in solid mechanics and in fluid mechanics. Usually, the stress is assumed to be a function of the velocity gradient when dealing with fluid mechanical problems and when a stress state in a solid is studied the stresses is most often assumed to be a function of the strain or of the strain rate (or both). Here the kinematic relation between the strain rate and the velocity gradient will be shown for the ‘Green-Lagrange’ strain rate measure. Therefore the results of the discussed topic in this section may be used as a link between the kinematical definitions used in classical solid mechanic problems and in fluid mechanics.

Consider, again, the length $ds$ between two points in the undeformed body and the length $dS$ in the deformed body (between the same to points), i.e.

$$|dx| = ds = \sqrt{dx \cdot dx}; \quad |dX| = dS = \sqrt{dX \cdot dX} \quad \text{(2.95)}$$

That is,

$$(ds)^2 = dx \cdot dx; \quad (dS)^2 = dX \cdot dX \quad \text{(2.96)}$$

By differentiating $(ds)^2$, using a dot denoting the material time derivative, one obtain

$$\frac{d(ds)^2}{dt} = \dot{dx} \cdot dx + dx \cdot \dot{dx} = 2dx \cdot \dot{dx} \quad \text{(2.97)}$$

where it also should be observed that the time derivative of $dS$, i.e. the length in the undeformed reference configuration is zero, due to $dS$ being constant.

Further, the relation between the distance vector $dx$ between two points in the deformed state and in the undeformed reference state $dX$ is given from the deformation gradient $F$ as

$$dx = FdX \quad \text{(2.98)}$$

Differentiation gives

$$\dot{dx} = \dot{F}dX + FD\dot{X}; \quad \ddot{dX} = 0 \quad \text{(2.99)}$$

i.e.

$$\frac{\ddot{dx}}{dt} = \dot{dx} = \dot{F}dX \quad \text{(2.100)}$$

where it should be noted that $dX$ is constant.

The velocity gradient $L$ describes the relation between the distance vector $dx$ between two points in the deformed state and its corresponding rate of change of length, i.e. $\dot{dx}$

$$L_{dx} = \dot{dx} = \dot{dX}$$

It is concluded from (2.100) and (2.101) that

$$\dot{dx} = \dot{F}dX = L_{dx} \quad \text{(2.102)}$$
That is, \( \mathbf{L} = \hat{\mathbf{F}} \frac{d \mathbf{X}}{d \mathbf{x}} \), or \( \mathbf{L} = \hat{\mathbf{F}} \mathbf{F}^{-1} \), which has been shown earlier.

By replacing \( \frac{d \mathbf{x}}{d \mathbf{x}} \) in (2.97) by the expression given by (2.101), one obtain

\[
\left( \frac{d \mathbf{x}}{d \mathbf{x}} \right)^2 = 2 \mathbf{x} \cdot (\mathbf{L} \frac{d \mathbf{x}}{d \mathbf{x}})
\]

(2.103)

Recall that the velocity gradient \( \mathbf{L} \) can be decomposed into a symmetric part \( \mathbf{D} \) and by a skew-symmetric part \( \mathbf{W} \) as

\[
\mathbf{L} = \mathbf{D} + \mathbf{W}
\]

(2.104)

where

\[
\mathbf{D} = \frac{1}{2} (\mathbf{L} + \mathbf{L}^T); \quad \mathbf{W} = \frac{1}{2} (\mathbf{L} - \mathbf{L}^T)
\]

(2.105)

This fact that \( \mathbf{W} \) is skew symmetric i.e. \( \mathbf{W} = -\mathbf{W}^T \), means that all diagonal element is zero. Insertion of the expression (2.104) into (2.103), gives

\[
\frac{1}{2} \left( \frac{d \mathbf{x}}{d \mathbf{x}} \right)^2 = d\mathbf{x} \cdot (\mathbf{D} d\mathbf{x}) + d\mathbf{x} \cdot (\mathbf{W} d\mathbf{x})
\]

\[
= d\mathbf{x} \cdot \left( \left( \frac{1}{2} (\mathbf{L} + \mathbf{L}^T) \right) d\mathbf{x} \right) + d\mathbf{x} \cdot \left( \left( \frac{1}{2} (\mathbf{L} - \mathbf{L}^T) \right) d\mathbf{x} \right)
\]

(2.106)

where the definitions in (2.105) is used. It is observed that \( 2d\mathbf{x} \cdot \left( \left( \frac{1}{2} (\mathbf{L} - \mathbf{L}^T) \right) d\mathbf{x} \right) = 0 \), due to \( \mathbf{W} \) being skew-symmetric. The rate of change of the cubic length obtained is

\[
\frac{1}{2} \left( \frac{d \mathbf{x}}{d \mathbf{x}} \right)^2 = d\mathbf{x} \cdot (\mathbf{D} d\mathbf{x})
\]

(2.107)

Consider, the ‘Green-Lagrange’ strain measure \( \varepsilon_{G-L} \) in the direction defined by \( d\mathbf{X}/d\mathbf{S} \), i.e.

\[
\varepsilon_{G-L} = \frac{(d\mathbf{x})^2 - (d\mathbf{S})^2}{2 (d\mathbf{S})^2} = \frac{d\mathbf{X}}{d\mathbf{S}} \cdot \left( \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{I}) \right) \frac{d\mathbf{X}}{d\mathbf{S}}
\]

(2.108)

where the ‘Green-Lagrange’ strain tensor \( \mathbf{E}^{G-L} \) for arbitrary direction is

\[
\mathbf{E}^{G-L} = \frac{1}{2} (\mathbf{F}^T \mathbf{F} - \mathbf{I})
\]

(2.109)

Combining (2.108) and (2.109), yields

\[
\varepsilon_{G-L} = \frac{(d\mathbf{x})^2 - (d\mathbf{S})^2}{2 (d\mathbf{S})^2} = \frac{d\mathbf{X}}{d\mathbf{S}} \cdot \left( \mathbf{E}^{G-L} \frac{d\mathbf{X}}{d\mathbf{S}} \right)
\]

(2.110)

The ‘Green-Lagrange’ strain measure \( \varepsilon_{G-L} \) will now be differentiated with respect to time (material time derivative), as

\[
\dot{\varepsilon}_{G-L} = \frac{(d\mathbf{x})^2 - (d\mathbf{S})^2}{2 (d\mathbf{S})^2} = \frac{d\mathbf{X}}{d\mathbf{S}} \cdot \left( \dot{\mathbf{E}}^{G-L} \frac{d\mathbf{X}}{d\mathbf{S}} \right)
\]

(2.111)

Since \( d\mathbf{S} \) and \( d\mathbf{X} \) are independent of time, expression (2.111) reduces to

\[
\dot{\varepsilon}_{G-L} = \frac{1}{2} \left( \frac{d \mathbf{x}}{d \mathbf{x}} \right)^2 = d\mathbf{x} \cdot \left( \dot{\mathbf{E}}^{G-L} d\mathbf{x} \right)
\]

(2.112)
But, it was also shown in (2.106) that

\[ \frac{1}{2} (ds)^2 = dx \cdot (Ddx) \]  

(2.113)

Now using \( dx = FdX \) to replace \( dx \) in (2.106) to yield

\[ \frac{1}{2} (ds)^2 = (FdX) \cdot (D(FdX)) = dX \cdot (F^TDFdX) \]  

(2.114)

By combining (2.112) and (2.113) the relation between the symmetric part of the velocity gradient \( D \) and the rate of change of the ‘Green-Lagrange’ strain tensor \( \dot{E}^{G-L} \) is obtained, i.e.

\[ dX \cdot (F^TDFdX) = dX \cdot \left( \dot{E}^{G-L}dX \right) \]  

(2.115)

Since \( dX \) is arbitrary one conclude that

\[ \dot{E}^{G-L} = F^TDF \]  

(2.116)

where it should be noted that the dot denotes the material time derivative, i.e. this time derivative is ‘following the motion’ of the body exhibiting strains. The result in (2.116) are due to E. and F. Cosserat in 1896.

By using the right Cauchy-Green tensor, i.e.

\[ C = F^TF \]  

(2.117)

and noting that

\[ E^{G-L} = \frac{1}{2} (F^TF - I) = \frac{1}{2} (C - I) \]  

(2.118)

when it is clear that the following holds

\[ \dot{E}^{G-L} = \frac{1}{2} \dot{C} \]  

(2.119)

Recall, further, that the deformation gradient \( F \) and its transpose can be expressed with its corresponding displacement gradient \( H^{G-L} \), i.e.

\[ F = \left( I + H^{G-L} \right) ; \quad F^T = \left( I + (H^{G-L})^T \right) \]  

(2.120)

If the displacement gradient \( H^{G-L} \) is very small, the approximation for \( \dot{E}^{G-L} \) is

\[ \dot{E}^{G-L} \approx F^TDF \approx IDI = D; \quad \text{if} \quad \left| \frac{\partial u_i}{\partial X_j} \right| \ll 1 \]  

(2.121)

Observe that \( D \) is shown to be frame-indifferent, see previous sections, however, \( \dot{E}^{G-L} \) is in general not frame-indifferent. Methods to tackle this dilemma, valid when significant displacement gradients is observed within a body will not be discussed in this work.
3. Two phase, N-constituent, structure of balance law’s

In this section mass balance equations for constituents appearing in different phases will be studied at macro scale. The consequences of requiring the sum of the mass balance equations for the individual constituents to be equal to the mass balance for the phase will be derived. The balance equations for the phases should, further be equal to the balance equation for the whole mixture.

Mass balance for constituent j in phase a is the postulate

\[
\frac{\partial}{\partial t} \int_{\mathbb{R}} \varepsilon_\alpha \rho_\alpha^j \, dv = \int_{\partial \mathbb{R}} \varepsilon_\alpha \rho_\alpha^j \mathbf{v}_\alpha^j \cdot ds + \int_{\mathbb{R}} (\dot{\varepsilon}_\alpha^j + \dot{\varepsilon}_\alpha^j) \, dv \tag{3.1}
\]

where \( \varepsilon_\alpha \) is the volume concentration of the \( \alpha \) phase, \( \rho_\alpha^j \) is the mass density concentration of the \( j \)th constituent in phase \( \alpha \), \( \mathbf{v}_\alpha^j \) is the velocity of the \( j \)th constituent, the mass exchange of \( j \)th constituent between phase boundaries is denoted \( \dot{\varepsilon}_\alpha^j \) and the chemical reaction of the \( j \)th constituent within the phase is denoted \( \dot{\varepsilon}_\alpha^j \).

Using the divergence theorem on the first term on the right-hand side of (3.1) gives

\[
\int_{\partial \mathbb{R}} \varepsilon_\alpha \rho_\alpha^j \mathbf{v}_\alpha^j \cdot ds = \int_{\mathbb{R}} \text{div} (\varepsilon_\alpha \rho_\alpha^j \mathbf{v}_\alpha^j) \, dv \tag{3.2}
\]

Combining (3.1) and (3.2) yields the local form of the balance of mass of the \( j \)th constituent in phase \( \alpha \), i.e.

\[
\frac{\partial (\varepsilon_\alpha \rho_\alpha^j)}{\partial t} + \text{div} (\varepsilon_\alpha \rho_\alpha^j \mathbf{v}_\alpha^j) = \dot{\varepsilon}_\alpha^j + \dot{\varepsilon}_\alpha^j, \quad j = 1, \ldots, N, \quad \alpha = l, s \tag{3.3}
\]

The mass balance for the phase \( \alpha \) can in an identical manner be brought to the local form

\[
\frac{\partial (\varepsilon_\alpha \rho_\alpha)}{\partial t} + \text{div} (\varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha) = \dot{\varepsilon}_\alpha \tag{3.4}
\]

where \( \dot{\varepsilon}_\alpha \) will be defined as the net gain of mass between phases, i.e.

\[
\sum_{j=1}^{N} \dot{\varepsilon}_\alpha^j = \dot{\varepsilon}_\alpha \tag{3.5}
\]

where \( N \) number of constituents are considered. This means that the chemical reaction \( \dot{\varepsilon}_\alpha^j \) do not affect the mass exchanges between phases.

The equations (3.3) and (3.4) can also be written in terms of the material time derivative instead of the spatial derivatives. Consider the relation (2.27) between the two derivatives, i.e.

\[
\frac{D_\alpha (\varepsilon_\alpha \rho_\alpha)}{Dt} = \frac{\partial (\varepsilon_\alpha \rho_\alpha)}{\partial t} + \mathbf{v}_\alpha \cdot \text{grad} (\varepsilon_\alpha \rho_\alpha) \tag{3.6}
\]

where \( D_\alpha (\varepsilon_\alpha \rho_\alpha) / Dt \) is the derivative with respect to the motion of the phase \( \alpha \). Combining (3.4) and (3.6), gives

\[
\frac{D_\alpha (\varepsilon_\alpha \rho_\alpha)}{Dt} - \mathbf{v}_\alpha \cdot \text{grad} (\varepsilon_\alpha \rho_\alpha) + \text{div} (\varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha) = \dot{\varepsilon}_\alpha \tag{3.7}
\]
Using the identity
\[
\text{div} (\varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha) = \varepsilon_\alpha \rho_\alpha \text{div} (\mathbf{v}_\alpha) + [\text{grad} (\varepsilon_\alpha \rho_\alpha)] \mathbf{v}_\alpha
\] (3.8)
gives the alternative version of (3.4), i.e. by combining the identity (3.8) with (3.7) one obtain
\[
\frac{D_\alpha (\varepsilon_\alpha \rho_\alpha)}{Dt} + \varepsilon_\alpha \rho_\alpha \text{div} (\mathbf{v}_\alpha) = \dot{\varepsilon}_\alpha
\] (3.9)

The definition of the phase velocity \(\mathbf{v}_\alpha\) is
\[
\mathbf{v}_\alpha = \frac{1}{\rho_\alpha} \sum_{j=1}^{N} \rho_\alpha^j \mathbf{v}_\alpha^j
\] (3.10)

The phase density \(\rho_\alpha\) is in the same manner defined as
\[
\rho_\alpha = \sum_{j=1}^{N} \rho_\alpha^j
\] (3.11)

In order to study the structure of the mass balance principals a summation of the \(N\) number of constituent equations building up phase \(\alpha\) will be performed, i.e.
\[
\sum_{j=1}^{N} \left( \rho_\alpha^j \frac{\partial (\varepsilon_\alpha \rho_\alpha^j)}{\partial t} + \text{div} (\varepsilon_\alpha \rho_\alpha^j \mathbf{v}_\alpha^j) - \dot{\varepsilon}_\alpha^j - \dot{\varepsilon}_\alpha^j \right) = 0, \quad j = 1, \ldots, N
\] (3.12)

Due to (3.10) and (3.11) this equation can be written as
\[
\frac{\partial (\varepsilon_\alpha \rho_\alpha)}{\partial t} + \text{div} (\varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha) = \sum_{j=1}^{N} (\dot{\varepsilon}_\alpha^j + \ddot{\varepsilon}_\alpha^j), \quad j = 1, \ldots, N
\] (3.13)

That is, by comparing (3.12) and (3.13) it immediately follows that
\[
\sum_{j=1}^{N} (\dot{\varepsilon}_\alpha^j + \ddot{\varepsilon}_\alpha^j) = \dot{\varepsilon}_\alpha + \sum_{j=1}^{N} \ddot{\varepsilon}_\alpha = \dot{\varepsilon}_\alpha
\] (3.14)

if one requires that the sum of the constituent equations should be equal to the phase equation. It is also noted that
\[
\sum_{j=1}^{N} \ddot{\varepsilon}_\alpha^j = 0
\] (3.15)

The local mass balance for the whole mixture is the postulate
\[
\frac{\partial (\varepsilon \rho)}{\partial t} + \text{div} (\varepsilon \rho \mathbf{v}) = 0
\] (3.16)
or equally
\[
\frac{\partial (\rho)}{\partial t} + \text{div} (\rho \mathbf{v}) = 0
\] (3.17)
which gives the proper interpretation of the volume concentrations, i.e.

\[ \sum_{\alpha=1}^{R} \varepsilon_{\alpha} = \varepsilon = 1 \quad (3.18) \]

The definition of the velocity of the mixture is

\[ v = \frac{1}{\rho} \sum_{\alpha=1,s}^{R} \rho_{\alpha} \mathbf{v}_{\alpha} = \frac{1}{\rho} \sum_{\alpha=1,s}^{R} \sum_{j=1}^{N} \rho_{\alpha}^j \mathbf{v}_{\alpha}^j \quad (3.19) \]

where also (3.10) is in use. With (3.11) the definition of the mass density of the whole mixture becomes

\[ \rho = \sum_{\alpha=1,s}^{R} \rho_{\alpha} = \sum_{\alpha=1,s}^{R} \sum_{j=1}^{N} \rho_{\alpha}^j \quad (3.20) \]

Summation of the \( R \) number of phases is

\[ \sum_{\alpha=1}^{R} \left( \frac{\partial (\varepsilon_{\alpha} \rho_{\alpha})}{\partial t} + \text{div} (\varepsilon_{\alpha} \rho_{\alpha} \mathbf{v}_{\alpha}) - \dot{e}_{\alpha} \right) = 0, \quad \alpha = 1, \ldots, R \quad (3.21) \]

Using (3.19) and (3.20) gives

\[ \frac{\partial (\varepsilon \rho)}{\partial t} + \text{div} (\varepsilon \rho \mathbf{v}) - \sum_{\alpha=1,s}^{R} \dot{e}_{\alpha} = 0 \quad (3.22) \]

By comparing (3.11) with (3.17) gives the conditions

\[ \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \rho_{\alpha} = \varepsilon \rho = \rho \quad (3.23) \]

and

\[ \sum_{\alpha=1,s}^{R} \dot{e}_{\alpha} = 0 \quad (3.24) \]

which is the consequence of requiring the sum of the phase mass balance equations to be identical with the balance principal for the whole mixture.

In different applications it is more convenient to adopt the concentration of constituent \( j \) in phase \( \alpha \), denoted \( C_{\alpha}^j \), instead of the mass density concentration. The concentration \( C_{\alpha}^j \) is defined as

\[ C_{\alpha}^j = \frac{\rho_{\alpha}^j}{\rho_{\alpha}} \quad (3.25) \]

That is, the concentration \( C_{\alpha}^j \) is related to the mass density of the phase \( \alpha \). It immediately follows that

\[ \sum_{j=1}^{N} C_{\alpha}^j = \frac{1}{\rho_{\alpha}} \sum_{j=1}^{N} \rho_{\alpha}^j = 1 \quad (3.26) \]
where (3.11) is used.

The definition of the so-called diffusion velocity \( \mathbf{u}_j^d \) of the \( j \)th constituent in phase \( \alpha \) is

\[
\mathbf{u}_j^d = \mathbf{v}_\alpha^d - \mathbf{v}_\alpha
\]  

(3.27)

Combining (3.27) with the mass balance equation expressed in terms of mass density concentrations, i.e. (3.3) one obtain

\[
\frac{\partial (\rho_\alpha \varepsilon_\alpha)}{\partial t} + \text{div} \left( \varepsilon_\alpha \rho_\alpha^2 \mathbf{u}_j^d \right) + \text{div} \left( \varepsilon_\alpha \rho_\alpha^2 \mathbf{v}_\alpha \right) = \dot{\varepsilon}_\alpha^j + \ddot{\varepsilon}_\alpha^j, \quad j = 1, \ldots, N
\]  

(3.28)

Noting that by use of the definition (3.25) the first term on the left-hand side of (3.28) can be written as

\[
\frac{\partial (\rho_\alpha \varepsilon_\alpha)}{\partial t} = \frac{\partial (C_\alpha^j \rho_\alpha)}{\partial t} = C_\alpha^j \frac{\partial (\rho_\alpha \varepsilon_\alpha)}{\partial t} + \rho_\alpha \varepsilon_\alpha \frac{\partial (C_\alpha^j)}{\partial t}
\]  

(3.29)

where standard partial derivatives is used. Further the second term on the left-hand side of (3.28) can be written as

\[
\text{div} \left( \varepsilon_\alpha \rho_\alpha^2 \mathbf{v}_\alpha \right) = \text{div} \left( \varepsilon_\alpha C_\alpha^j \rho_\alpha \mathbf{v}_\alpha \right) = C_\alpha^j \text{div} \left( \varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha \right) + \varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha \cdot \text{grad} \left( C_\alpha^j \right)
\]  

(3.30)

Using (3.29) and (3.30) in (3.27) yields

\[
C_\alpha^j \left[ \frac{\partial (\rho_\alpha \varepsilon_\alpha)}{\partial t} + \text{div} \left( \varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha \right) \right] + \rho_\alpha \varepsilon_\alpha \frac{\partial (C_\alpha^j)}{\partial t} + \varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha \cdot \text{grad} \left( C_\alpha^j \right) = \text{div} \left( \varepsilon_\alpha \rho_\alpha^2 \mathbf{u}_j^d \right) + \dot{\varepsilon}_\alpha^j + \ddot{\varepsilon}_\alpha^j
\]  

(3.31)

From the balance of mass of the phase \( \alpha \), i.e. equation (3.4), it is concluded that

\[
C_\alpha^j \left[ \frac{\partial (\rho_\alpha \varepsilon_\alpha)}{\partial t} + \text{div} \left( \varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha \right) \right] = C_\alpha^j \dot{\varepsilon}_\alpha
\]  

(3.32)

That is, combining (3.31) and (3.32) gives the mass balance for the \( j \)th component in phase \( \alpha \) expressed in terms of the concentration \( C_\alpha^j \) instead of the mass density concentration \( \rho_\alpha^j \), one obtain

\[
\varepsilon_\alpha \rho_\alpha \frac{\partial (C_\alpha^j)}{\partial t} + \text{div} \left( \varepsilon_\alpha \rho_\alpha^2 \mathbf{u}_j^d \right) + \varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha \cdot \text{grad} \left( C_\alpha^j \right) = \dot{\varepsilon}_\alpha^j + \ddot{\varepsilon}_\alpha^j - C_\alpha^j \dot{\varepsilon}_\alpha
\]  

(3.33)

By noting that the material derivative \( \frac{D_\alpha}{Dt} \) is related to the spatial derivative \( \frac{\partial(\cdot)}{\partial t} \) through the velocity of the phase \( \alpha \) as: \( \frac{D_\alpha}{Dt} = \frac{\partial(\cdot)}{\partial t} + \left[ \text{grad} \left( \cdot \right) \right] \mathbf{v}_\alpha \), one can write the first term on the left-hand side of (3.33) as

\[
\varepsilon_\alpha \rho_\alpha \frac{D_\alpha}{Dt} (C_\alpha^j) = \varepsilon_\alpha \rho_\alpha \frac{\partial (C_\alpha^j)}{\partial t} + \left[ \text{grad} \left( C_\alpha^j \right) \right] \varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha
\]  

(3.34)

That is, the material derivative of the concentration \( C_\alpha^j \) can be expressed as

\[
\varepsilon_\alpha \rho_\alpha \frac{D_\alpha}{Dt} (C_\alpha^j) + \text{div} \left( \varepsilon_\alpha \rho_\alpha^2 \mathbf{u}_j^d \right) = \dot{\varepsilon}_\alpha^j + \ddot{\varepsilon}_\alpha^j - C_\alpha^j \dot{\varepsilon}_\alpha
\]  

(3.35)

which is an alternative version to (3.3) of the mass balance of the \( j \)th constituent in the \( \alpha \) phase.
Consider, finally, the derivation of the mass balance equation for the $j$th constituent in $\alpha$ phase using the material time derivative instead of the spatial derivative used in (3.3). The relation between the derivatives becomes

$$\frac{D_{\alpha} (\varepsilon_{\alpha} \rho_{\alpha}^j)}{Dt} = \frac{\partial (\varepsilon_{\alpha} \rho_{\alpha}^j)}{\partial t} + v_{\alpha}^j \cdot \text{grad} (\varepsilon_{\alpha} \rho_{\alpha}^j)$$  \hspace{1cm} (3.36)$$

where (2.27) is used. Hence, the balance equation (3.3) can be written as

$$\frac{D_{\alpha} (\varepsilon_{\alpha} \rho_{\alpha}^j)}{Dt} = v_{\alpha}^j \cdot \text{grad} (\varepsilon_{\alpha} \rho_{\alpha}^j) + \text{div} (\varepsilon_{\alpha} \rho_{\alpha}^j v_{\alpha}^j) = \delta_{\alpha}^j + \bar{\delta}_{\alpha}^j$$  \hspace{1cm} (3.37)$$

Noting that the following identity is valid

$$\text{div} (\varepsilon_{\alpha} \rho_{\alpha}^j v_{\alpha}^j) = \varepsilon_{\alpha} \rho_{\alpha}^j \text{div} (v_{\alpha}^j) + v_{\alpha}^j \cdot \text{grad} (\varepsilon_{\alpha} \rho_{\alpha}^j)$$  \hspace{1cm} (3.38)$$

Combining (3.36) and (3.37) gives

$$\frac{D_{\alpha} (\varepsilon_{\alpha} \rho_{\alpha}^j)}{Dt} + \varepsilon_{\alpha} \rho_{\alpha}^j \text{div} (v_{\alpha}^j) = \delta_{\alpha}^j + \bar{\delta}_{\alpha}^j$$  \hspace{1cm} (3.39)$$

The summation of (3.39) yields the already derived condition for the $\alpha$ phase, i.e. (3.14).

4. Balance of linear momentum

The momentum balance for the $j$th constituent in phase $\alpha$ is the postulate

$$\frac{\partial}{\partial t} \int_{\mathbb{R}} \varepsilon_{\alpha} \rho_{\alpha}^j v_{\alpha}^j \, dv = - \int_{\partial \mathbb{R}} \varepsilon_{\alpha} \rho_{\alpha}^j v_{\alpha}^j \cdot (v_{\alpha}^j - ds) + \int_{\partial \mathbb{R}} t_{\alpha}^j \, ds \hspace{1cm} (4.1)$$

where $t_{\alpha}^j$ is the stress tensor of $j$th constituent, $g_{\alpha}^j$ the body force, $\hat{T}_{\alpha}^j$ is the net gain of momentum for the $j$th component of the $\alpha$-phase due to interactions with the other phases. $\bar{\delta}_{\alpha}^j$ measures the gain of momentum for the $j$th component of the $\alpha$-phase through interactions with other species in the same phase.

Using the divergence theorems

$$\int_{\partial \mathbb{R}} \varepsilon_{\alpha} \rho_{\alpha}^j v_{\alpha}^j \cdot (v_{\alpha}^j - ds) = \int_{\mathbb{R}} \text{div} (\varepsilon_{\alpha} \rho_{\alpha}^j v_{\alpha}^j \otimes v_{\alpha}^j) \, dv$$  \hspace{1cm} (4.2)$$

and

$$\int_{\partial \mathbb{R}} t_{\alpha}^j \, ds = \int_{\mathbb{R}} \text{div} (\varepsilon_{\alpha} t_{\alpha}^j) \, dv$$  \hspace{1cm} (4.3)$$

one can write the local form (4.1) as
Partial differentiation of the left-hand side of (4.4) gives

\[
\frac{\partial (\epsilon_\alpha \rho_\alpha^j v_\alpha^j)}{\partial t} = -\text{div} (\epsilon_\alpha \rho_\alpha^j v_\alpha^j \otimes v_\alpha^j) + \text{div} (\epsilon_\alpha t_\alpha^j)
\]

\[
+ \epsilon_\alpha \rho_\alpha^j g_\alpha^j + \dot{T}_\alpha^j + \ddot{v}_\alpha^j + \dddot{v}_\alpha^j + \dddot{v}_\alpha^j
\]

where the relation between the material and spatial derivatives, i.e. \( \frac{D_\alpha^j}{Dt} = \frac{\partial }{\partial t} + [\text{grad }()] v_\alpha^j \), is used. Noting that the identity

\[
\text{div} (\epsilon_\alpha \rho_\alpha^j v_\alpha^j \otimes v_\alpha^j) = v_\alpha^j \text{div} (\epsilon_\alpha \rho_\alpha^j v_\alpha^j) + \epsilon_\alpha \rho_\alpha^j [\text{grad } (v_\alpha^j)] v_\alpha^j
\]

holds, the momentum balance (4.4) can by (4.5) and (4.6) be written as

\[
\epsilon_\alpha \rho_\alpha^j \frac{D_\alpha^j (v_\alpha^j)}{Dt} = -v_\alpha^j \left[ \frac{\partial (\epsilon_\alpha \rho_\alpha^j)}{\partial t} + \text{div} (\epsilon_\alpha \rho_\alpha^j v_\alpha^j) - \dddot{v}_\alpha^j - \dddot{v}_\alpha^j \right]
\]

\[
+ \text{div} (\epsilon_\alpha \dddot{v}_\alpha^j) + \epsilon_\alpha \rho_\alpha^j g_\alpha^j + \dot{T}_\alpha^j + \dddot{v}_\alpha^j
\]

where it is concluded that the terms in the bracket cancels due to the balance of mass for the \( j \)-th constituent in phase \( \alpha \), i.e. see equation (3.3). The momentum balance reduces to

\[
\epsilon_\alpha \rho_\alpha^j \frac{D_\alpha^j (v_\alpha^j)}{Dt} = \text{div} (\epsilon_\alpha \dddot{v}_\alpha^j) + \epsilon_\alpha \rho_\alpha^j g_\alpha^j + \dot{T}_\alpha^j + \dddot{v}_\alpha^j
\]

In the same manner one can show that the same condition for the phase \( \alpha \) becomes

\[
\epsilon_\alpha \rho_\alpha \frac{D_\alpha (v_\alpha)}{Dt} = \text{div} (\epsilon_\alpha \dddot{t}_\alpha) + \epsilon_\alpha \rho_\alpha g_\alpha + \dot{T}_\alpha + \dddot{v}_\alpha
\]

where \( \dot{T}_\alpha \) is the net gain of momentum for the \( \alpha \)-phase due to interaction with the other phases.

Summation of the constituent equation (4.8) i.e.

\[
\sum_{j=1}^{N} \epsilon_\alpha \rho_\alpha^j \frac{D_\alpha^j (v_\alpha^j)}{Dt} = \sum_{j=1}^{N} \text{div} (\epsilon_\alpha \dddot{t}_\alpha^j) + \sum_{j=1}^{N} \epsilon_\alpha \rho_\alpha^j g_\alpha^j + \sum_{j=1}^{N} \dot{T}_\alpha^j + \sum_{j=1}^{N} \dddot{v}_\alpha^j
\]

should result in the postulate for the phase \( \alpha \), i.e. equation (4.9). The restriction imposed by this fact will be examined. Consider first the definition of the so-called inner stress tensor

\[
t_\alpha = \sum_{j=1}^{N} t_\alpha^j
\]
The body force for the phase is, further, defined as

\[ g_{\alpha} = \frac{1}{\rho_{\alpha}} \sum_{j=1}^{N} \rho_{\alpha}^j \mathbf{g}_{\alpha}^j \]

(4.12)

From the above definitions the equation (4.10) can be written

\[ \sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha}^j \frac{D_a}{Dt} (\mathbf{v}_{\alpha}^j) = \text{div} (\varepsilon_{\alpha} \mathbf{t}_{\alpha}) + \varepsilon_{\alpha} \rho_{\alpha} g_{\alpha} + \sum_{j=1}^{N} \dot{\mathbf{T}}_{\alpha}^j + \sum_{j=1}^{N} \dot{\mathbf{v}}_{\alpha}^j \]

(4.13)

Consider the arbitrary property \( \Gamma_{\alpha} (x, t) \). Assume that the property for the constituents \( \Gamma_{\alpha}^j \) can be weighted as

\[ \Gamma_{\alpha} = \frac{1}{\rho_{\alpha}} \sum_{j=1}^{N} \rho_{\alpha}^j \Gamma_{\alpha}^j = \sum_{j=1}^{N} C_{\alpha}^j \Gamma_{\alpha}^j \]

(4.14)

The material time derivative of \( \Gamma_{\alpha} \) is by use of (4.14) written as

\[ \frac{D_a (\Gamma_{\alpha})}{Dt} = \sum_{j=1}^{N} \frac{D_a (C_{\alpha}^j \Gamma_{\alpha}^j)}{Dt} = \sum_{j=1}^{N} \left( C_{\alpha}^j \frac{D_a (\Gamma_{\alpha}^j)}{Dt} + \Gamma_{\alpha}^j \frac{D_a (C_{\alpha}^j)}{Dt} \right) \]

(4.15)

where also partial differentiation is performed. It has been shown earlier that the material time derivative of the arbitrary property \( \Gamma_{\alpha} \) following the motion of the phase \( \alpha \) and the property following the motion of the constituent \( j \) in the \( \alpha \) phase can be related through the diffusion velocity for the \( j \)th constituent as:

\[ \frac{D_a (\Gamma_{\alpha}^j)}{Dt} - \frac{D_a (\Gamma_{\alpha}^j)}{Dt} = (\text{grad} \ \Gamma_{\alpha}^j) \mathbf{u}_{\alpha}^j. \]

Further, it has been shown that the mass balance for the \( j \)th constituent in phase \( \alpha \) can be expressed as:

\[ \varepsilon_{\alpha} \rho_{\alpha} \frac{D_a (C_{\alpha}^j)}{Dt} + \text{div} (\varepsilon_{\alpha} \rho_{\alpha}^j \mathbf{u}_{\alpha}^j) = \dot{\varepsilon}_{\alpha}^j + \dot{\varepsilon}_{\alpha} - C_{\alpha}^j \dot{\varepsilon}_{\alpha} \]

where the concentration of \( j \)th constituent is defined as:

\[ C_{\alpha}^j = \rho_{\alpha}^j / \rho_{\alpha}. \]

From this it is concluded that (4.15) multiplied with \( \varepsilon_{\alpha} \rho_{\alpha} \) can be formulated as

\[ \varepsilon_{\alpha} \rho_{\alpha} \frac{D_a (\Gamma_{\alpha})}{Dt} = \varepsilon_{\alpha} \rho_{\alpha} \sum_{j=1}^{N} \left( C_{\alpha}^j \frac{D_a (\Gamma_{\alpha}^j)}{Dt} + \Gamma_{\alpha}^j \frac{D_a (C_{\alpha}^j)}{Dt} \right) \]

(4.16)

\[ + \sum_{j=1}^{N} \left( \varepsilon_{\alpha} \rho_{\alpha}^j \frac{D_a (\Gamma_{\alpha}^j)}{Dt} - \varepsilon_{\alpha} \rho_{\alpha}^j (\text{grad} \ \Gamma_{\alpha}^j) \mathbf{u}_{\alpha}^j \right) \]

\[ + \sum_{j=1}^{N} (-\Gamma_{\alpha}^j \text{div} (\varepsilon_{\alpha} \rho_{\alpha}^j \mathbf{u}_{\alpha}^j) + \Gamma_{\alpha}^j (\dot{\varepsilon}_{\alpha}^j + \dot{\varepsilon}_{\alpha} - C_{\alpha}^j \dot{\varepsilon}_{\alpha})) \]

Using the identity

\[ \text{div} (\varepsilon_{\alpha} \rho_{\alpha}^j \Gamma_{\alpha}^j \mathbf{u}_{\alpha}^j) = \varepsilon_{\alpha} \rho_{\alpha}^j (\text{grad} \ \Gamma_{\alpha}^j) \mathbf{u}_{\alpha}^j + \Gamma_{\alpha}^j \text{div} (\varepsilon_{\alpha} \rho_{\alpha}^j \mathbf{u}_{\alpha}^j) \]

(4.17)

equation (4.16) takes the form

\[ \varepsilon_{\alpha} \rho_{\alpha} \frac{D_a (\Gamma_{\alpha})}{Dt} = \sum_{j=1}^{N} \left( \varepsilon_{\alpha} \rho_{\alpha}^j \frac{D_a (\Gamma_{\alpha}^j)}{Dt} - \text{div} (\varepsilon_{\alpha} \rho_{\alpha}^j \Gamma_{\alpha}^j \mathbf{u}_{\alpha}^j) + \Gamma_{\alpha}^j (\dot{\varepsilon}_{\alpha}^j + \dot{\varepsilon}_{\alpha} - C_{\alpha}^j \dot{\varepsilon}_{\alpha}) \right) \]

(4.18)
By identifying the arbitrary properties \( \Gamma^j_\alpha \) and \( \Gamma_\alpha \) as: \( \Gamma^j_\alpha = \mathbf{v}^j_\alpha \) and \( \Gamma_\alpha = \mathbf{v}_\alpha \), equation (4.18) gives

\[
\varepsilon_\alpha \rho_\alpha \frac{D\mathbf{v}_\alpha}{Dt} = \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_\alpha \frac{D\mathbf{v}^j_\alpha}{Dt} \right) - \text{div} \left( \varepsilon_\alpha \rho_\alpha \mathbf{v}^j_\alpha \otimes \mathbf{u}^j_\alpha \right) + \mathbf{v}^j_\alpha \left( \dot{\varepsilon}^j_\alpha + \ddot{\varepsilon}^j_\alpha - C^j_\alpha \ddot{\varepsilon}_\alpha \right) \tag{4.19}\]

Noting that the velocity of the \( j \)th constituent \( \mathbf{v}^j_\alpha \) can be expressed by the diffusion velocity \( \mathbf{u}^j_\alpha \) and the velocity of the \( \alpha \) phase \( \mathbf{v}_\alpha \) as: \( \mathbf{v}^j_\alpha = \mathbf{u}^j_\alpha + \mathbf{v}_\alpha \), one can use equation (4.18) to establish that

\[
\varepsilon_\alpha \rho_\alpha \frac{D\mathbf{v}^j_\alpha}{Dt} = \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_\alpha \frac{D\mathbf{v}_\alpha}{Dt} \right) - \text{div} \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_\alpha \mathbf{u}^j_\alpha \otimes \mathbf{u}^j_\alpha \right) \tag{4.20}\]

\[
- \text{div} \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_\alpha \mathbf{u}^j_\alpha \otimes \mathbf{v}_\alpha \right) + \sum_{j=1}^{N} \left( \dot{\varepsilon}^j_\alpha + \ddot{\varepsilon}^j_\alpha - C^j_\alpha \ddot{\varepsilon}_\alpha \right) \mathbf{u}^j_\alpha \]

Using, further, the restriction for the diffusion velocities, i.e. \( \sum_{j=1}^{N} \rho_\alpha^j \mathbf{u}^j_\alpha = 0 \) and the relation \( \sum_{j=1}^{N} \dot{\varepsilon}^j_\alpha = \dot{\varepsilon}_\alpha \) together with \( \sum_{j=1}^{N} C^j_\alpha = 1 \) and \( \sum_{j=1}^{N} \left( \dot{\varepsilon}^j_\alpha + \ddot{\varepsilon}^j_\alpha - C^j_\alpha \ddot{\varepsilon}_\alpha \right) = 0 \), that is (4.20) takes the form

\[
- \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_\alpha \frac{D\mathbf{v}^j_\alpha}{Dt} \right) = -\varepsilon_\alpha \rho_\alpha \frac{D\mathbf{v}_\alpha}{Dt} - \text{div} \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_\alpha \mathbf{u}^j_\alpha \otimes \mathbf{u}^j_\alpha \right) \tag{4.21}\]

\[
+ \sum_{j=1}^{N} \left( \dot{\varepsilon}^j_\alpha + \ddot{\varepsilon}^j_\alpha - C^j_\alpha \ddot{\varepsilon}_\alpha \right) \mathbf{u}^j_\alpha \]

Combining (4.13) and (4.21) results in

\[
\varepsilon_\alpha \rho_\alpha \frac{D\mathbf{v}_\alpha}{Dt} = \text{div} \left( \varepsilon_\alpha \mathbf{t}_\alpha - \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_\alpha \mathbf{u}^j_\alpha \otimes \mathbf{u}^j_\alpha \right) \right) + \varepsilon_\alpha \rho_\alpha \mathbf{b}_\alpha + \sum_{j=1}^{N} \mathbf{T}^j_\alpha + \sum_{j=1}^{N} \mathbf{j}^j_\alpha \tag{4.22}\]

\[
+ \sum_{j=1}^{N} \dot{\varepsilon}^j_\alpha \mathbf{u}^j_\alpha + \sum_{j=1}^{N} \ddot{\varepsilon}^j_\alpha \mathbf{u}^j_\alpha - \frac{\dot{\varepsilon}_\alpha}{\rho_\alpha} \sum_{j=1}^{N} \rho^j_\alpha \mathbf{u}^j_\alpha \]

where also \( C^j_\alpha = \rho^j_\alpha / \rho_\alpha \) is used.

According to (4.22) the stress tensor for the \( \alpha \) phase, \( \mathbf{t}_\alpha \), takes the form

\[
\mathbf{t}_\alpha = \sum_{j=1}^{N} \mathbf{t}^j_\alpha - \sum_{j=1}^{N} \left( \rho^j_\alpha \mathbf{u}^j_\alpha \otimes \mathbf{u}^j_\alpha \right) = \mathbf{t}_\alpha - \sum_{j=1}^{N} \left( \rho^j_\alpha \mathbf{u}^j_\alpha \otimes \mathbf{u}^j_\alpha \right) \tag{4.23}\]

where the definition of the inner stress tensor (4.11) is used. The second order tensor \( \rho^j_\alpha \mathbf{u}^j_\alpha \otimes \mathbf{u}^j_\alpha \) is the so-called Reinholds stress tensor which is observed to be symmetric.
The local form of the moment equation for the $\alpha$ phase is the postulate

$$
\varepsilon_\alpha \rho_\alpha \frac{D\alpha}{Dt} = \text{div} (\varepsilon_\alpha t_\alpha) + \varepsilon_\alpha \rho_\alpha g_\alpha + \mathbf{T}_\alpha
$$

(4.24)

By comparing (4.22) with (4.24) the following choice will be adopted

$$
\sum_{j=1}^{N} \mathbf{T}_\alpha^j + \sum_{j=1}^{N} \varepsilon_\alpha^j \mathbf{u}_\alpha^j = \mathbf{T}_\alpha
$$

(4.25)

and

$$
\sum_{j=1}^{N} \varepsilon_\alpha^j + \sum_{j=1}^{N} \varepsilon_\alpha^j \mathbf{u}_\alpha^j = 0
$$

(4.26)

The relations (4.25) and (4.26) are the conditions that must be fulfilled in order to assure that the momentum balance equations for the constituents and the phase are compatible.

The local postulate for momentum balance of the whole mixture is

$$
\rho \frac{D (v)}{Dt} = \text{div} (\mathbf{t}) + \rho g
$$

(4.27)

The summation of the phase equations, i.e.

$$
\sum_{\alpha=1}^{R} \varepsilon_\alpha \rho_\alpha \frac{D\alpha}{Dt} = \sum_{\alpha=1}^{R} \text{div} (\varepsilon_\alpha t_\alpha) + \sum_{\alpha=1}^{R} \varepsilon_\alpha \rho_\alpha g_\alpha + \sum_{\alpha=1}^{R} \mathbf{T}_\alpha
$$

(4.28)

should result in the equation for the whole mixture. The condition for $\mathbf{T}_\alpha$, i.e. the net gain of momentum for the $\alpha$-phase due to interaction with the other phases, must be

$$
\sum_{\alpha=1}^{R} \mathbf{T}_\alpha + \sum_{\alpha=1}^{R} \varepsilon_\alpha \mathbf{u}_\alpha = 0
$$

(4.29)

in order to fulfill this condition. The relation (4.29) can be derived in the same manner as the relations for the constituents within phases, see equations (4.25) and (4.26).

5. Balance of angular momentum for the mixture

The angular momentum is usually used only to show that the stress tensor for a single constituent material must be symmetric. This derivation will be performed in this section.

The postulate for angular momentum is

$$
\frac{\partial}{\partial t} \int_{\Omega} (\mathbf{x} \times \mathbf{v}) \, dv = - \oint_{\partial \Omega} \mathbf{x} \times \rho \mathbf{v} \, ds + \oint_{\partial \Omega} \mathbf{x} \times \mathbf{T} \, ds + \int_{\Omega} \mathbf{x} \times \rho g \, dv
$$

(5.1)

where $\mathbf{x}$ is an arbitrary place. The divergence theorem gives

$$
\oint_{\partial \Omega} \mathbf{x} \times \mathbf{v} \, ds = \int_{\Omega} \text{div} (\rho (\mathbf{x} \times \mathbf{v}) \otimes \mathbf{v}) \, dv
$$

(5.2)
and
\[ \int_{\partial \mathbb{R}} x \times T \, ds = \int_{\mathbb{R}} \text{div} (x \times T) \, dv \] (5.3)
which means that the local form of the angular momentum is
\[ \frac{\partial (x \times v \rho)}{\partial t} = -\text{div} (\rho (x \times v) \otimes v) + \text{div} (x \times T) + x \times \rho g \] (5.4)

This equation will now be simplified further. Consider the identity
\[ \frac{\partial}{\partial t} (x \times v \rho) = (x \times v) \frac{\partial \rho}{\partial t} + \rho \frac{\partial (x \times v)}{\partial t} \]
\[ = (x \times v) \frac{\partial \rho}{\partial t} + \rho \frac{D(x \times v)}{Dt} - \rho [\text{grad} (x \times v)] v \] (5.5)

where
\[ \frac{D\Gamma}{Dt} (x, t) = \frac{\partial \Gamma}{\partial t} (x, t) + [\text{grad} \Gamma (x, t)] v (x, t) \] (5.6)

is used with \( \Gamma \equiv x \times v \), i.e.
\[ \frac{D(x \times v)}{Dt} = \frac{\partial (x \times v)}{\partial t} + [\text{grad} (x \times v)] v \] (5.7)

Equations (5.4) and (5.5) combine to yield
\[ (x \times v) \frac{\partial \rho}{\partial t} + \rho \frac{D(x \times v)}{Dt} = \rho [\text{grad} (x \times \dot{x})] \dot{x} - \text{div} (\rho (x \times \dot{x}) \otimes \dot{x}) + \text{div} (x \times T) + x \times \rho g \] (5.8)

The first term on the right hand side of (5.4) is rewritten with the identity
\[ \text{div} (\rho (x \times v) \otimes v) = (x \times v) \text{div} (\rho v) + \rho [\text{grad} (x \times v)] v \] (5.9)

Combining (5.8) and (5.9) to yield
\[ (x \times v) \frac{\partial \rho}{\partial t} + \rho \frac{D(x \times v)}{Dt} = \rho [\text{grad} (x \times v)] v - (x \times v) \text{div} (\rho v) \]
\[ -\rho [\text{grad} (x \times v)] v \]
\[ + \text{div} (x \times T) + x \times \rho g \] (5.10)

i.e.
\[ (x \times v) \frac{\partial \rho}{\partial t} + \rho \frac{D(x \times v)}{Dt} = - (x \times v) \text{div} (\rho v) + \text{div} (x \times T) + x \times \rho g \] (5.11)

This equation is further rearranged to yield
\[ (x \times v) \left( \frac{\partial \rho}{\partial t} + \text{div} (\rho v) \right) + \rho \frac{D(x \times v)}{Dt} = \text{div} (x \times T) + x \times \rho g \] (5.12)
The balance of mass for the whole mixture is

\[ \frac{\partial \rho}{\partial t} + \text{div} (\rho \mathbf{v}) = 0 \]  

(5.13)

And due to this the balance of angular momentum reduces to

\[ \rho \frac{D (\mathbf{x} \times \mathbf{v})}{Dt} = \text{div} (\mathbf{x} \times \mathbf{T}) + \mathbf{x} \times \rho \mathbf{g} \]  

(5.14)

This equation will be analyzed further to show that the stress tensor \( \mathbf{T} \) is symmetric.

Consider the identity

\[ \rho \frac{D (\mathbf{x} \times \mathbf{v})}{Dt} = \rho \mathbf{x} \times \frac{D (\mathbf{v})}{Dt} \]  

(5.15)

and also the identity

\[ \text{div} (\mathbf{x} \times \mathbf{T}) = \mathbf{x} \times \text{div} (\mathbf{T}) \]

(5.16)

\[ + (T_{32} - T_{23}) i_1 + (T_{13} - T_{31}) i_2 + (T_{21} - T_{12}) i_3 \]

The verification of this identity will be left to the reader. Combining (5.15) and (5.16) with (5.14) yields

\[ \rho \mathbf{x} \times \frac{D (\mathbf{v})}{Dt} = \mathbf{x} \times \text{div} (\mathbf{T}) \]

(5.17)

\[ + (T_{32} - T_{23}) i_1 + (T_{13} - T_{31}) i_2 + (T_{21} - T_{12}) i_3 + \mathbf{x} \times \rho \mathbf{b} \]

Rearrangement of this equation gives

\[ \mathbf{x} \times \left( \rho \frac{D (\mathbf{v})}{Dt} - \text{div} (\mathbf{T}) - \rho \mathbf{b} \right) = (T_{32} - T_{23}) i_1 \]

(5.18)

\[ + (T_{13} - T_{31}) i_2 + (T_{21} - T_{12}) i_3 \]

Due to the linear balance of momentum, i.e.

\[ \rho \frac{D (\mathbf{v})}{Dt} - \text{div} (\mathbf{T}) - \rho \mathbf{b} = 0 \]  

(5.19)

Equation (5.18) simplifies to

\[ 0 = (T_{32} - T_{23}) i_1 + (T_{13} - T_{31}) i_2 + (T_{21} - T_{12}) i_3 \]  

(5.20)

Using the rectangular base vectors \( i_1 = [1 \ 0 \ 0]^T, i_2 = [0 \ 1 \ 0]^T, i_3 = [0 \ 0 \ 1]^T \)

one obtain

\[ \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} T_{32} - T_{23} \\ T_{13} - T_{31} \\ T_{21} - T_{12} \end{bmatrix} \]  

(5.21)
from equation (5.20). That is, the stress tensor

\[
T = \begin{bmatrix}
T_{11} & T_{12} & T_{13} \\
T_{21} & T_{22} & T_{23} \\
T_{31} & T_{32} & T_{33}
\end{bmatrix}
\]  \hspace{1cm} (5.22)

is symmetric. This fact can be illustrated by writing \( T_{32} = T_{23}, \) \( T_{13} = T_{31} \) and \( T_{21} = T_{12} \) or equally

\[
T = T^T
\]  \hspace{1cm} (5.23)

Cauchy’s laws of motion is simply the linear momentum equation (??) together with the fact that the stress tensor is symmetric which was shown by using the postulate of angular momentum (5.14), compare previous sections. That is

\[
\rho \frac{D (\mathbf{v})}{Dt} = \text{div} \, T + \rho \mathbf{g}; \quad \text{and} \quad T = T^T
\]  \hspace{1cm} (5.24)

This, further implies that the stress tensors for the constituents indeed can be unsymmetrical.

6. Energy balance

The energy balance postulate for the \( j \)th constituent in the \( \alpha \)-phase is

\[
\frac{\partial}{\partial t} \int_R \varepsilon_{\alpha} \rho_{\alpha} \left( E_{\alpha}^j + \frac{1}{2} \left( v_{\alpha}^j \right)^2 \right) \, dv = - \oint_{\partial R} \varepsilon_{\alpha} \rho_{\alpha} \left( E_{\alpha}^j + \frac{1}{2} \left( v_{\alpha}^j \right)^2 \right) v_{\alpha}^j \cdot ds + \oint_{\partial R} \varepsilon_{\alpha} \left( \mathbf{t}_{\alpha}^j \cdot \mathbf{v}_{\alpha}^j - q_{\alpha}^j \right) \cdot ds \\
+ \int_R \left( \varepsilon_{\alpha} \rho_{\alpha} \left( \dot{r}_{\alpha}^j v_{\alpha}^j + \varepsilon_{\alpha} \rho_{\alpha} v_{\alpha}^j \cdot q_{\alpha}^j \right) \right) \, dv + \int_R \left( \mathbf{v}_{\alpha}^j \cdot \left( \dot{\mathbf{T}}_{\alpha} + \dot{\mathbf{v}}_{\alpha} \right) \right) \, dv \\
+ \int_R \left( \dot{q}_{\alpha}^j + \dot{\mathcal{E}}_{\alpha}^j \right) \, dv + \int_R \left( .\right) \left( E_{\alpha}^j + \frac{1}{2} \left( v_{\alpha}^j \right)^2 \right) \, dv + \int_R \left( v_{\alpha} \right)^2 \, dv + \int_R \left( v_{\alpha} \right)^2 \, dv
\]

where \( E_{\alpha}^j \) is the internal energy density for the \( j \)th constituent in phase \( \alpha \), \( q_{\alpha}^j \) is the heat flux vector for \( j \)th constituent, \( \dot{E}_{\alpha}^j \) is the heat supply to \( j \)th constituent from all other constituents in phase \( \alpha \), \( \dot{Q}_{\alpha}^j \) is the heat supply to \( j \)th constituent from other phases than \( \alpha \), \( r_{\alpha}^j \) is the external heat source and \( \left( v_{\alpha}^j \right)^2 = v_{\alpha}^j \cdot v_{\alpha}^j \).

Using the divergence theorem on the term on the left-hand side of (6.1), i.e.

\[
\oint_{\partial R} \varepsilon_{\alpha} \rho_{\alpha} \left( E_{\alpha}^j + \frac{1}{2} \left( v_{\alpha}^j \right)^2 \right) v_{\alpha}^j \cdot ds = \int_R \text{div} \left( \varepsilon_{\alpha} \rho_{\alpha} \left( E_{\alpha}^j + \frac{1}{2} \left( v_{\alpha}^j \right)^2 \right) \right) v_{\alpha}^j \, dv
\]  \hspace{1cm} (6.2)
and on the first term on the right-hand side of (6.1), as

$$\int_{\partial R} \varepsilon_\alpha (t^j_\alpha v^j_\alpha - q^j_\alpha) \cdot ds = \int_R \text{div} (\varepsilon_\alpha (t^j_\alpha v^j_\alpha - q^j_\alpha)) \, dv$$

(6.3)

the energy balance for the constituents (6.1) can by (6.2) and (6.3) be brought to the local form

$$\frac{\partial}{\partial t} \varepsilon_\alpha \rho^j_\alpha \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) = \text{div} \left( \varepsilon_\alpha \rho^j_\alpha \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) v^j_\alpha \right)$$

(6.4)

Partial differentiation of the term on left-hand side of (6.4) gives

$$\frac{\partial}{\partial t} \varepsilon_\alpha \rho^j_\alpha \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) = \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) \frac{\partial (\varepsilon_\alpha \rho^j_\alpha)}{\partial t}$$

(6.5)

Further, partial differentiation of first term on right-hand side of (6.4) gives

$$\text{div} \left( \varepsilon_\alpha \rho^j_\alpha \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) v^j_\alpha \right) = \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) \text{div} (\varepsilon_\alpha \rho^j_\alpha v^j_\alpha)$$

(6.6)

By using the relation between material derivative and spatial derivative, i.e.

$$\frac{D^j_\alpha}{Dt} (\Gamma^j_\alpha) = \frac{\partial (\Gamma^j_\alpha)}{\partial t} = (\text{grad} \, \Gamma^j_\alpha) \cdot v^j_\alpha$$

with \( \Gamma^j_\alpha = E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \) one obtain

$$D^j_\alpha \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) = \frac{\partial (E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2)}{\partial t} + \left[ \text{grad} \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) \right] \cdot v^j_\alpha$$

(6.7)

By multiplying (6.7) with \( \varepsilon_\alpha \rho^j_\alpha \) and eliminating the term \( \text{grad} \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) \cdot \varepsilon_\alpha \rho^j_\alpha v^j_\alpha \) in (6.6), yields

$$\text{div} \left( \varepsilon_\alpha \rho^j_\alpha \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) v^j_\alpha \right) = \left( E^i_\alpha + \frac{1}{2} (v^j_\alpha)^2 \right) \text{div} (\varepsilon_\alpha \rho^j_\alpha v^j_\alpha)$$

(6.8)
Consider next the mass balance for the $j$th component in phase $\alpha$, i.e., $\frac{\partial (\rho^i_{\alpha} \rho^j_{\alpha})}{\partial t} + \text{div} (\rho^i_{\alpha} \rho^j_{\alpha} \mathbf{v}_{\alpha}) = \dot{\varepsilon}^j_{\alpha} + \varepsilon^j_{\alpha}$, multiplied with $\left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right)$, i.e.

$$
\left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \frac{\partial (\rho^i_{\alpha} \rho^j_{\alpha})}{\partial t} = - \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \text{div} (\rho^i_{\alpha} \rho^j_{\alpha} \mathbf{v}_\alpha)
+ \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \dot{\varepsilon}^j_{\alpha}
+ \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \varepsilon^j_{\alpha}
$$

(6.9)

By eliminating the term $\left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \text{div}(\rho^i_{\alpha} \rho^j_{\alpha} \mathbf{v}_\alpha)$ in (6.8) and (6.9), one obtain

$$
0 = \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \frac{\partial (\rho^i_{\alpha} \rho^j_{\alpha})}{\partial t}
+ \rho^i_{\alpha} \rho^j_{\alpha} \frac{\partial (E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2)}{\partial t}
+ \text{div} \left( \rho^i_{\alpha} \rho^j_{\alpha} \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \mathbf{v}_\alpha \right)
- \rho^i_{\alpha} \frac{D^j_{\alpha}}{D t} \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right)
- \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \dot{\varepsilon}^j_{\alpha}
- \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \varepsilon^j_{\alpha}
$$

(6.10)

Combining (6.10) and (6.5) the result is

$$
\frac{\partial}{\partial t} \rho^j_{\alpha} \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) = - \text{div} \left( \rho^i_{\alpha} \rho^j_{\alpha} \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \mathbf{v}_\alpha \right)
+ \rho^i_{\alpha} \frac{D^j_{\alpha}}{D t} \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right)
+ \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \dot{\varepsilon}^j_{\alpha}
+ \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) \varepsilon^j_{\alpha}
$$

(6.11)

Combining, further, (6.11) with the energy balance equation (6.4) one obtain

$$
\frac{\varepsilon^j_{\alpha}}{\rho^i_{\alpha}} \frac{D^j_{\alpha}}{D t} \left( E^i_{\alpha} + \frac{1}{2} (v^j_{\alpha})^2 \right) = \text{div} \left( \rho^i_{\alpha} \left( t^j_{\alpha} \mathbf{v}_\alpha - q^j_{\alpha} \right) \right)
+ \varepsilon^j_{\alpha} \rho^j_{\alpha} \rho^i_{\alpha} \mathbf{v}_\alpha \cdot \mathbf{w}^j_{\alpha}
+ \mathbf{v}^i_{\alpha} \cdot \left( \mathbf{T}^j_{\alpha} + \mathbf{v}^j_{\alpha} \right) + \dot{Q}^j_{\alpha} + \dot{E}^j_{\alpha}
$$

(6.12)
Since the following identity

\[
\frac{D_j^i \left( \frac{1}{2} (v^i)^2 \right)}{Dt} = v^i \cdot \frac{D^i_j (v^i)}{Dt} \tag{6.13}
\]

and

\[
\text{div} (\varepsilon_i \text{grad} v^i) = v^i \cdot \text{div} (\varepsilon_i \text{grad} v^i) + \varepsilon_i \text{grad} v^i
\]

\[
= v^i \cdot \text{div} (\varepsilon_i \text{grad} v^i) + \text{tr} (\varepsilon_i T^j_q^i a^j)
\tag{6.14}
\]

holds, where \( d^j_i = \text{grad} v^i \) is the velocity gradient, the equation (6.12) can be brought to the form

\[
\varepsilon_i \rho_i \frac{D^i_j (E^i)}{Dt} = \text{tr} (\varepsilon_i T^j_q^i a^j) - \text{div} (\varepsilon_i q^i) + \text{tr} (\varepsilon_i \rho_i r^j a^j)
\tag{6.15}
\]

Due to the equation for the momentum balance: \( \varepsilon_i \rho_i \frac{D^i_j (E^i)}{Dt} = \text{div} (\varepsilon_i t^i a^j) + \varepsilon_i \rho_i r^j a^j + \hat{Q}^j a^j + \hat{E}^j_a \),

\[
\text{i.e. equation (4.8), the third term on the right-hand side of (6.15) cancels, i.e.}
\]

\[
\varepsilon_i \rho_i \frac{D^i_j (E^i)}{Dt} = \text{tr} (\varepsilon_i T^j_q^i a^j) - \text{div} (\varepsilon_i q^i) + \varepsilon_i \rho_i r^j a^j + \hat{Q}^j a^j + \hat{E}^j_a \tag{6.16}
\]

which is the local form of the energy balance (6.1).

Consider next the postulate for the phases building up the whole mixture, which can be written

\[
\frac{\partial}{\partial t} \int_{\mathbb{R}} \varepsilon_i \rho_i \left( E^i + \frac{1}{2} (v^i)^2 \right) dv = - \int_{\partial \mathbb{R}} \varepsilon_i \rho_i \left( E^i + \frac{1}{2} (v^i)^2 \right) v^i \cdot ds \tag{6.17}
\]

\[
+ \int_{\partial \mathbb{R}} \varepsilon_i (t^i a^i - q^i) \cdot ds
\]

\[
+ \int_{\mathbb{R}} \left( \varepsilon_i \rho_i r^i a^i + \sum_{j=1}^{N} \varepsilon_i \rho_i v^i \cdot g^i \right) dv
\]

\[
+ \int_{\mathbb{R}} (v^i \cdot \hat{T} a + \hat{Q} a) dv
\]

\[
+ \int_{\mathbb{R}} \varepsilon_i (E^i + \frac{1}{2} (v^i)^2) dv
\]

According to the same procedure used to obtain the local statement (4.24) for the constituents in phase \( \alpha \), one obtain the local version of the whole phase, as

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The following definitions for the external heat \( r_\alpha \) and the inner internal heat density \( E_{1\alpha} \) of the phase \( \alpha \) will be adopted,

\[
r_\alpha = \frac{1}{\rho_\alpha} \sum_{j=1}^{N} \rho_\alpha^j r_\alpha^j; \quad E_{1\alpha} = \frac{1}{\rho_\alpha} \sum_{j=1}^{N} \rho_\alpha^j E_{1\alpha}^j,
\]

where the internal heat density \( E_\alpha \) is related to the inner internal heat density \( E_{1\alpha} \) by the diffusion velocity, as

\[
E_\alpha = E_{1\alpha} + \frac{1}{2\rho_\alpha} \sum_{j=1}^{N} \rho_\alpha^j u_\alpha^j
\]

The inner heat flux vector \( \mathbf{q}_{1\alpha} \) is defined as

\[
\mathbf{q}_{1\alpha} = \sum_{j=1}^{N} \left( \mathbf{q}_\alpha^j - \mathbf{t}_\alpha^T u_\alpha^j + \rho_\alpha^j E_{1\alpha}^j u_\alpha^j \right)
\]

where the heat flux vector \( \mathbf{q}_\alpha \) is given by

\[
\mathbf{q}_\alpha = \mathbf{q}_{1\alpha} + \frac{1}{2} \sum_{j=1}^{N} \rho_\alpha^j u_\alpha^j^2 u_\alpha^j
\]

Another quantity \( k_\alpha \), which is related to the heat flux, will also be introduced:

\[
k_\alpha = \sum_{j=1}^{N} \left( \mathbf{q}_\alpha^j + \rho_\alpha^j E_{1\alpha}^j u_\alpha^j \right)
\]

\[
= \mathbf{q}_{1\alpha} + \sum_{j=1}^{N} \mathbf{t}_\alpha^T u_\alpha^j
\]

\[
= \mathbf{q}_\alpha - \sum_{j=1}^{N} \rho_\alpha^j \left( -\mathbf{t}_\alpha^T / \rho_\alpha^j + \frac{1}{2} u_\alpha^j^2 I \right) u_\alpha^j
\]

where the definitions (6.21) and (6.22) are used.

Consider the identities valid for the terms in (6.18), the left-hand side can be written as

\[
\varepsilon_\alpha \rho_\alpha \frac{D_\alpha \left( E_\alpha + \frac{1}{2} (v_\alpha)^2 \right)}{Dt} = \varepsilon_\alpha \rho_\alpha \frac{D_\alpha (E_\alpha)}{Dt} + \varepsilon_\alpha \rho_\alpha \frac{D_\alpha \left( \frac{1}{2} (v_\alpha \cdot v_\alpha) \right)}{Dt}
\]

(6.24)
Partial derivative of the last term in (6.24) makes it possible to re-write the expression to yield

\[ \varepsilon_\alpha \rho_\alpha \frac{D_\alpha \left( E_\alpha + \frac{1}{2} (v_\alpha)^2 \right)}{Dt} = \varepsilon_\alpha \rho_\alpha \frac{D_\alpha (E_\alpha)}{Dt} + \varepsilon_\alpha \rho_\alpha \cdot \frac{D_\alpha (v_\alpha)}{Dt} \]  

(6.25)

Using the definition of the diffusion velocity \( u^j_\alpha \), i.e. \( u^j_\alpha = v^j_\alpha - v_\alpha \), the third term on the right-hand side of (6.18) can be written

\[ \sum_{j=1}^{N} \varepsilon_\alpha \rho_\alpha^j v^j_\alpha \cdot g^j_\alpha = \sum_{j=1}^{N} \varepsilon_\alpha \rho_\alpha^j \left( u^j_\alpha + v_\alpha \right) \cdot g^j_\alpha \]  

= \varepsilon_\alpha \sum_{j=1}^{N} \left( \rho_\alpha^j g^j_\alpha \right) \cdot v_\alpha + \varepsilon_\alpha \sum_{j=1}^{N} \left( \rho_\alpha^j u^j_\alpha \right) \cdot g^j_\alpha \]  

(6.26)

Using the definition of the body force \( g_\alpha = \frac{1}{\rho_\alpha} \sum_{j=1}^{N} \rho_\alpha^j g^j_\alpha \), expression (6.26) becomes

\[ \sum_{j=1}^{N} \varepsilon_\alpha \rho_\alpha^j v^j_\alpha \cdot g^j_\alpha = \varepsilon_\alpha \rho_\alpha g_\alpha \cdot v_\alpha + \varepsilon_\alpha \sum_{j=1}^{N} \left( \rho_\alpha^j u^j_\alpha \right) \cdot g^j_\alpha \]  

(6.27)

The term \( \text{div}(\varepsilon_\alpha (t_\alpha v_\alpha)) \) in (6.18) can be written as

\[ \text{div}(\varepsilon_\alpha (t_\alpha v_\alpha)) = v_\alpha \cdot \text{div}(\varepsilon_\alpha t_\alpha) + \varepsilon_\alpha \text{tr}(t_\alpha d_\alpha) \]  

(6.28)

where partial differentiation is used and where \( d_\alpha = \text{grad}v_\alpha \).

Using the identities (6.27) and (6.28) in (6.18) one obtain

\[ \varepsilon_\alpha \rho_\alpha \frac{D_\alpha (E_\alpha)}{Dt} = v_\alpha \cdot \text{div}(\varepsilon_\alpha t_\alpha) + \varepsilon_\alpha \text{tr}(t_\alpha d_\alpha) - \text{div}(\varepsilon_\alpha q_\alpha) \]  

+ \varepsilon_\alpha \rho_\alpha^r \alpha + \varepsilon_\alpha \rho_\alpha g_\alpha \cdot v_\alpha + \varepsilon_\alpha \sum_{j=1}^{N} \left( \rho_\alpha^j u^j_\alpha \right) \cdot g^j_\alpha

+ v_\alpha \cdot (\dot{T}_\alpha + \dot{Q}_\alpha - \varepsilon_\alpha \rho_\alpha v_\alpha \cdot \frac{D_\alpha (v_\alpha)}{Dt}) \]  

(6.29)

By collecting terms including \( v_\alpha \), the expression (6.29) becomes

\[ \varepsilon_\alpha \rho_\alpha \frac{D_\alpha (E_\alpha)}{Dt} = \varepsilon_\alpha \text{tr}(t_\alpha d_\alpha) - \text{div}(\varepsilon_\alpha q_\alpha) \]  

+ \varepsilon_\alpha \sum_{j=1}^{N} \left( \rho_\alpha^j u^j_\alpha \right) \cdot g^j_\alpha + \dot{Q}_\alpha + \varepsilon_\alpha \rho_\alpha^r \alpha

- v_\alpha \cdot \left( \varepsilon_\alpha \rho_\alpha \frac{D_\alpha (v_\alpha)}{Dt} - \text{div}(\varepsilon_\alpha t_\alpha) - \varepsilon_\alpha \rho_\alpha g_\alpha - \dot{T}_\alpha \right) \]  

(6.30)
Noting that the momentum balance for the α-phase is: 
\[ \dot{t}_\alpha(\mathbf{u}_\alpha^{\alpha}), = \text{div}(\varepsilon_\alpha \mathbf{t}_\alpha) + \varepsilon_\alpha \rho_\alpha \mathbf{g}_\alpha + \dot{\mathbf{f}}_\alpha, \]
i.e. see equation (4.24), the local form of the energy balance for the phase α becomes

\[ \varepsilon_\alpha \rho_\alpha \frac{D_\alpha (E_\alpha)}{D_t} = \varepsilon_\alpha \text{tr} (\mathbf{t}_\alpha \mathbf{d}_\alpha) - \text{div} (\varepsilon_\alpha \mathbf{q}_\alpha) + \varepsilon_\alpha \sum_{j=1}^{N} (\rho_j^j \mathbf{u}_j^j) \cdot \mathbf{g}_\alpha + \dot{Q}_\alpha + \varepsilon_\alpha \rho_\alpha \mathbf{r}_\alpha \]

Next the condition of the heat supply term \( \dot{Q}_\alpha \) will be examined.

Consider equation (6.20) written as

\[ \rho_\alpha \frac{D_\alpha (E_\alpha)}{D_t} = \rho_\alpha \frac{D_\alpha (E_\alpha)}{D_t} + \frac{\rho_\alpha}{2} \sum_{j=1}^{N} D_\alpha \left( \frac{C_j^j \mathbf{u}_j^2}{2} \right) \]

where \( C_j^j \rho_\alpha = \rho_j^j \) is used. According to equation (4.18) one can establish that

\[ \varepsilon_\alpha \rho_\alpha \frac{D_\alpha (\Gamma_\alpha)}{D_t} = \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_\alpha \frac{\Gamma_j^j}{D_t} - \text{div} (\varepsilon_\alpha \rho_\alpha \Gamma_j^j \mathbf{u}_\alpha) + \frac{\Gamma_j^j}{D_t} (\hat{\mathbf{e}}_\alpha^j + \hat{\mathbf{c}}_\alpha^j - C_j^j \hat{\mathbf{e}}_\alpha) \right) \]

with \( \Gamma_j^j = \frac{1}{2} u_j^2 \) and observing that \( \Gamma_\alpha \) is the mass density weighted value of \( \Gamma_j^j \), i.e. \( \Gamma_\alpha = C_j^j \frac{1}{2} u_j^2 \) one obtain

\[ \varepsilon_\alpha \rho_\alpha \sum_{j=1}^{N} \frac{1}{2} C_j^j \frac{\mathbf{u}_\alpha^2}{D_t} = \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_\alpha \frac{\mathbf{u}_\alpha^2}{D_t} - \text{div} (\varepsilon_\alpha \rho_\alpha \Gamma_j^j \mathbf{u}_\alpha) + \frac{\Gamma_j^j}{D_t} (\hat{\mathbf{e}}_\alpha^j + \hat{\mathbf{c}}_\alpha^j - C_j^j \hat{\mathbf{e}}_\alpha) \right) \]

Noting also that

\[ \frac{D_j^j \mathbf{u}_\alpha^2}{D_t} = \frac{D_j^j \mathbf{u}_\alpha^2}{D_t} = 2 \mathbf{u}_\alpha \cdot \frac{D_j^j \mathbf{u}_\alpha}{D_t} \]

is valid, one can write (6.34), as

\[ \varepsilon_\alpha \rho_\alpha \sum_{j=1}^{N} \frac{1}{2} C_j^j \frac{\mathbf{u}_\alpha^2}{D_t} = \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_\alpha \frac{\mathbf{u}_\alpha^2}{D_t} - \text{div} (\varepsilon_\alpha \rho_\alpha \Gamma_j^j \mathbf{u}_\alpha) + \frac{\Gamma_j^j}{D_t} (\hat{\mathbf{e}}_\alpha^j + \hat{\mathbf{c}}_\alpha^j - C_j^j \hat{\mathbf{e}}_\alpha) \right) \]

The term \( \varepsilon_\alpha \rho_\alpha \mathbf{u}_\alpha \cdot \frac{D_j^j (\mathbf{u}_\alpha^j)}{D_t} \) in (6.36) can further be written, using \( \mathbf{u}_\alpha = \mathbf{v}_\alpha - \mathbf{v}_\alpha \), to obtain

\[ \sum_{j=1}^{N} \varepsilon_\alpha \rho_\alpha \mathbf{u}_\alpha \cdot \frac{D_j^j (\mathbf{v}_\alpha^j)}{D_t} = \sum_{j=1}^{N} \varepsilon_\alpha \rho_\alpha \mathbf{u}_\alpha \cdot \left( \frac{D_j^j (\mathbf{v}_\alpha^j)}{D_t} - \frac{D_j^j (\mathbf{v}_\alpha)}{D_t} \right) \]
Following the relation: \( \frac{D\phi_i(r_0)}{Dt} = D_\alpha(\Gamma_\alpha) = (\text{grad } \Gamma_\alpha) \mathbf{u}_\alpha^i, \) i.e. equation (2.29), with \( \frac{D\phi_i(r_0)}{Dt} = \frac{D\phi_i(x_\alpha)}{Dt}, \) the equation (6.37) becomes

\[
\sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha}^j \mathbf{u}^j_\alpha \cdot \frac{D\phi_i}{Dt} = \sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha}^j \mathbf{u}^j_\alpha \cdot \left( \frac{D\phi_i}{Dt} - \frac{D_\alpha(\mathbf{v}_\alpha)}{Dt} - (\text{grad } \mathbf{v}_\alpha) \mathbf{u}_\alpha^j \right)
\]

(6.38)

The term \( \sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha}^j \mathbf{u}^j_\alpha \cdot (d_\alpha \mathbf{u}^j_\alpha) \) can, further, be identified as

\[
\sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha}^j \mathbf{u}^j_\alpha \cdot (d_\alpha \mathbf{u}^j_\alpha) = \sum_{j=1}^{N} \varepsilon_{(\alpha)} \rho_{(\alpha)}^j \mathbf{v}^j_{(\alpha)} \cdot (d_{(\alpha)} \mathbf{u}_{(\alpha)}^m \mathbf{u}_{(\alpha)}^m)
\]

(6.39)

From equations (6.39), (6.38) and (6.36) it is concluded that

\[
\varepsilon_{\alpha} \rho_{\alpha} \sum_{j=1}^{N} \frac{1}{2} \frac{D_\alpha(C_{ij} \mathbf{u}^j_\alpha)}{Dt} = \sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha}^j \mathbf{u}^j_\alpha \cdot \left( \frac{D\phi_i}{Dt} - \frac{D_\alpha(\mathbf{v}_\alpha)}{Dt} - (\text{grad } \mathbf{v}_\alpha) \mathbf{u}_\alpha^j \right)
\]

(6.40)

Due to the condition \( \sum_{j=1}^{N} (\rho_{\alpha}^j \mathbf{u}^j_\alpha) = 0, \) i.e. equation (2.17), it is concluded that the second term on the right-hand cancels.
Consider next equation (6.31) written as

\[
\varepsilon_\alpha \rho_\alpha \frac{D_a (E_{1\alpha})}{Dt} + \frac{\varepsilon_\alpha \rho_\alpha}{2} \sum_{j=1}^{N} D_{\alpha} \left( C_{\alpha j}^2 u_{\alpha j}^2 \right) = \varepsilon_\alpha \text{tr} \left( t_{1\alpha} - \sum_{j=1}^{N} \left( \rho_{\alpha j} u_{\alpha j} \otimes u_{\alpha j} \right) \right) d_{\alpha} \quad (6.41)
\]

\[
- \text{div} \left( \varepsilon_\alpha \left( q_{1\alpha} + \frac{1}{2} \sum_{j=1}^{N} \rho_{\alpha j}^2 u_{\alpha j}^2 \right) \right)
\]

\[
+ \varepsilon_\alpha \sum_{j=1}^{N} (\rho_{\alpha j} u_{\alpha j}) \cdot s_{\alpha j} + \hat{Q}_{1\alpha} + \varepsilon_\alpha \rho_\alpha r_{\alpha}
\]

where the definitions (6.32), (4.23) and (6.22) is used. Combining (6.41) with (6.40), using the condition \( \sum_{j=1}^{N} (\rho_{\alpha j} u_{\alpha j}) = 0 \), yields

\[
\varepsilon_\alpha \rho_\alpha \frac{D_a (E_{1\alpha})}{Dt} = \varepsilon_\alpha \text{tr} \left( t_{1\alpha} d_{\alpha} \right) - \text{div} (\varepsilon_\alpha q_{1\alpha}) \quad (6.42)
\]

\[
+ \varepsilon_\alpha \rho_\alpha r_{\alpha} + \hat{Q}_{1\alpha}
\]

\[
- \frac{1}{2} \rho_\alpha \sum_{j=1}^{N} \left( \rho_{\alpha j}^2 u_{\alpha j}^2 s_{\alpha j} ight)
\]

\[
- \sum_{j=1}^{N} (\frac{1}{2} u_{\alpha j}^2 (s_{\alpha j}^2 + e_{\alpha j}^2 - C_{\alpha j}^j \hat{e}_{\alpha j}))
\]

Considering the term \( \text{tr}(t_{1\alpha} d_{\alpha}) \) which can be introduced by the following identities by using the relation: \( u_{\alpha}^j = v_{\alpha}^j - v_{\alpha} \), i.e.

\[
\text{tr} \sum_{j=1}^{N} (t_{\alpha j}^T d_{\alpha j}) = \text{tr} \sum_{j=1}^{N} (t_{\alpha j}^T \text{grad} v_{\alpha}) = \text{tr} \sum_{j=1}^{N} (t_{\alpha j}^T \text{grad} (u_{\alpha j} + v_{\alpha})) \quad (6.43)
\]

\[
= \text{tr} \sum_{j=1}^{N} (t_{\alpha j}^T \text{grad} u_{\alpha j}) + \text{tr} \sum_{j=1}^{N} (t_{\alpha j}^T d_{\alpha j})
\]

\[
= \text{tr} \sum_{j=1}^{N} (t_{\alpha j}^T \text{grad} u_{\alpha j}) + \text{tr} (t_{1\alpha} d_{\alpha})
\]

Further the following holds

\[
\text{tr} \sum_{j=1}^{N} (t_{\alpha j}^T \text{grad} u_{\alpha j}) = \text{div} \sum_{j=1}^{N} (t_{\alpha j}^T u_{\alpha j}) - \sum_{j=1}^{N} u_{\alpha j}^j \cdot \text{div} t_{\alpha j}^j \quad (6.44)
\]

That is, equation (6.43) can be written

\[
\text{tr} \sum_{j=1}^{N} (t_{\alpha j}^T d_{\alpha j}) = \text{div} \sum_{j=1}^{N} (t_{\alpha j}^T u_{\alpha j}) - \sum_{j=1}^{N} u_{\alpha j}^j \cdot \text{div} t_{\alpha j}^j + \text{tr} (t_{1\alpha} d_{\alpha}) \quad (6.45)
\]
The derived equations (6.42) and (6.45) combines to yield

\[ \frac{\varepsilon_{\alpha} \rho_{\alpha}}{D_{\alpha}} \frac{D (E_{1 \alpha})}{D t} = \varepsilon_{\alpha} \text{tr} \sum_{j=1}^{N} \left( \mathbf{T}_{\alpha}^{T} \mathbf{d}_{\alpha}^{j} \right) - \text{div} \sum_{j=1}^{N} \left( \mathbf{T}_{\alpha}^{T} \mathbf{u}_{\alpha}^{j} \right) \]

\[ + \varepsilon_{\alpha} \rho_{\alpha} v_{\alpha} + \dot{Q}_{\alpha} - \text{div} (\varepsilon_{\alpha} \mathbf{q}_{\alpha}) \]

\[ - \sum_{j=1}^{N} \mathbf{u}_{\alpha}^{j} \cdot \left( \varepsilon_{\alpha} \rho_{\alpha}^{j} \mathbf{d}_{\alpha}^{j} - \varepsilon_{\alpha} \rho_{\alpha}^{j} \mathbf{g}_{\alpha}^{j} + \varepsilon_{\alpha} \text{div} \mathbf{t}_{\alpha}^{j} + \varepsilon_{\alpha} \text{div} \mathbf{r}_{\alpha}^{j} \right) \]

\[ - \sum_{j=1}^{N} \left( \frac{1}{2} \mathbf{u}_{\alpha}^{j} \mathbf{u}_{\alpha}^{j} \right) \left( \varepsilon_{\alpha}^{j} + \dot{\varepsilon}_{\alpha}^{j} - C_{\alpha}^{j} \dot{\varepsilon}_{\alpha}^{j} \right) \]  

Using the momentum balance for the \( j \)th component, i.e. \( \varepsilon_{\alpha} \rho_{\alpha}^{j} \frac{D}{D t} \left( \mathbf{u}_{\alpha}^{j} \right) = \text{div} (\varepsilon_{\alpha} \mathbf{t}_{\alpha}^{j} + \varepsilon_{\alpha} \rho_{\alpha}^{j} \mathbf{g}_{\alpha}^{j} + \varepsilon_{\alpha} \text{div} \mathbf{t}_{\alpha}^{j} + \varepsilon_{\alpha} \text{div} \mathbf{r}_{\alpha}^{j} + \varepsilon_{\alpha} \mathbf{q}_{\alpha}) \), i.e. equation (4.8), and the definition of \( k_{\alpha} \) i.e. \( k_{\alpha} = q_{\alpha} + \sum_{j=1}^{N} \mathbf{u}_{\alpha}^{j} \mathbf{u}_{\alpha}^{j} \), see equation (6.23), one obtain

\[ \frac{\varepsilon_{\alpha} \rho_{\alpha}}{D_{\alpha}} \frac{D (E_{1 \alpha})}{D t} = \varepsilon_{\alpha} \text{tr} \sum_{j=1}^{N} \left( \mathbf{T}_{\alpha}^{T} \mathbf{d}_{\alpha}^{j} \right) - \text{div} (\varepsilon_{\alpha} k_{\alpha}) \]

\[ + \varepsilon_{\alpha} \rho_{\alpha} v_{\alpha} + \dot{Q}_{\alpha} \]

\[ - \sum_{j=1}^{N} \mathbf{u}_{\alpha}^{j} \cdot \left( \mathbf{t}_{\alpha}^{j} + \mathbf{r}_{\alpha}^{j} \right) \]

\[ - \sum_{j=1}^{N} \left( \frac{1}{2} \mathbf{u}_{\alpha}^{j} \mathbf{u}_{\alpha}^{j} \right) \left( \varepsilon_{\alpha}^{j} + \dot{\varepsilon}_{\alpha}^{j} - C_{\alpha}^{j} \dot{\varepsilon}_{\alpha}^{j} \right) \]

The balance principle for the constituents within the \( \alpha \)-phase must be consistent with the equation for the whole phase. Consider, therefore, the sum of the equations of (6.16), i.e.

\[ \varepsilon_{\alpha} \sum_{j=1}^{N} \rho_{\alpha}^{j} \frac{D (E_{1 \alpha}^{j})}{D t} = \sum_{j=1}^{N} \text{tr} (\varepsilon_{\alpha} \mathbf{t}_{\alpha}^{j} \mathbf{d}_{\alpha}^{j}) - \sum_{j=1}^{N} \text{div} (\varepsilon_{\alpha} \mathbf{q}_{\alpha}^{j}) \]

\[ + \varepsilon_{\alpha} \rho_{\alpha} v_{\alpha} + \sum_{j=1}^{N} \dot{Q}_{\alpha}^{j} + \sum_{j=1}^{N} \dot{E}_{\alpha}^{j} \]

The term \( \varepsilon_{\alpha} \sum_{j=1}^{N} \rho_{\alpha}^{j} \frac{D (E_{1 \alpha}^{j})}{D t} \) in (6.48) can be written as

\[ \varepsilon_{\alpha} \sum_{j=1}^{N} \rho_{\alpha}^{j} \frac{D (E_{1 \alpha}^{j})}{D t} = \varepsilon_{\alpha} \rho_{\alpha} \frac{D (E_{1 \alpha})}{D t} + \sum_{j=1}^{N} \text{div} (\varepsilon_{\alpha} \rho_{\alpha}^{j} E_{\alpha}^{j} \mathbf{u}_{\alpha}^{j}) \]

\[ + \dot{E}_{\alpha}^{j} \left( \varepsilon_{\alpha}^{j} + \dot{\varepsilon}_{\alpha}^{j} - C_{\alpha}^{j} \dot{\varepsilon}_{\alpha}^{j} \right) \]

Using the relation:

\[ \varepsilon_{\alpha} \rho_{\alpha} \frac{D (\Gamma_{\alpha})}{D t} = \sum_{j=1}^{N} \left( \varepsilon_{\alpha} \rho_{\alpha}^{j} \frac{D (\Gamma_{\alpha}^{j})}{D t} - \text{div} (\varepsilon_{\alpha} \rho_{\alpha}^{j} \Gamma_{\alpha}^{j} \mathbf{u}_{\alpha}^{j}) + \Gamma_{\alpha}^{j} \left( \varepsilon_{\alpha}^{j} + \dot{\varepsilon}_{\alpha}^{j} - C_{\alpha}^{j} \dot{\varepsilon}_{\alpha}^{j} \right) \right) \]
that is equation (4.18), with $\Gamma_\alpha = E_\alpha^2$.

Combining (6.48) and (6.49) results in the expression

$$
\varepsilon_\alpha \rho_\alpha \frac{D_\alpha (E_{1\alpha})}{Dt} = \sum_{j=1}^{N} \text{tr} (\varepsilon_\alpha t_{\alpha}^{ij} d_{\alpha}^{ij}) - \sum_{j=1}^{N} \text{div} (\varepsilon_\alpha q_{\alpha}^{i}) + \varepsilon_\alpha \rho_\alpha r_\alpha + \sum_{j=1}^{N} \hat{Q}_{\alpha}^{ij} + \sum_{j=1}^{N} \hat{E}_{\alpha}^{ij}
$$

$$
- \sum_{j=1}^{N} \text{div} (\varepsilon_\alpha \rho_\alpha E_{\alpha}^{ij} u_{\alpha}^{ij})
$$

$$
- E_{\alpha}^{ij} (\dot{e}_{\alpha}^{ij} + \ddot{e}_{\alpha}^{ij} - C_{\alpha}^{ij} \dot{e}_{\alpha})
$$

Using, further, equation (6.23) i.e. $k_\alpha = \sum_{j=1}^{N} (q_{\alpha}^{i} + \rho_\alpha E_{\alpha}^{ij} u_{\alpha}^{ij})$ in (6.50), one obtains

$$
\varepsilon_\alpha \rho_\alpha \frac{D_\alpha (E_{1\alpha})}{Dt} = \sum_{j=1}^{N} \text{tr} (\varepsilon_\alpha t_{\alpha}^{ij} d_{\alpha}^{ij}) - \sum_{j=1}^{N} \text{div} (\varepsilon_\alpha k_{\alpha}) + \varepsilon_\alpha \rho_\alpha r_\alpha + \sum_{j=1}^{N} \hat{Q}_{\alpha}^{ij} + \sum_{j=1}^{N} \hat{E}_{\alpha}^{ij}
$$

$$
- E_{\alpha}^{ij} (\dot{e}_{\alpha}^{ij} + \ddot{e}_{\alpha}^{ij} - C_{\alpha}^{ij} \dot{e}_{\alpha})
$$

A direct comparison between (6.51) and (6.47) gives the condition

$$
\sum_{j=1}^{N} (\hat{Q}_{\alpha}^{ij} + \hat{E}_{\alpha}^{ij} + u_{\alpha}^{i} \cdot (\hat{T}_{\alpha}^{ij} + \hat{v}_{\alpha}^{ij}) + (\dot{e}_{\alpha}^{ij} + \ddot{e}_{\alpha}^{ij} - C_{\alpha}^{ij} \dot{e}_{\alpha}) (\frac{1}{2} u_{\alpha}^{ij2} + E_{\alpha}^{ij})) = \hat{Q}_{\alpha}
$$

which is the proper expression that must be fulfilled in order to assure that the phase equations to be compatible with the equations of the constituents within the phase.

In the same manner one can establish that the following condition

$$
\sum_{\alpha=1}^{R} \left( \hat{Q}_{\alpha} + u_{\alpha} \cdot \hat{T}_{\alpha} + \dot{e}_{\alpha} \left( \frac{1}{2} u_{\alpha}^{2} + E_{\alpha} \right) \right) = 0
$$

should hold when comparing the phase equations with the whole mixture.

Combining (6.52) and (6.53) yields

$$
\sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \hat{Q}_{\alpha}^{ij} + \hat{E}_{\alpha}^{ij} + u_{\alpha}^{i} \cdot (\hat{T}_{\alpha}^{ij} + \hat{v}_{\alpha}^{ij}) + (\dot{e}_{\alpha}^{ij} + \ddot{e}_{\alpha}^{ij} - C_{\alpha}^{ij} \dot{e}_{\alpha}) (\frac{1}{2} u_{\alpha}^{ij2} + E_{\alpha}^{ij}) \right) = \sum_{\alpha} \hat{Q}_{\alpha}
$$

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We shall later need the expression for \( \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \dot{Q}_{\alpha}^{j} + \dot{E}_{\alpha}^{j} \right) \) which becomes

\[
\sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \dot{Q}_{\alpha}^{j} + \dot{E}_{\alpha}^{j} \right) = - \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \mathbf{u}_{\alpha}^{j} \cdot \left( \dot{\mathbf{T}}_{\alpha}^{j} + \dot{r}_{\alpha}^{j} \right) \tag{6.55}
\]

- \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \dot{e}_{\alpha}^{j} + \dot{r}_{\alpha}^{j} - C_{\alpha}^{j} \dot{e}_{\alpha} \right) \frac{1}{2} u_{\alpha}^{j2}
- \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \dot{e}_{\alpha}^{j} + \dot{r}_{\alpha}^{j} - C_{\alpha}^{j} \dot{e}_{\alpha} \right) \mathbf{E}_{\alpha}^{j}
- \sum_{\alpha=1}^{R} \mathbf{u}_{\alpha} \cdot \dot{\mathbf{T}}_{\alpha} - \sum_{\alpha=1}^{R} \dot{e}_{\alpha} \left( \frac{1}{2} u_{\alpha}^{2} + E_{\alpha} \right)

7. Second axiom of thermodynamics

A form of the second axiom of thermodynamics in which all constituents and phases has the same temperature will be considered. One postulate for the phase \( \alpha \) is

\[
\frac{\partial}{\partial t} \int_{\mathbb{R}} \varepsilon_{\alpha} \rho_{\alpha} \eta_{\alpha} \, dv \geq - \int_{\mathbb{R}} \varepsilon_{\alpha} \rho_{\alpha} \eta_{\alpha} \mathbf{v}_{\alpha} \cdot ds - \int_{\mathbb{R}} \sum_{j=1}^{N} \left( \frac{\varepsilon_{\alpha} \mathbf{h}_{\alpha}^{j}}{T} \right) \cdot ds \tag{7.1}
\]

\[
+ \int_{\mathbb{R}} \varepsilon_{\alpha} \sum_{j=1}^{N} \rho_{\alpha} \tau_{\alpha}^{j} \, dv
\]

where \( \eta_{\alpha} \) is the entropy density for phase \( \alpha \), \( \mathbf{h}_{\alpha}^{j} \) is the entropy flux vector for the \( j \)th constituent in \( \alpha \)-phase, not necessarily equal to the heat flux vector and \( T \) is the absolute temperature.

The entropy density for \( \alpha \)-phase \( \eta_{\alpha} \) is defined to be related to the entropy density of constituents in phase, as

\[
\eta_{\alpha} = \frac{1}{\rho_{\alpha}} \sum_{j=1}^{N} \rho_{\alpha} \dot{r}_{\alpha}^{j} = \sum_{j=1}^{N} C_{\alpha}^{j} \eta_{\alpha}^{j} \tag{7.2}
\]

Using the divergence theorem on the first term on the right-hand side of (7.1), i.e.

\[
\int_{\partial \mathbb{R}} \varepsilon_{\alpha} \rho_{\alpha} \eta_{\alpha} \mathbf{v}_{\alpha} \cdot ds = \int_{\mathbb{R}} \text{div} \left( \varepsilon_{\alpha} \rho_{\alpha} \eta_{\alpha} \mathbf{v}_{\alpha} \right) \, dv \tag{7.3}
\]

and on the second term on the right-hand side of (7.1), as

\[
\int_{\partial \mathbb{R}} \varepsilon_{\alpha} \sum_{j=1}^{N} \left( \frac{\mathbf{h}_{\alpha}^{j}}{T} \right) \cdot ds = \int_{\mathbb{R}} \text{div} \left( \varepsilon_{\alpha} \sum_{j=1}^{N} \left( \frac{\mathbf{h}_{\alpha}^{j}}{T} \right) \right) \, dv \tag{7.4}
\]

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the local form corresponding to equation (7.1), becomes

$$\frac{\partial (\varepsilon_\alpha \rho_\alpha \eta_\alpha)}{\partial t} \geq - \text{div} (\varepsilon_\alpha \rho_\alpha \eta_\alpha \mathbf{v}_\alpha) - \text{div} \left( \sum_{j=1}^{N} \left( \frac{\varepsilon_\alpha h_j^\alpha}{T} \right) \right) + \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j r_\alpha^j \tag{7.5}$$

Consider the identity

$$\text{div} (\varepsilon_\alpha \rho_\alpha \eta_\alpha \mathbf{v}_\alpha) = \eta_\alpha \text{div} (\varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha) + \varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha \cdot \text{grad} \eta_\alpha \tag{7.6}$$

and also the partial derivative

$$\frac{\partial (\varepsilon_\alpha \rho_\alpha \eta_\alpha)}{\partial t} = \varepsilon_\alpha \frac{\partial \eta_\alpha}{\partial t} + \eta_\alpha \frac{\partial \varepsilon_\alpha \rho_\alpha}{\partial t} \tag{7.7}$$

Combining (7.5), (7.6) and (7.7), one obtain

$$\eta_\alpha \left( \frac{\partial \varepsilon_\alpha \rho_\alpha}{\partial t} + \text{div} (\rho_\alpha \mathbf{v}_\alpha) - \varepsilon_\alpha \right) \geq - \varepsilon_\alpha \rho_\alpha \frac{\partial \eta_\alpha}{\partial t} - \varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha \cdot \text{grad} \eta_\alpha$$

$$- \text{div} \left( \sum_{j=1}^{N} \left( \frac{\varepsilon_\alpha h_j^\alpha}{T} \right) \right) + \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j r_\alpha^j - (\varepsilon_\alpha \eta_\alpha) \tag{7.8}$$

The balance of mass for the $\alpha$-phase is:

$$\frac{\partial (\varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha)}{\partial t} + \text{div} (\varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha) = \dot{\varepsilon}_\alpha, \text{ which means that } \tag{7.8}$$

Reduces to the form

$$\varepsilon_\alpha \rho_\alpha \frac{\partial \eta_\alpha}{\partial t} \geq - \varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha \cdot \text{grad} \eta_\alpha - \text{div} \left( \sum_{j=1}^{N} \left( \frac{\varepsilon_\alpha h_j^\alpha}{T} \right) \right) + \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j r_\alpha^j - (\varepsilon_\alpha \eta_\alpha) \tag{7.9}$$

Expressing the inequality (7.9) in terms of the material time derivative using the relation:

$$\frac{\partial \varepsilon_\alpha \rho_\alpha}{\partial t} = \mathbf{v} \cdot \text{grad} \Gamma_\alpha + \frac{\partial \varepsilon_\alpha \rho_\alpha}{\partial t}, \text{ with } \Gamma_\alpha = \eta_\alpha \tag{7.10}$$

is yielded. That is the corresponding version of (7.9) is

$$\varepsilon_\alpha \rho_\alpha \frac{D \eta_\alpha}{Dt} \geq - \text{div} \left( \varepsilon_\alpha \sum_{j=1}^{N} \left( \frac{h_j^\alpha}{T} \right) \right) + \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j r_\alpha^j - (\varepsilon_\alpha \eta_\alpha) \tag{7.11}$$

Another postulate for entropy for the phase $\alpha$, than equation (7.1), will be considered in order to examine the meaning of the property $h_j^\alpha$. This postulate is

$$\frac{\partial}{\partial t} \int_{\mathbb{R}} \varepsilon_\alpha \rho_\alpha \eta_\alpha d\nu \geq - \int_{\partial \Omega} \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j r_\alpha^j \mathbf{v}_\alpha \cdot d\mathbf{s} - \int_{\partial \Omega} \varepsilon_\alpha \sum_{j=1}^{N} \left( \frac{\varepsilon_\alpha h_j^\alpha}{T} \right) \cdot d\mathbf{s} \tag{7.12}$$

$$+ \int_{\mathbb{R}} \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j r_\alpha^j d\nu \tag{7.12}$$
Performing the divergence theorem on the surface integrals, gives

$$\int_{\partial R} \epsilon_\alpha \rho_\alpha^{i} \eta_\alpha^{i} \vec{v}_\alpha^{i} \cdot d\vec{s} = \int_{R} \text{div} \left( \epsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^{j} \eta_\alpha^{j} \vec{v}_\alpha^{j} \right) d\vec{v}$$

(7.13)

and

$$\int_{\partial R} \epsilon_\alpha \sum_{j=1}^{N} \left( \frac{q_\alpha^{j}}{T_\alpha} \right) \cdot d\vec{s} = \int_{R} \text{div} \left( \epsilon_\alpha \sum_{j=1}^{N} \left( \frac{q_\alpha^{j}}{T_\alpha} \right) \right) d\vec{v}$$

(7.14)

By using the definition $\vec{v}_\alpha^{i} = \vec{v}_\alpha + \vec{u}_\alpha^{i}$ and $\rho_\alpha \eta_\alpha = \sum_{j=1}^{N} \rho_\alpha^{j} \eta_\alpha^{j}$ the term on the right-hand side of (7.13) can be written as

$$\text{div} \left( \epsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^{j} \eta_\alpha^{j} \vec{v}_\alpha^{j} \right) = \text{div} (\epsilon_\alpha \rho_\alpha \eta_\alpha \vec{v}_\alpha) + \text{div} \left( \epsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^{j} \eta_\alpha^{j} \vec{u}_\alpha^{j} \right)$$

(7.15)

That is the expressions (7.13), (7.14) and (7.15) makes it possible to write (7.12) in its local form

$$\frac{\partial (\epsilon_\alpha \rho_\alpha \eta_\alpha)}{\partial t} \geq -\text{div} (\epsilon_\alpha \rho_\alpha \eta_\alpha \vec{v}_\alpha) - \text{div} \left( \epsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^{j} \eta_\alpha^{j} \vec{u}_\alpha^{j} \right)$$

(7.16)

$$-\text{div} \left( \epsilon_\alpha \sum_{j=1}^{N} \left( \frac{q_\alpha^{j}}{T_\alpha} \right) \right)$$

$$+ \epsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^{j} \eta_\alpha^{j} \vec{u}_\alpha^{j}$$

The partial differentiations

$$\text{div} (\epsilon_\alpha \rho_\alpha \eta_\alpha \vec{v}_\alpha) = \eta_\alpha \text{div} (\epsilon_\alpha \rho_\alpha \vec{v}_\alpha) + \epsilon_\alpha \rho_\alpha \vec{v}_\alpha \cdot \text{grad} \eta_\alpha$$

(7.17)

and

$$\frac{\partial (\epsilon_\alpha \rho_\alpha \eta_\alpha)}{\partial t} = \epsilon_\alpha \rho_\alpha \frac{\partial \eta_\alpha}{\partial t} + \eta_\alpha \frac{\partial \epsilon_\alpha \rho_\alpha}{\partial t}$$

(7.18)

will be used. Further, consider the relation between the material derivative and spatial derivatives of the entropy density, i.e.

$$\frac{D \eta_\alpha}{Dt} = \vec{v}_\alpha \cdot \text{grad} \eta_\alpha + \frac{\partial \eta_\alpha}{\partial t}$$

(7.19)

Combining (7.18) and (7.19), yields

$$\frac{\partial (\epsilon_\alpha \rho_\alpha \eta_\alpha)}{\partial t} = \epsilon_\alpha \rho_\alpha \frac{D \eta_\alpha}{Dt} - \epsilon_\alpha \rho_\alpha \vec{v}_\alpha \cdot \text{grad} \eta_\alpha + \eta_\alpha \frac{\partial \epsilon_\alpha \rho_\alpha}{\partial t}$$

(7.20)
The expressions (7.17) and (7.20) gives together with (7.16) the inequality

\[ \varepsilon_\alpha \rho_\alpha \frac{D_\alpha \eta_\alpha}{Dt} \geq -\eta_\alpha \left( \frac{\partial \varepsilon_\alpha \rho_\alpha}{\partial t} + \text{div} (\varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha) - \dot{\varepsilon}_\alpha \right) \]  
\[ + \text{div} \left( \varepsilon_\alpha \sum_{j=1}^{N} \rho_{\alpha j} \eta_{\alpha j} \mathbf{u}_{\alpha j} \right) - \text{div} \left( \varepsilon_\alpha \sum_{j=1}^{N} \left( \frac{\rho_{\alpha j}}{T} \right) \right) \]  
\[ + \varepsilon_\alpha \sum_{j=1}^{N} \rho_{\alpha j} \dot{r}_{\alpha j} - \left( (\dot{\varepsilon}_\alpha \eta_\alpha) \right) \]  

(7.21)

where term \( \dot{\varepsilon}_\alpha \eta_\alpha - \dot{\varepsilon}_\alpha \eta_\alpha = 0 \) has been added to the expression. This makes it possible to use the mass balance equation for the \( \alpha \)-phase, i.e. \[ \frac{\partial \varepsilon_\alpha \rho_\alpha}{\partial t} + \text{div} (\varepsilon_\alpha \rho_\alpha \mathbf{v}_\alpha) - \dot{\varepsilon}_\alpha = 0, \] in order to reduce equation (7.21) to

\[ \varepsilon_\alpha \rho_\alpha \frac{D_\alpha \eta_\alpha}{Dt} \geq -\text{div} \left( \varepsilon_\alpha \sum_{j=1}^{N} \left( \rho_{\alpha j} \eta_{\alpha j} \mathbf{u}_{\alpha j} + \frac{\rho_{\alpha j}}{T} \right) \right) \]  
\[ + \varepsilon_\alpha \sum_{j=1}^{N} \rho_{\alpha j} \dot{r}_{\alpha j} - \left( (\dot{\varepsilon}_\alpha \eta_\alpha) \right) \]  

(7.22)

A direct comparison between (7.11) and (7.22) immediately validates that the entropy flux \( \mathbf{h}_\alpha^j \) is related to the heat flux \( \mathbf{q}_\alpha^j \), as

\[ \mathbf{h}_\alpha^j = \mathbf{q}_\alpha^j + \rho_{\alpha j} \dot{r}_{\alpha j} T \mathbf{u}_{\alpha j} \]  

(7.23)

The entropy inequality, such as equation (7.22), is often combined with the energy equation in order to obtain a more physical intuitive and instructive version of the second axiom of thermodynamics. Consider first the inequality (7.22) re-written in terms of the material time derivative of \( \eta_\alpha \) following the motion of the \( j \)-th constituent instead of the phase motion. The relation between the time derivatives can be expressed as

\[ \varepsilon_\alpha \rho_\alpha \frac{D_\alpha (\eta_\alpha)}{Dt} = \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_{\alpha j} \frac{D_\alpha \eta_{\alpha j}}{Dt} - \text{div} (\varepsilon_\alpha \rho_{\alpha j} \eta_{\alpha j} \mathbf{u}_{\alpha j}) + \Gamma_{\alpha j} \left( \dot{\varepsilon}_\alpha + \varepsilon_{\alpha j} - C_{\alpha j} \varepsilon_\alpha \right) \right) \]  

(7.24)

which is equation (4.18) repeated. With \( \Gamma_{\alpha j} = \eta_{\alpha j} \) one obtain

\[ \varepsilon_\alpha \rho_\alpha \frac{D_\alpha (\eta_\alpha)}{Dt} = \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_{\alpha j} \frac{D_\alpha \eta_{\alpha j}}{Dt} - \text{div} (\varepsilon_\alpha \rho_{\alpha j} \eta_{\alpha j} \mathbf{u}_{\alpha j}) + \eta_{\alpha j} \left( \dot{\varepsilon}_\alpha + \varepsilon_{\alpha j} - C_{\alpha j} \varepsilon_\alpha \right) \right) \]  

(7.25)

Combining (7.22) and (7.25) yields the inequality

\[ 0 \leq \varepsilon_\alpha \sum_{j=1}^{N} \rho_{\alpha j} \frac{D_\alpha \eta_{\alpha j}}{Dt} + \text{div} \left( \varepsilon_\alpha \sum_{j=1}^{N} \frac{\mathbf{q}_{\alpha j}}{T} \right) \]  
\[ - \varepsilon_\alpha \sum_{j=1}^{N} \rho_{\alpha j} \dot{r}_{\alpha j} + \sum_{j=1}^{N} \eta_{\alpha j} \left( \dot{\varepsilon}_\alpha + \varepsilon_{\alpha j} - C_{\alpha j} \varepsilon_\alpha \right) + \left( (\dot{\varepsilon}_\alpha \eta_\alpha) \right) \]  

(7.26)
This expression is multiplied with the temperature \( T \), i.e.

\[
0 \leq T \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j \frac{D_j^i (\eta_\alpha^j)}{D_t} + T \text{div} \left( \varepsilon_\alpha \sum_{j=1}^{N} \frac{q_j^i}{T} \right) - T \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j r^j_\alpha + \sum_{j=1}^{N} T \eta_\alpha^j \left( \varepsilon_\alpha^i + \varepsilon_\alpha^j - C_\alpha^j \varepsilon_\alpha^j \right) + \left( \dot{\varepsilon}_\alpha T \eta_\alpha \right) \tag{7.27}
\]

The second term on the right-hand side of (7.27) can be re-written by using the partial derivative

\[
\text{div} \left( \varepsilon_\alpha \mathbf{q}_\alpha^j \right) = \text{div} \left( \varepsilon_\alpha \frac{T \mathbf{q}_\alpha^j}{T} \right) = T \text{div} \left( \varepsilon_\alpha \frac{\mathbf{q}_\alpha^j}{T} \right) + \varepsilon_\alpha \frac{q_j^i}{T} \cdot \text{grad} \left( T \right) \tag{7.28}
\]

The equations (7.27) and (7.28) gives

\[
0 \leq T \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j \frac{D_j^i (\eta_\alpha^j)}{D_t} + \text{div} \left( \varepsilon_\alpha \sum_{j=1}^{N} \frac{q_j^i}{T} \right) - \varepsilon_\alpha \sum_{j=1}^{N} \frac{q_j^i}{T} \cdot \text{grad} \left( T \right) \tag{7.29}
\]

The local energy balance equation for the \( j \)-th component in the \( \alpha \)-phase is

\[
\varepsilon_\alpha \rho_\alpha^j \frac{D_j^i (E_\alpha^i)}{D_t} = \text{tr} \left( \varepsilon_\alpha T^i_j \frac{q_j^i}{T} \right) - \text{div} \left( \varepsilon_\alpha \mathbf{q}_\alpha^j \right) + \varepsilon_\alpha \rho_\alpha^j r^j_\alpha + \dot{Q}_\alpha^j + \dot{E}_\alpha^j \tag{7.30}
\]

which is (6.16) repeated. Summation of the energy balance equations for all \( N \) constituents building up the \( \alpha \)-phase is expressed as

\[
\frac{\varepsilon_\alpha}{T} \sum_{j=1}^{N} \rho_\alpha^j r^j_\alpha = -\frac{1}{T} \text{tr} \left( \varepsilon_\alpha \sum_{j=1}^{N} T^i_j \frac{q_j^i}{T} \right) + \frac{1}{T} \text{div} \left( \varepsilon_\alpha \sum_{j=1}^{N} \frac{q_j^i}{T} \right) - \sum_{j=1}^{N} \frac{1}{T} \left( \dot{Q}_\alpha^j + \dot{E}_\alpha^j \right) + \frac{\varepsilon_\alpha}{T} \sum_{j=1}^{N} \rho_\alpha^j \frac{D_j^i (E_\alpha^i)}{D_t} \tag{7.31}
\]

in which the whole equation has been divided by the temperature \( T \). The inequality (7.29) divided by the temperature \( T \) is

\[
0 \leq \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j \frac{D_j^i (\eta_\alpha^j)}{D_t} + \frac{1}{T} \text{div} \left( \varepsilon_\alpha \sum_{j=1}^{N} \frac{q_j^i}{T} \right) - \varepsilon_\alpha \sum_{j=1}^{N} \frac{q_j^i}{T^2} \cdot \text{grad} \left( T \right) \tag{7.32}
\]

\[
-\varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j r^j_\alpha + \sum_{j=1}^{N} T \eta_\alpha^j \left( \varepsilon_\alpha^i + \varepsilon_\alpha^j - C_\alpha^j \varepsilon_\alpha^j \right) + \left( \dot{\varepsilon}_\alpha T \eta_\alpha \right)
\]
Combining the expressions (7.31) and (7.32) yields an alternative version of the inequality (7.22), i.e.,

\[
\varepsilon_{\alpha} \sum_{j=1}^{N} \rho_{\alpha} \frac{D^{j}_{\alpha} (\eta^{j}_{\alpha})}{D t} - \frac{1}{T} \sum_{j=1}^{N} \rho_{\alpha} \frac{D^{j}_{\alpha} (E^{j}_{\alpha})}{D t} \geq \varepsilon_{\alpha} q^{j}_{\alpha} \cdot \text{grad} (T) \tag{7.33}
\]

\[
-\frac{1}{T} \text{tr} \left( \varepsilon_{\alpha} \sum_{j=1}^{N} T^{j}_{\alpha} d^{j}_{\alpha} \right)
\]
\[
-\frac{1}{T} \sum_{j=1}^{N} \left( \dot{Q}^{j}_{\alpha} + \dot{E}^{j}_{\alpha} \right)
\]
\[
-\sum_{j=1}^{N} T_{\eta^{j}_{\alpha}} (\dot{\varepsilon}^{j}_{\alpha} + \dot{\varepsilon}^{j}_{\alpha} - C^{j}_{\alpha} \dot{\varepsilon}^{j}_{\alpha}) - \left( (\varepsilon_{\alpha} T_{\eta^{j}_{\alpha}}) \right)
\]

Summing the equation (7.33) over all phases building up the whole mixture gives

\[
\sum_{\alpha=1}^{R} \sum_{\alpha=1}^{N} \varepsilon_{\alpha} \rho_{\alpha} \frac{D^{j}_{\alpha} (\eta^{j}_{\alpha})}{D t} - \frac{1}{T} \sum_{\alpha=1}^{R} \sum_{\alpha=1}^{N} \rho_{\alpha} \frac{D^{j}_{\alpha} (E^{j}_{\alpha})}{D t} \geq \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \sum_{j=1}^{N} q^{j}_{\alpha} \cdot \text{grad} (T) \tag{7.34}
\]

\[
-\frac{1}{T} \text{tr} \left( \sum_{\alpha=1}^{R} \sum_{\alpha=1}^{N} T^{j}_{\alpha} d^{j}_{\alpha} \right)
\]
\[
-\sum_{\alpha=1}^{R} \sum_{j=1}^{N} \frac{1}{T} \left( \dot{Q}^{j}_{\alpha} + \dot{E}^{j}_{\alpha} \right)
\]
\[
-\sum_{j=1}^{N} T_{\eta^{j}_{\alpha}} (\dot{\varepsilon}^{j}_{\alpha} + \dot{\varepsilon}^{j}_{\alpha} - C^{j}_{\alpha} \dot{\varepsilon}^{j}_{\alpha}) - \left( (\sum_{\alpha=1}^{R} \varepsilon_{\alpha} T_{\eta^{j}_{\alpha}}) \right)
\]

The expression for \( \sum_{\alpha=1}^{R} \sum_{j=1}^{N} (\dot{Q}^{j}_{\alpha} + \dot{E}^{j}_{\alpha}) \) in (6.55), i.e.,

\[
\sum_{\alpha=1}^{R} \sum_{j=1}^{N} (\dot{Q}^{j}_{\alpha} + \dot{E}^{j}_{\alpha}) = -\sum_{\alpha=1}^{R} \sum_{\alpha=1}^{N} u^{j}_{\alpha} \cdot \left( \dot{T}^{j}_{\alpha} + \gamma^{j}_{\alpha} \right) \tag{7.35}
\]

\[
-\sum_{\alpha=1}^{R} \sum_{j=1}^{N} (\dot{\varepsilon}^{j}_{\alpha} + \dot{\varepsilon}^{j}_{\alpha} - C^{j}_{\alpha} \dot{\varepsilon}^{j}_{\alpha}) \frac{1}{2} u_{\alpha}^{j^{2}}
\]
\[
-\sum_{\alpha=1}^{R} \sum_{j=1}^{N} (\dot{\varepsilon}^{j}_{\alpha} + \dot{\varepsilon}^{j}_{\alpha} - C^{j}_{\alpha} \dot{\varepsilon}^{j}_{\alpha}) E^{j}_{\alpha}
\]
\[
-\sum_{\alpha=1}^{R} u_{\alpha} \cdot \dot{T}_{\alpha} - \sum_{\alpha=1}^{R} \dot{\varepsilon}_{\alpha} \left( \frac{1}{2} u_{\alpha}^{2} + E_{\alpha} \right)
\]
can be combined with the inequality (7.34), yielding

\[ \sum_{\alpha=1}^{R} \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j T \frac{\partial \alpha^j}{\partial T} - \sum_{\alpha=1}^{R} \varepsilon_\alpha \sum_{j=1}^{N} \rho_\alpha^j \frac{D^i_\alpha (E^i_\alpha)}{D^i} \geq 0 \]  

(7.36)

\[ \sum_{\alpha=1}^{R} \varepsilon_\alpha \sum_{j=1}^{N} \frac{D^j_\alpha T}{T} \cdot \text{grad}(T) \]

\[ - \text{tr} \left( \sum_{\alpha=1}^{R} \varepsilon_\alpha \sum_{j=1}^{N} t^j T^j_\alpha \right) \]

\[ + \sum_{\alpha=1}^{R} \sum_{j=1}^{N} (\hat{\varepsilon}_\alpha^j + \hat{\varepsilon}_\alpha^j - C^j_\alpha \hat{\varepsilon}_\alpha^j) \frac{1}{2} u^2_\alpha \]

\[ + \sum_{\alpha=1}^{R} \varepsilon_\alpha \frac{1}{2} u^2_\alpha + \sum_{\alpha=1}^{R} \varepsilon_\alpha E_\alpha - \sum_{\alpha=1}^{R} \varepsilon_\alpha T \eta_\alpha \]

\[ + \sum_{\alpha=1}^{R} \sum_{j=1}^{N} u^i_\alpha \cdot (\hat{T}_\alpha^j + \hat{\varepsilon}_\alpha^j) \]

\[ + \sum_{\alpha=1}^{R} \sum_{j=1}^{N} (\hat{\varepsilon}_\alpha^j + \hat{\varepsilon}_\alpha^j - C^j_\alpha \hat{\varepsilon}_\alpha^j) E^i_\alpha \]

\[ - \sum_{\alpha=1}^{R} T \eta_\alpha \left( \hat{\varepsilon}_\alpha^j + \hat{\varepsilon}_\alpha^j - C^j_\alpha \hat{\varepsilon}_\alpha^j \right) \]

It is most often convenient to express the entropy inequality in other variables than the internal energy \( E_\alpha^i \). Here the Helmholtz free energy will be adopted \( A_\alpha^i \). The Helmholtz free energy is related to the internal energy, temperature and entropy with the following definition

\[ A_\alpha^i = E_\alpha^i - T \eta_\alpha^j \]  

(7.37)

Partial differentiation of the Helmholtz free energy gives

\[ \frac{D^i_\alpha (A_\alpha^i)}{D^i} = \frac{D^i_\alpha (E_\alpha^i)}{D^i} - T \frac{D^i_\alpha (\eta_\alpha^j)}{D^i} - \eta_\alpha^j \frac{D^i_\alpha (T)}{D^i} \]  

(7.38)

where \( A_\alpha^i \) is related to \( A_\alpha \) with the definition

\[ A_\alpha = \frac{1}{\rho_\alpha} \sum_{j=1}^{N} \rho_\alpha^j A_\alpha^i = \sum_{j=1}^{N} C^j_\alpha A_\alpha^i \]  

(7.39)

The term of interest in the inequality (7.36) therefore can be written

\[ T \frac{D^i_\alpha (\eta_\alpha^j)}{D^i} - \frac{D^i_\alpha (E_\alpha^i)}{D^i} = - \frac{D^i_\alpha (A_\alpha^i)}{D^i} - \eta_\alpha^j \frac{D^i_\alpha (T)}{D^i} \]  

(7.40)
Using the definition (7.36) and (7.40), the inequality (7.36) can be expressed as

\[
- \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \sum_{j=1}^{N} \left( \rho_{\alpha}^{j} \left( \frac{D_{\alpha}^{j} (A_{\alpha}^{i})}{Dt} + \eta_{\alpha}^{j} \frac{D_{\alpha}^{j} (T)}{Dt} \right) \right) \geq 0
\]  
(7.41)

\[
\sum_{\alpha=1}^{R} \varepsilon_{\alpha} \sum_{j=1}^{N} \frac{q_{\alpha}^{j}}{T} \cdot \text{grad} (T)
\]

\[
- \text{tr} \left( \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \sum_{j=1}^{N} \mathbf{r}_{\alpha}^{j} \mathbf{d}_{\alpha}^{j} \right)
\]

\[
+ \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \varepsilon_{\alpha}^{j} + \varepsilon_{\alpha}^{j} - C_{\alpha}^{j} \varepsilon_{\alpha}^{j} \right) \frac{1}{2} u_{\alpha}^{j 2} + \sum_{\alpha=1}^{R} \varepsilon_{\alpha}^{j} u_{\alpha}^{2} + \sum_{\alpha=1}^{R} \varepsilon_{\alpha} A_{\alpha}
\]

\[
\sum_{\alpha=1}^{R} \sum_{j=1}^{N} \mathbf{u}_{\alpha}^{j} \cdot \left( \mathbf{T}_{\alpha}^{j} + \mathbf{v}_{\alpha}^{j} \right) + \sum_{\alpha=1}^{R} \mathbf{u}_{\alpha} \cdot \mathbf{T}_{\alpha}
\]

\[
+ \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \varepsilon_{\alpha}^{j} + \varepsilon_{\alpha}^{j} - C_{\alpha}^{j} \varepsilon_{\alpha}^{j} \right) A_{\alpha}^{i}
\]

in which the internal energy \(E_{\alpha}^{i}\) in (7.36) is replaced by the Helmholtz free energy \(A_{\alpha}^{i}\).

Consider next the equation (2.29) with \(\Gamma_{\alpha} = T\), i.e.

\[
\frac{D_{\alpha}^{j} (T)}{Dt} = \frac{D_{\alpha} (T)}{Dt} + \text{grad} (T) \cdot \mathbf{u}_{\alpha}^{j}
\]  
(7.42)

Multiplying the whole expression (7.42) with \(\rho_{\alpha}^{j} \eta_{\alpha}^{j}\) and summing over all \(N\) constituents in the \(\alpha\)-phase, gives

\[
\sum_{j=1}^{N} \rho_{\alpha}^{j} \eta_{\alpha}^{j} \frac{D_{\alpha}^{j} (T)}{Dt} = \rho_{\alpha} \eta_{\alpha} \frac{D_{\alpha} (T)}{Dt} + \sum_{j=1}^{N} \rho_{\alpha}^{j} \eta_{\alpha}^{j} \text{grad} (T) \cdot \mathbf{u}_{\alpha}^{j}
\]  
(7.43)

The definition of the entropy flux \(h_{\alpha}^{j}\) will also be used, i.e. equation (7.23) is

\[
h_{\alpha}^{j} = q_{\alpha}^{j} + \rho_{\alpha}^{j} \eta_{\alpha}^{j} T \mathbf{u}_{\alpha}^{j}
\]  
(7.44)

A summation of (7.44) is

\[
\sum_{j=1}^{N} q_{\alpha}^{j} = h_{\alpha} - \sum_{j=1}^{N} \rho_{\alpha}^{j} \eta_{\alpha}^{j} T \mathbf{u}_{\alpha}^{j}
\]  
(7.45)

where it is noted that \(\sum_{j=1}^{N} h_{\alpha}^{j} = h_{\alpha}\). Multiplying (7.45) with \(\text{grad}(T) / T\) gives

\[
\sum_{j=1}^{N} q_{\alpha}^{j} \cdot \text{grad} (T) / T = h_{\alpha} \cdot \text{grad} (T) / T - \sum_{j=1}^{N} \rho_{\alpha}^{j} \eta_{\alpha}^{j} \mathbf{u}_{\alpha}^{j} \cdot \text{grad} (T)
\]  
(7.46)
Combining (7.43) and (7.46), further, results in that the inequality (7.41) can be written as

\[
- \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \rho_{\alpha} \frac{D_{\alpha} A_{\alpha}^{j}}{Dt} \right) - \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \rho_{\alpha} \frac{D_{\alpha} (T) }{Dt} \geq (7.47)
\]

\[
\sum_{\alpha=1}^{R} \varepsilon_{\alpha} h_{\alpha} \cdot \text{grad} (T)/T - \text{tr} \left( \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \varepsilon_{\alpha}^{T} d_{\alpha}^{j} \right)
\]

\[
+ \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \varepsilon_{\alpha}^{j} + \varepsilon_{\alpha}^{j} - C_{\alpha}^{j} e_{\alpha} \right) \frac{1}{2} u_{\alpha}^{2} + \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \frac{1}{2} u_{\alpha}^{2}
\]

\[
+ \sum_{\alpha=1}^{R} \varepsilon_{\alpha} E_{\alpha} + \sum_{\alpha=1}^{R} \varepsilon_{\alpha} A_{\alpha}
\]

\[
+ \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \sum_{u_{\alpha}^{j} \cdot \left( T_{\alpha}^{j} + \varepsilon_{\alpha}^{j} \right) + \sum_{\alpha=1}^{R} u_{\alpha} \cdot T_{\alpha}
\]

\[
+ \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \varepsilon_{\alpha}^{j} + \varepsilon_{\alpha}^{j} - C_{\alpha}^{j} e_{\alpha} \right) A_{\alpha}^{j}
\]

Consider next equation (4.18) with \( \Gamma_{\alpha} = A_{\alpha}^{j} \) which gives

\[
\sum_{\alpha=1}^{R} \sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha} \frac{D_{\alpha} A_{\alpha}^{j}}{Dt} + \sum_{\alpha=1}^{R} \sum_{j=1}^{N} A_{\alpha}^{j} \left( \varepsilon_{\alpha}^{j} + \varepsilon_{\alpha}^{j} - C_{\alpha}^{j} e_{\alpha} \right) = \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \rho_{\alpha} \frac{D_{\alpha} (A_{\alpha})}{Dt} (7.48)
\]

\[
+ \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \text{div} \left( \varepsilon_{\alpha} \rho_{\alpha} A_{\alpha}^{j} u_{\alpha}^{j} \right)
\]
The inequality (7.47) combined with (7.48) yields

\[
-R \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \rho_{\alpha} \frac{D_{\alpha}(A_{\alpha})}{Dt} - R \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \rho_{\alpha} \eta_{\alpha} \frac{D_{\alpha}(T)}{Dt} \geq 0
\]  

(7.49)

\[
\sum_{\alpha=1}^{R} \varepsilon_{\alpha} h_{\alpha} \cdot \text{grad} (T) / T
\]

\[
- \text{tr} \left( \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \sum_{j=1}^{N} t_{\alpha}^{ij} d_{\alpha}^{ij} \right)
\]

\[
+ R \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left( \sigma_{\alpha}^{j} + \sigma_{\alpha}^{j} - C_{\alpha} \dot{\varepsilon}_{\alpha} \right) \frac{1}{2} u_{\alpha}^{2} + \sum_{\alpha=1}^{R} \dot{\varepsilon}_{\alpha} \frac{1}{2} u_{\alpha}^{2} + \sum_{\alpha=1}^{R} \varepsilon_{\alpha} A_{\alpha}
\]

\[
+ R \sum_{\alpha=1}^{R} \sum_{j=1}^{N} u_{\alpha}^{j} \cdot \left( \tilde{T}_{\alpha}^{j} + \tilde{\tau}_{\alpha}^{j} \right) + \sum_{\alpha=1}^{R} u_{\alpha} \cdot \tilde{T}_{\alpha}
\]

\[
+ \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \text{div} \left( \varepsilon_{\alpha} \rho_{\alpha} A_{\alpha}^{j} u_{\alpha}^{j} \right)
\]

which is the version of second axiom of thermodynamics for the whole mixture expressed with the material time derivatives following the motion of the \( \alpha \)-phase. The inequality, such as (7.49), is used when deriving constitutive equations. It is, however, of interest to make some further manipulations.

Consider the term \( \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \left[ \varepsilon_{\alpha} \text{tr} \left( t_{\alpha}^{ij} d_{\alpha}^{ij} \right) \right] \) in the inequality (7.49). By combining the equations (2.21) and (2.23) it is clear that \( \sum_{j=1}^{N} \varepsilon_{\alpha}^{j} d_{\alpha}^{ij} \) can be written as

\[
\sum_{j=1}^{N} \varepsilon_{\alpha}^{j} d_{\alpha}^{ij} = \varepsilon_{\alpha} d_{\alpha} + \sum_{j=1}^{N} \varepsilon_{\alpha}^{j} \text{grad} u_{\alpha}^{j}
\]  

(7.50)

Hence, one also obtains

\[
\sum_{\alpha=1}^{R} \sum_{j=1}^{N} \text{tr} \varepsilon_{\alpha} d_{\alpha} t_{\alpha}^{ij} = \sum_{\alpha=1}^{R} \left( \text{tr} \varepsilon_{\alpha} d_{\alpha} \sum_{j=1}^{N} t_{\alpha}^{ij} + \sum_{j=1}^{N} \text{tr} \varepsilon_{\alpha}^{j} \text{grad} u_{\alpha}^{j} t_{\alpha}^{ij} \right)
\]  

(7.51)

which is the trace of equation (7.50). The term \( \sum_{\alpha=1}^{R} \left( \text{tr} \varepsilon_{\alpha} d_{\alpha} \sum_{j=1}^{N} t_{\alpha}^{ij} \right) \) in (7.51) can by aid of (4.23) be written as

\[
\sum_{\alpha=1}^{R} \left( \text{tr} \varepsilon_{\alpha} d_{\alpha} \sum_{j=1}^{N} t_{\alpha}^{ij} \right) = \sum_{\alpha=1}^{R} \left( \text{tr} \varepsilon_{\alpha} d_{\alpha} \left( t_{\alpha} + \sum_{j=1}^{N} \rho_{\alpha}^{j} u_{\alpha}^{j} \otimes u_{\alpha}^{j} \right) \right)
\]  

(7.52)
The term \( \sum_{j=1}^{N} \text{tr} \varepsilon_{\alpha} \text{grad} \mathbf{u}_{\alpha}^{j} t_{\alpha}^{j} \) in (7.51) can be written

\[
\sum_{\alpha=1}^{R} \left( \sum_{j=1}^{N} \text{tr} \varepsilon_{\alpha} \text{grad} \mathbf{u}_{\alpha}^{j} t_{\alpha}^{j} \right) = \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \sum_{j=1}^{N} \text{tr} \left( \text{grad} \mathbf{u}_{\alpha}^{j} t_{\alpha}^{j} \right)
\] (7.53)

That is, (7.51), (7.52) and (7.53) combined, yields

\[
\sum_{\alpha=1}^{R} \sum_{j=1}^{N} \text{tr} \varepsilon_{\alpha} \mathbf{d}_{\alpha}^{j} t_{\alpha}^{j} = \sum_{\alpha=1}^{R} \left( \text{tr} \varepsilon_{\alpha} \mathbf{d}_{\alpha} \left( \mathbf{t}_{\alpha} + \sum_{j=1}^{N} \rho_{\alpha}^{j} \mathbf{u}_{\alpha}^{j} \otimes \mathbf{u}_{\alpha}^{j} \right) \right) + \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \sum_{j=1}^{N} \text{tr} \left( \text{grad} \mathbf{u}_{\alpha}^{j} t_{\alpha}^{j} \right)
\] (7.54)

Noting, also, that the following identity holds

\[
\sum_{\alpha=1}^{R} \text{div} \left( \sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha}^{j} A_{\alpha}^{j} \mathbf{u}_{\alpha}^{j} \right) = \sum_{\alpha=1}^{R} \sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha}^{j} A_{\alpha}^{j} \text{div} \mathbf{u}_{\alpha}^{j} + \sum_{\alpha=1}^{R} \sum_{i,j=1}^{N} \mathbf{u}_{\alpha}^{j} \cdot \text{grad} \left( \varepsilon_{\alpha} \rho_{\alpha}^{j} A_{\alpha}^{j} \right)
\] (7.55)

which is obtained by taking partial derivatives. Further the first term on the right-hand side of (7.55) can be re-written by the identity

\[
\sum_{\alpha=1}^{R} \sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha}^{j} A_{\alpha}^{j} \text{div} \mathbf{u}_{\alpha}^{j} = \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \sum_{j=1}^{N} \text{tr} \left( \text{grad} \mathbf{u}_{\alpha}^{j} \left( \rho_{\alpha}^{j} A_{\alpha}^{j} \mathbf{I} \right) \right)
\] (7.56)

i.e. the expression (7.55) can be formulated as

\[
\sum_{\alpha=1}^{R} \text{div} \left( \sum_{j=1}^{N} \varepsilon_{\alpha} \rho_{\alpha}^{j} A_{\alpha}^{j} \mathbf{u}_{\alpha}^{j} \right) = \sum_{\alpha=1}^{R} \varepsilon_{\alpha} \sum_{j=1}^{N} \text{tr} \left( \text{grad} \mathbf{u}_{\alpha}^{j} \left( \rho_{\alpha}^{j} A_{\alpha}^{j} \mathbf{I} \right) \right) + \sum_{\alpha=1}^{R} \sum_{i,j=1}^{N} \mathbf{u}_{\alpha}^{j} \cdot \text{grad} \left( \varepsilon_{\alpha} \rho_{\alpha}^{j} A_{\alpha}^{j} \right)
\] (7.57)
The expressions (7.54) and (7.57) is used in the inequality (7.49), i.e.

\[
- \sum_{\alpha=1}^{R} \epsilon_\alpha \rho_\alpha \frac{D_a (A_\alpha)}{Dt} - \sum_{\alpha=1}^{R} \epsilon_\alpha \rho_\alpha \eta_\alpha \frac{D_a (T)}{Dt} \geq 0 \tag{7.58}
\]

Collecting terms including \( \text{tr}(\text{grad} u^j_\alpha) \) and \( u^j_\alpha \) simply gives

\[
- \sum_{\alpha=1}^{R} \epsilon_\alpha \rho_\alpha \frac{D_a (A_\alpha)}{Dt} - \sum_{\alpha=1}^{R} \epsilon_\alpha \rho_\alpha \eta_\alpha \frac{D_a (T)}{Dt} \geq 0 \tag{7.59}
\]

Finally consider the meaning of \( h_\alpha \) expressed in terms of the Helmholtz free energy \( A^j_\alpha \). The
The definition of the heat flux $q_{\alpha}$ in the $\alpha$-phase is
\[ q_{\alpha} = \sum_{j=1}^{N} \left( q_{\alpha}^{j} - t_{\alpha}^{jT} u_{\alpha}^{j} + \rho_{\alpha}^{j} \mathbf{E}_{\alpha}^{j} u_{\alpha}^{j} + \frac{1}{2} \rho_{\alpha}^{j} \mathbf{u}_{\alpha}^{jT} \mathbf{u}_{\alpha}^{j} \right) \]  
(7.60)
which is obtained by combining (6.21) and (6.22). The heat flux $q_{\alpha}^{j}$ is related to $h_{\alpha}$, as
\[ \sum_{j=1}^{N} q_{\alpha}^{j} = h_{\alpha} - \sum_{j=1}^{N} \rho_{\alpha}^{j} \gamma_{\alpha}^{j} T u_{\alpha}^{j} \]  
(7.61)
i.e. compare with equation (7.23). The equations (7.60) and (7.61) gives the proper expression for $h_{\alpha}$, i.e.
\[ h_{\alpha} = q_{\alpha} + \sum_{j=1}^{N} t_{\alpha}^{jT} u_{\alpha}^{j} + \sum_{j=1}^{N} \rho_{\alpha}^{j} \gamma_{\alpha}^{j} T u_{\alpha}^{j} - \sum_{j=1}^{N} \rho_{\alpha}^{j} \mathbf{E}_{\alpha}^{j} u_{\alpha}^{j} + \frac{1}{2} \sum_{j=1}^{N} \rho_{\alpha}^{j} \mathbf{u}_{\alpha}^{jT} \mathbf{u}_{\alpha}^{j} \]  
(7.62)
This equation reduces when using the definition of the Helmholtz free energy, i.e. $A_{\alpha}^{j} = E_{\alpha}^{j} - T \gamma_{\alpha}^{j}$, and one obtain
\[ h_{\alpha} = q_{\alpha} + \sum_{j=1}^{N} t_{\alpha}^{jT} u_{\alpha}^{j} - \sum_{j=1}^{N} \rho_{\alpha}^{j} A_{\alpha}^{j} u_{\alpha}^{j} + \frac{1}{2} \sum_{j=1}^{N} \rho_{\alpha}^{j} \mathbf{u}_{\alpha}^{jT} \mathbf{u}_{\alpha}^{j} \]  
(7.63)
which is the proper identification of the entropy flux included in the inequality (7.59).

8. General principles for developing constitutive relations

Here different theories will be discussed how to develop stringent physical assumptions concerning material behavior for different material. However, the assumptions involved in determining the material behavior for fluids will serve as an important example.

8.1. Introductory remarks

In developing constitutive relations several powerful theories can be adopted to make sure that nothing unphysical sneaks into the model. Here some of the different approaches will be discussed.

In order, to understand these classical continuum approaches the concept of tensors must be dealt with. A brief discussion of the subject will be performed.

8.2. Vectors, first order Cartesian tensors

A vector is a 'geometrical' object representing physical properties such as displacements $w$, velocities $\dot{x}$, accelerations $\ddot{x}$, forces, momentum etc.

The characteristic properties of a vector is that one must specify a direction and, furthermore, one must use the parallelogram law when the sum of two vectors is to be computed. That is if two vectors $r$ and $s$ are represented by a direction and length by two 'arrows' in a Cartesian coordinate system, then these vectors are 'moved' in its corresponding directions so that its
origins coincide and so that its sides is the sides in a parallelogram. The diagonal in this parallelogram (from corner to corner) is the sum of the vectors \( r \) and \( s \). This means, in general, that this new vector has an new direction and length.

Another important property of vectors is that the length, e.g. \(|r|\) and \(|s|\) remains the same if another origo and directions of axis is used to describe the vectors \( r \) and \( s \). In other words, \(|r|\) and \(|s|\) remains the same irrespectively of which Cartesian coordinate system one happens to choose to represent the vectors. Indeed, the length of a vector is independent of any introduced coordinate system such as cylindrical or curve linear systems and also independent of transformations between such different systems, here the traditional Cartesian coordinate system will be considered by simplicity, without losing the generality of the concept of vector properties.

A Cartesian vector can also be seen as an ‘arrows’ between two points in (a rectangular) space, say \( a \) and \( b \), and the corresponding vector is then written as \( \overrightarrow{ab} \). It seems intuitively correct that this ‘arrow’ between two points is \textit{physically independent} of which coordinate system one happens to used since the two points \( a \) and \( b \) can easily be described (represented) in different types of coordinate systems and therefore summation of different vectors in such coordinate systems can also be defined.

We now starts to reach the physical relevance for the introduction of so-called first order tensors. Above the phrase ‘physically independent’ was used, this means, loosely speaking, that a physical event such as acceleration of a body in space, do not care about any coordinate system which has been introduce (by someone to relate the numerical value of this acceleration). Naturally, we often want to relate a physical phenomenon to a certain coordinate system, but indeed, from a purely physical point of view is seem unnecessary to even specify a coordinate system since the physical events that we which to study acts independently of them. The so-called tensors is introduced without any attention to any special coordinate system. However, for example, the first order tensor (a vector) includes three pieces of information corresponding to directions in space (not necessary three perpendicular Cartesian axis \( x_1, x_2 \) and \( x_3 \)), this mean that a first order tensor can be bound to a coordinate system whenever one which to do so. When, for example, describing the physical balance laws, e.g. balance of energy and balance of momentum, one often use this ‘coordinate free’ tensor description since these physical balance principles has nothing to do with which type of coordinate system we happens to relate a physical balance principle to.

Why not always introduce a coordinate system in advance and, moreover, why not choose a simple Cartesian coordinate system when describing physical events? It turns out that there is several reasons that motivates the use of a ‘coordinate free’ tensor description. Perhaps, the most important issue is that the tensor description opens up possibilities to study the reasonableness of different material assumptions in a very stringent way. This stems from the fact that tensors take certain different ‘values’ when they are described in different coordinate systems. By rather intuitively argument it is tempting to postulate that the general behavior of the response of a material during, for example, mechanical loading should be independent of the orientation of the observer. That is one want to assure that two different observers having different coordinate systems to relate the same physical behavior can communicate and agree that they observe the same thing. In general one need a transformation to relate what the two observers record, i.e. they communicate through a proper transformation and the same transformation is the guarantee that the two observers can agree that the record the same physical event. If the same two observers attached to different coordinate systems cannot under any circumstances agree how
the real physical event should be transformed between them something unphysical takes place since the physical event is independent of any coordinate system. For example, an introduced material assumption which results in that a simulated response cannot be interpreted correctly by two observers attached to different coordinate systems. i.e. a proper transformation between them cannot be obtained, then the material assumption must be considered to be irrelevant and cannot therefore be used.

Another, useful, feature of (second order) tensors is that certain mathematical operations among the (nine) component in such a tensor results in a scalar property which is invariant. An invariant is some kind of physical property which is completely independent of which coordinate system attached.. That is, not even a transformation between two observers is needed since the same number is recorded in both coordinate systems. Invariants is very useful when establishing relevant material assumptions since it describes a fundamental process which is completely independent of how the observer is oriented relative to the process. An invariant measure can, for example, be a volume change (a scalar number) or a hydrostatic mechanical pressure.

When using tensors to describe physical events one certainly expect that when attaching a certain coordinate system to it, lets call this coordinate system O, a known physical event such as a known acceleration of a body can be described with three numerical values. But, on the other hand, if one of some reason want to observe the same acceleration from another coordinate system O* (which, for example, has another origo and directions of the axis than compared to the O-system) one will obtain three numerical values which (in general) differs from the values recorded with the O-system as an reference to the event. In the next section it will be shown how the three numerical values in the two different frames can be related to each other, i.e. a transformation between the values in the O-system and O*-system will be explained. It should be observed that the real physical event is independent of both the O-system and the O*-system as we have introduced them only to record the event relatively to some arbitrary reference. Indeed, the transformation rule of a vector between to different coordinate systems, say O and O* can be used as an definition of a first order tensor. Or, perhaps, more correctly a column matrix including three pieces of information is a first order tensor if a given transformation rule gives a new column matrix including three pieces of information which can be correctly represented in another coordinate system (this ‘new’ coordinate system is given explicitly from the transformation).

8.3. Point transformation, change of coordinate system

In order to obtain a transformation of properties such as a vectors between different coordinate systems the transformation of points between coordinate systems will be discussed. A point transformation between two Cartesian coordinate systems can be expressed, with a general relation, as

\[ \mathbf{x}' = \mathbf{c}(t) + \mathbf{Q}(t) \mathbf{x} \quad (8.1) \]

where \( \mathbf{c}(t) \) represents a translation and \( \mathbf{Q}(t) \) is a rotation.

The rotation \( \mathbf{Q}(t) \) is always orthogonal i.e.

\[ \mathbf{QQ}^T = 1 \quad (8.2) \]
or equally

\[ Q^{-1} = Q^T \]  

(8.3)

Consider a point vector, i.e. a vector between points \( a \) and \( b \) in space given by

\[ \mathbf{r} = \overline{ab} \]  

(8.4)

i.e.

\[ \mathbf{r} = x^a - x^b \]  

(8.5)

where \( x^a \) are the coordinates (place) for the point \( a \) and \( x^b \) for the point \( b \) described in the \( x \)-frame. This the same vector observed in another coordinate system \( x^* \) is

\[ \mathbf{r}^* = x^{a*} - x^{b*} \]  

(8.6)

where \( x^{a*} \) are the coordinates for the same point \( a \) and \( x^{b*} \) for the same point \( b \) in the \( x^* \)-frame.

According to the point transformation (8.1) one obtain the following relation between the same vector recorded in the \( x \)-frame and in the \( x^* \)-frame, one obtain

\[
\begin{align*}
\mathbf{x}^{a*} &= \mathbf{c}(t) + \mathbf{Q}(t) \mathbf{x}^a \\
\mathbf{x}^{b*} &= \mathbf{c}(t) + \mathbf{Q}(t) \mathbf{x}^b \\
\mathbf{r}^* &= \mathbf{x}^{a*} - \mathbf{x}^{b*} = \mathbf{c}(t) + \mathbf{Q}(t) \mathbf{x}^a - \mathbf{c}(t) - \mathbf{Q}(t) \mathbf{x}^b \\
\mathbf{r}^* &= \mathbf{Q}(t) (\mathbf{x}^a - \mathbf{x}^b) = \mathbf{Q}(t) \mathbf{r}
\end{align*}
\]

That is, a vector transforms between two Cartesian coordinate system as

\[ \mathbf{r}^* = \mathbf{Q}(t) \mathbf{r} \]  

(8.7)

This can also be seen as an definition of a first order (Cartesian) tensor. Note also that a vector is independent of the translation \( \mathbf{c}(t) \) which corresponds to the definition of a vector only having a direction and a length, i.e. no information is included telling anything about its actual place in space.

All introduced physical vector properties in the balance principles are first order tensors, i.e.

\[ \mathbf{x}^* = \mathbf{Q}(t) \mathbf{x}; \quad \mathbf{x}^* = \mathbf{Q}(t) \mathbf{x}; \quad \mathbf{b}^* = \mathbf{Q}(t) \mathbf{b}; \quad \mathbf{q}^* = \mathbf{Q}(t) \mathbf{q} \]  

(8.8)

A second order tensor is a linear combination of two first order tensors \( s \) and \( r \), e.g. \( \mathbf{U} \) and \( \mathbf{U}^* \) is a second order tensor if

\[ \mathbf{s} = \mathbf{U} \mathbf{r}; \quad \mathbf{s}^* = \mathbf{U}^* \mathbf{r}^* \]  

(8.9)

The transformation rule for the second order tensor follows by considering the transformation rule for the first order tensors \( \mathbf{r} \) and \( \mathbf{s} \), i.e.

\[ \mathbf{s}^* = \mathbf{Q}(t) \mathbf{s}; \quad \mathbf{r}^* = \mathbf{Q}(t) \mathbf{r} \]  

(8.10)

Insertion of (8.10a) and (8.10b) into (8.9b) yields

\[ \mathbf{Q}(t) \mathbf{s} = \mathbf{U}^* \mathbf{Q}(t) \mathbf{r} \]  

(8.11)
Multiplying both sides with $Q(t)^T$, i.e.

$$Q(t)^T Q(t) s = Q(t)^T U^* Q(t) r$$

(8.12)

and using that the rotation is orthogonal, i.e. (8.2) is

$$Q(t)^T Q(t) = I$$

(8.13)

Insertion of (8.14) into (8.12), gives

$$s = Q(t)^T T^* Q(t) r$$

(8.14)

Comparison with (8.9a), yields

$$U = Q(t)^T U^* Q(t)$$

(8.15)

which is the transformation rule for a second order tensor.

That is, all introduced physical second order tensor properties in the physical balance principle descriptions are transformed according to (8.15), e.g.

$$T = Q(t)^T T^* Q(t); \quad L = Q(t)^T L^* Q(t); \quad W = Q(t)^T W^* Q(t);$$

(8.16)

At last, it is mentioned that all scalar properties are independent of different frames, e.g.

$$\theta^* = \theta; \quad \rho^* = \rho; \quad \varepsilon^* = \varepsilon;$$

(8.17)

That is, no transformations is needed for scalar properties when the coordinate system is changed.

8.4. Observing a physical event in two different frames moving relatively to each others in the time domain

Given a deformation function $\chi$, a change of frame is a mapping that yields a new deformation function $\chi^*$, defined by

$$\chi^*(X,t) = c(t) + Q(t) \chi(X,t) \quad \text{(event)}$$

(8.18)

which follows from (8.1) where $c(t)$ is an arbitrary time-dependent vector representing a translation and $Q(t)$ a time-dependent orthogonal linear transformation representing a rigid rotation. Physically, $\chi$ and $\chi^*$ describe the same motion, but mathematical $\chi^*$ is the motion obtained from $\chi$ by the superposition of a time dependent rigid transformation. It is important to stress that (8.18) represents a transformation of points and does not alter the reference configuration, i.e. $X$ is the 'name' (this 'name' is actually the initial (reference) coordinates $X$ at some time level $t_0$) of a particle in its reference configuration which is independent of the transformation (8.18).

The sequences of position vectors $x^*$ following the motion with reference to the $x^*$-frame can be written

$$x^* = \chi^*(X,t)$$

(8.19)
and the same motion recorded by sequences of position vectors \( \mathbf{x} \) in the \( x \)-frame can be written

\[ \mathbf{x} = \chi (\mathbf{X},t) \]  

(8.20)

Observe, that the reference position \( \mathbf{X} \) is the same for the motion observed in the different frames.

The velocity \( \dot{x}^* \) and acceleration \( \ddot{x}^* \) observed in the \( x^* \)-frame are by definition time derivatives of the motion, i.e.

\[ \dot{x}^* = \frac{\partial \mathbf{x}^* (\mathbf{X},t)}{\partial t} \]  

(8.21)

\[ \ddot{x}^* = \frac{\partial^2 \mathbf{x}^* (\mathbf{X},t)}{\partial t^2} \]  

(8.22)

and in the \( x \)-frame the velocities is defined as

\[ \dot{x} = \frac{\partial \chi (\mathbf{X},t)}{\partial t} \]  

(8.23)

\[ \ddot{x} = \frac{\partial^2 \chi (\mathbf{X},t)}{\partial t^2} \]  

(8.24)

Noting, that \( \mathbf{c} (t) \), i.e. the translation and \( \mathbf{Q} (t) \) i.e. the rotation, in general, must be allowed to change with time. This corresponds to

\[ \ddot{x}^* (\mathbf{X},t) = \ddot{\mathbf{c}} (t) + \mathbf{Q} (t) \ddot{x} + \dot{\mathbf{Q}} (t) \chi (\mathbf{X},t) \]  

(8.25)

or equally

\[ \ddot{x}^* (\mathbf{X},t) = \ddot{\mathbf{c}} (t) + \mathbf{Q} (t) \ddot{x} + \dot{\mathbf{Q}} (t) \chi (\mathbf{X},t) \]  

(8.25)

where (8.20) has been used. Note that, the \( x \)-frame is moving relatively to the \( x^* \)-frame.

Indeed, a transformation of a first order tensor is defined as in (8.8a), i.e. for the velocity which certainly is a tensor one have \( \dot{x}^* = \mathbf{Q} (t) \ddot{x} \), but the reason for the expression (8.25) and (8.8a) being different is that the condition for \( \ddot{x}^* \) in (8.25) is that the two different frames considered is allowed to ‘move’ relatively to each other with a speed given by \( \mathbf{c} \) and \( \mathbf{Q} \). This means that the transformation rules which defined the first and second order tensors, discussed in the previous section, is ‘time independent’. That is, a tensor itself is not affected by the time aspect, the only restriction on a tensor is that a physical correct interpretation of it should be obtained (at an instantaneous time level) in two frames and the two different interpretations of it should be related through the transformation rules (8.8a) (first order tensor) and (8.15) (second order tensor). However, the transformation (8.25) tells us that observers attached to two different frames which moves relative to each other with a given speed (here, speed can be referred to a time dependent translation and rotation), will measure two different velocities which not communicates with each other with the transformation (8.8a). Therefore, such time dependent properties are said to be a frame-different tensor. A frame-indifferent tensor (such as the heat flux vector) is then a property which can be measured by to observers moving relatively each other, these to measurements should then be related by the standard time independent tensor transformation (8.7).

The acceleration \( \ddot{x} \) as observed from the \( x \)-frame (note that, the \( x \)-frame is moving with a speed relatively to the \( x^* \)-frame) is transformed to the acceleration \( \ddot{x}^* \) in the \( x^* \)-frame, as

\[ \ddot{x}^* (\mathbf{X},t) = \ddot{\mathbf{c}} (t) + \mathbf{Q} (t) \ddot{x} + \dot{\mathbf{Q}} (t) \chi (\mathbf{X},t) \]  

(8.26)
The deformation gradient is transformed as a vector, i.e.

\[ \mathbf{F}^* (\mathbf{X}, t) = \mathbf{Q} (t) \mathbf{F} (\mathbf{X}, t) \]  \hspace{1cm} (8.28)

This will be shown below, and the velocity gradient is transformed between two different frames, as

\[ \mathbf{L}^* = \dot{\mathbf{F}}^* \mathbf{F}^*^{-1} = \mathbf{Q} (t) \dot{\mathbf{L}} \mathbf{Q} (t)^T + \dot{\mathbf{Q}} (t) \mathbf{Q} (t)^T \]  \hspace{1cm} (8.29)

where

\[ \mathbf{L}^* = \mathbf{D}^* + \mathbf{W}^* \]  \hspace{1cm} (8.30)

The transformation (8.29) will also be shown below.

The second order deformation gradient tensor \( \mathbf{F} \) transforms like a vector under change of frame at time \( t \). Assuming that the two frames had the same orientation at time \( t_0 \) when the neighborhood of a point was in the reference configuration so that \( d\mathbf{X}^* = d\mathbf{X} \) at \( t_0 \)

\[ d\mathbf{x}^* = \mathbf{F}^* d\mathbf{x}^* = \mathbf{F}^* d\mathbf{X}; \quad d\mathbf{x} = \mathbf{F} d\mathbf{X} \]  \hspace{1cm} (8.31)

i.e. from (8.7) and (8.31b) one obtain

\[ d\mathbf{x}^* = \mathbf{Q} (t) d\mathbf{x} \]  \hspace{1cm} (8.32)

= \mathbf{Q} (t) (\mathbf{F} d\mathbf{X})

= (\mathbf{Q} (t) \mathbf{F}) d\mathbf{X}

thus by replacing \( d\mathbf{x}^* \) by \( d\mathbf{x}^* = \mathbf{F}^* d\mathbf{X} \), yields

\[ \mathbf{F}^* d\mathbf{X} = (\mathbf{Q} (t) \mathbf{F}) d\mathbf{X} \]  \hspace{1cm} (8.33)

i.e.

\[ (\mathbf{F}^* - \mathbf{Q} (t) \mathbf{F}) d\mathbf{X} = 0 \]  \hspace{1cm} (8.34)

since \( d\mathbf{X} \) can be chosen arbitrary the expression (8.34) becomes

\[ \mathbf{F}^* (\mathbf{X}, t) = \mathbf{Q} (t) \mathbf{F} (\mathbf{X}, t) \]  \hspace{1cm} (8.35)

which is the result to be derived, i.e. expression (8.28).

In order to show how the transformation of the velocity gradient (8.29) can be obtained, consider the material time derivative of (8.35), i.e.

\[ \dot{\mathbf{F}}^* (\mathbf{X}, t) = \mathbf{Q} (t) \dot{\mathbf{F}} (\mathbf{X}, t) + \dot{\mathbf{Q}} (t) \mathbf{F} (\mathbf{X}, t) \]  \hspace{1cm} (8.36)

Furthermore, the inverse of the deformation gradient \( \mathbf{F}^{-1} \) can be transformed as a vector in the same manner as \( \mathbf{F} \) being transformed, that is

\[ \mathbf{F}^{-1} (\mathbf{X}, t) = \mathbf{F}^{-1} \mathbf{Q} (t)^T \]  \hspace{1cm} (8.37)
Since we have
\[ F^{*-1}(X,t) = Q(t) F^{-1}(X,t) = Q(t)^{-1} Q(t) F^{-1} Q(t) = F^{-1} Q(t)^T \quad (8.38) \]
where (8.2) and (8.3) has been used. Noting further that \( L^* \) can be expressed in terms of the deformation gradient and its material time derivative, as
\[ L^* = \dot{F}^* F^{*-1} \quad (8.39) \]
and in the same manner in the \( x \)-frame, as
\[ L = \dot{F} F^{-1} \quad (8.40) \]
Noting, that the following, also, holds
\[ F^* F^{*-1} = 1; \quad FF^{-1} = 1 \quad (8.41) \]
Using, the expressions (8.39) and the transformation rule (8.36), gives
\[ L^* = \dot{F}^* F^{*-1} = \left( Q(t) \dot{F} + \dot{Q}(t) F \right) F^{-1} Q(t)^T \quad (8.42) \]
i.e.
\[ L^* = \dot{F}^* F^{*-1} = Q(t) \dot{F} F^{-1} Q(t)^T + \dot{Q}(t) FF^{-1} Q(t)^T \quad (8.43) \]
by using the expressions (8.41b) and (8.40) gives the transformation for the velocity gradient
\[ L^* = \dot{F}^* F^{*-1} = Q(t) L Q(t)^T + \dot{Q}(t) Q(t)^T \quad (8.44) \]
Which is the expression presented in (8.29).

8.5. Objectivity, or frame-indifference

A scalar \( \phi \) and a vector (or equally a first-order tensor) \( r \) is said to be objective or frame-indifferent if the tensor transformation is independent of the rate of change of relative translation \( \dot{c}(t) \) and rotation \( \dot{Q}(t) \) between two different frames moving relatively to each other. That is, for frame-indifferent tensors in this case denoted \( \phi \) and \( r \) should be transformed as
\[ \phi^*(x^*,t) = \phi(x,t) \quad (8.45) \]
\[ r^*(x^*,t) = Q(t) r(x,t) \quad (8.46) \]
For example, the time \( t \) is objective since \( t = t^* \). The transformation (8.46) follows directly from the point relation between the two frames in equation (??). This is due to the translation \( c(t) \) not contributing to any change of vector properties (or equally a line between points in space) transformed between different frames. However, the translation \( c(t) \) do effect the transformation of points (but, again, not vectors between point).

 Constitutive equations 'must' be invariant (objective) under changes of reference frame. If a dynamic constitutive equation with a motion and a stress tensor satisfied in one frame, let's say
in the x-frame, one have \( x = \mathbf{x}(X,t) \) and \( T(X,t) \) it must also be satisfied for any equivalent process in the \( x^* \)-frame. This means that the constitutive equation must also be satisfied by the motion and the stress tensor given by

\[
\begin{align*}
x^* &= \mathbf{x}^*(X,t) = c(t) + \mathbf{Q}(t) \mathbf{x}(X,t) \\
T^* &= T^*(X,t) = Q(t) T(X,t) Q(t)^T
\end{align*}
\] (8.47)

which follows from the expressions (8.15) and (8.15) (where the arbitrary tensor \( U \) is identified as the stress tensor \( T \)).

The velocity gradient \( L \) is a second order tensor, but is the velocity gradient \( L \) a frame-indifferent tensor property according to (8.47)? Actually, the physical property \( L \) is not a frame-indifferent tensor since it was shown that \( L^* \) is related to \( L \) as

\[
L^* = \mathbf{F}^* F^{-1} = Q(t) L Q(t)^T + \dot{Q}(t) Q(t)^T
\] (8.48)

which is (8.29) repeated. That is, the term \( \dot{Q}(t) Q(t)^T \) is not ‘allowed’ when a property is to be frame-indifferent. It is noted that the transformation between \( L^* \) and \( L \) is dependent of the rate of change of a ‘hypothetical’ rate of change of the relative rotation between different frames. Due to this fact, one usually, avoid to constitute the stress as a function of \( L \) since it is supposed that a ‘hypothetical’ relative rotation of two different frames with attached observers should not affect the material behavior itself in terms of a response.

It has been discussed earlier that the velocity gradient can be decomposed into a symmetric part and a skew symmetric part as

\[
L = D + W
\] (8.49)

Where \( D \) is the symmetric part of the velocity gradient is defined as

\[
D = \frac{1}{2} (L + L^T)
\] (8.50)

and the skew part is defined as

\[
W = \frac{1}{2} (L - L^T)
\] (8.51)

Is the symmetric part of the velocity gradient, i.e. \( D \), a frame-indifferent tensor property according to (8.47)? By using (8.50) and the transformation rule for \( L \), i.e. equation (8.29), one obtain

\[
D^* = \frac{1}{2} L^* + \frac{1}{2} L^{*T}
\] (8.52)

\[
= \frac{1}{2} Q(t) L Q(t)^T + \frac{1}{2} Q(t) L^T Q(t)^T + \frac{1}{2} \dot{Q}(t) Q(t)^T + \frac{1}{2} \left( \dot{Q}(t) Q(t)^T \right)^T
\]

i.e.

\[
D^* = Q(t) D Q(t)^T + \frac{1}{2} \dot{Q}(t) Q(t)^T + \frac{1}{2} \left( \dot{Q}(t) Q(t)^T \right)^T
\] (8.53)

Moreover, from (8.2) we have

\[
Q(t) Q(t)^T - 1 = 0
\] (8.54)
differentiation of (8.54) with respect to the material time derivative, i.e.

$$\dot{Q}(t)Q(t)^T - \mathbf{1} = 0$$  \hspace{1cm} (8.55)

This expression can be written as

$$\dot{Q}(t)Q(t)^T + Q(t)\dot{Q}(t)^T = 0$$  \hspace{1cm} (8.56)

where partial differentiation is used. A pure mathematical rearrangement with help from the mathematical rules for the transpose operator, gives

$$\left(\dot{Q}(t)Q(t)^T\right)^T = \left(Q(t)^T\right)^T\dot{Q}(t)^T = Q(t)\dot{Q}(t)^T$$  \hspace{1cm} (8.57)

The expressions (8.56) and (8.57) combine to yield

$$\dot{Q}(t)Q(t)^T = -\left(\dot{Q}(t)Q(t)^T\right)^T$$  \hspace{1cm} (8.58)

It can be noted that $\dot{Q}(t)Q(t)^T$ is skew symmetric and more important, by using (8.58) in (8.53) one can obtain

$$D^* = Q(t)DQ(t)^T$$  \hspace{1cm} (8.59)

which is due to

$$\frac{1}{2}\dot{Q}(t)Q(t)^T + \frac{1}{2}\dot{Q}(t)Q(t)^T = -\frac{1}{2}\left(\dot{Q}(t)Q(t)^T\right)^T + \frac{1}{2}\left(\dot{Q}(t)Q(t)^T\right)^T = 0$$  \hspace{1cm} (8.60)

Hence, the symmetric part of the velocity gradient $D$ is an objective tensor or equally a frame-indifferent tensor.

In fluid mechanics one usually prefer to choose the stress to be a function of $D$ rather than of $L$. This is due to the symmetric part of the velocity gradient $D$ remaining unaffected by the time aspects of two different observers attached to two different frames moving and rotating relatively to each others. That is $D$ is a frame-indifferent tensor.

8.6. More about frame indifference an constitutive equations

The important physical message of the frame-indifference when establishing constitutive functions is that the response function $f$ should be independent of which time dependent frame one happens to choose.

Consider, for example, a stress $T$ which is assumed to depend on the symmetric part of the velocity gradient $D$, the spin $W$, the density $\rho$, the temperature gradient $g$, the velocity $\dot{x}$ and the place $x$

$$T = f(D, W, \rho, g, \dot{x}, x)$$  \hspace{1cm} (8.61)

where $g = \text{grad} \theta$. The same physical event in terms of stresses must be obtained in the $x*$-frame

$$T^* = f(D^*, W^*, \rho^*, g^*, \dot{x}^*, x^*)$$  \hspace{1cm} (8.62)
Not that the response function \( f \) must be independent of the transformation, indeed, it is independent of any introduced coordinate system. Loosely speaking, this means that if the stress can be determined with a (hypothetical) experiments with the \( x \)-frame as an reference, then it should also be possible to observe the same physical process having the observer attached to the \( x^\ast \)-frame. This means, further, that the material itself is subjected to a stress (determined by the response function \( f \)) when a hypothetical motion is given (this motion is really the same for two different frames, but the motion is recorded by two different observers one of them attached to \( x \)-frame and the other to the \( x^\ast \)-frame), it then seems natural to assume that the response function \( f \) is independent of how the two different observers like to interpret physical events to their attached frames. Due to this, the assumption behind frame-indifference of constitutive equations is also called isotropy of space, yet another illustrative (alternative) name is material objectivity. Indeed, the concept of frame-indifference are so obvious to our physical intuition that we do not even recognize in most cases that we are applying a very useful general principle.

The objectivity principal gives the transformation rule

\[
T^\ast = Q(t) T Q(t)^T
\]  
(8.63)

for the stresses as observed from two different frames moving relatively to each others. From (8.48) one obtain

\[
L^\ast = D^\ast + W^\ast = Q(t) L Q(t)^T + \dot{Q}(t) Q(t)^T
\]  
(8.64)

and from (8.59) one obtain

\[
L^\ast = D^\ast + W^\ast = Q(t) D Q(t)^T + Q(t) W Q(t)^T + \dot{Q}(t) Q(t)^T
\]  
(8.65)

since

\[
W^\ast = Q(t) W Q(t)^T + \dot{Q}(t) Q(t)^T
\]  
(8.66)

The density transforms as

\[
\rho^\ast = \rho
\]  
(8.67)

and the temperature as

\[
\theta^\ast = \theta
\]  
(8.68)

hence, \( g = \text{grad} \theta \), transforms as

\[
g^\ast = Q(t) g
\]  
(8.69)

The velocity \( \dot{x} \) transforms as

\[
\dot{x}^\ast = \dot{c}(t) + Q(t) \dot{x} + \dot{Q}(t) x
\]  
(8.70)

and the point relation is

\[
x^\ast = c(t) + Q(t) x
\]  
(8.71)

The constitutive relation (8.59) can the be written

\[
T^\ast = f(Q(t) D Q(t)^T, Q(t) W Q(t)^T + \dot{Q}(t) Q(t)^T, \rho, Q(t) g, \dot{c}(t) + Q(t) \dot{x} + \dot{Q}(t) x, c(t) + Q(t) x)
\]  
(8.72)

63
where the above transformation rules, given above have been adopted.

By testing a given value of the otherwise arbitrary rotation tensor \( Q(t) \), conclusions can be drawn concerning if the frame-indifference is fulfilled. Choose, for example, \( Q(t) = 1 \), \( \dot{Q}(t) = 0 \), insertion of this choice into (8.72), gives

\[
T^* = f(D, W, \rho, g, \dot{c}(t) + \dot{x}, c(t) + x)
\]  

(8.73)

Since \( \dot{c}(t) \) and \( c(t) \) must be allowed to be chosen arbitrary one concludes that the constitutive relation \( f(D, W, \rho, g, \dot{x}, x) \) must be reduced to \( f(D, W, \rho, g) \) in order to fulfill the frame-indifference postulate. That is (8.72) is reduced to

\[
T^* = f(Q(t) DQ(t)^T, Q(t) WQ(t)^T + \dot{Q}(t) Q(t)^T, \rho, Q(t) g)
\]  

(8.74)

Next, choose the otherwise arbitrary rotation to the value \( Q(t) = 1 \)

\[
T^* = f(D, W + \dot{Q}(t), \rho, g)
\]  

(8.75)

which says that the response function \( f \) cannot depend on \( W \), since \( \dot{Q}(t) \) is completely arbitrary, i.e. \( f(D, W, \rho, g) = f(D, \rho, g) \). That is, the rate of rotation of a frame (which has nothing to do with the actual motion of the body) is not allowed to effect the response function \( f \).

Another, often used, argument which perhaps is more illustrative is to set \( \dot{Q}(t) = -W \) and \( Q(t) = 1 \) which yields \( T^* = f(D, O, \rho, g) \). By using this choice of rotation and rate of rotation of the observers frames it is, again, clear that \( f \) cannot depend on the spin \( W \) when not allowing for any dependence of \( Q(t) \), i.e. when adopting the frame-indifference principle.

Another important issue is to show that velocity differences or equally relative velocities fulfill the frame-indifference postulate. Consider two velocities \( \dot{x}_a^* \) and \( \dot{x}_b^* \) which transforms as

\[
\dot{x}_a^* = \dot{c}(t) + Q(t) \dot{x}_a + \dot{Q}(t) x
\]  

(8.76)

and

\[
\dot{x}_b^* = \dot{c}(t) + Q(t) \dot{x}_b + \dot{Q}(t) x
\]  

(8.77)

The difference of the two velocities denoted \( \dot{x}_{a-b} \) can according two (8.76) and (8.77) be transformed as

\[
\dot{x}_{a-b}^* = \dot{x}_a^* - \dot{x}_b^* = Q(t) (\dot{x}_a - \dot{x}_b) = Q(t) \dot{x}_{a-b}
\]  

(8.78)

which is the desired property and it is concluded that \( \dot{x}_{a-b} \) is a frame-indifferent property. The stress could therefore, for example be constituted as \( T = f(\dot{x}_{a-b}) \) since \( T^* = f(\dot{x}_{a-b}^*) = f(Q(t) \dot{x}_{a-b}) \). It should be noted, however, that other postulates, such as the second axiom of thermodynamics, may be in conflict with such constitutive assumptions. This subject will be discussed later.

Spin tensor

\[
W_a^* = Q(t) W_a Q(t)^T + \dot{Q}(t) Q(t)^T
\]  

(8.79)

\[
W_b^* = Q(t) W_b Q(t)^T + \dot{Q}(t) Q(t)^T
\]  

(8.80)

\[
W_{a-b}^* = W_a^* - W_b^* = Q(t) (W_a - W_b) Q(t)^T = Q(t) W_{a-b} Q(t)^T
\]  

(8.81)

which means that the difference of spin as defined above is a reference indifferent property.
8.7. The Rivling-Eriksen tensor of second order

Consider the constitutive assumption for the stress as

\[ T = f(\text{grad}\hat{\mathbf{x}}, \text{grad}\hat{\mathbf{x}}) \]  

(8.82)

Denoting the symmetric part of the velocity gradient in the fashion of Rivling-Eriksen, i.e.

\[ \mathbf{A}_1 = \mathbf{L} + \mathbf{L}^T = 2\mathbf{D} \]  

(8.83)

From earlier we know that the part of the velocity gradient denoted \( \mathbf{D} \) is symmetric and frame indifferent i.e.

\[ \mathbf{A}_1 = \mathbf{A}_1^T; \quad \text{and} \quad \mathbf{A}_1^* = \mathbf{Q}(t) \mathbf{A}_1 \mathbf{Q}(t)^T \]  

(8.84)

Referring to the material time derivative of the rotation times rotation as: \( \dot{\mathbf{Q}}(t) \mathbf{Q}(t)^T = \mathbf{\Omega} \), that is, one obtain

\[ \mathbf{L}^* = \mathbf{Q}(t) \mathbf{L} \mathbf{Q}(t)^T + \dot{\mathbf{Q}}(t) \mathbf{Q}(t)^T = \mathbf{Q}(t) \mathbf{L} \mathbf{Q}(t)^T + \mathbf{\Omega} \]  

(8.85)

Again, it is shown that the velocity gradient is not frame indifferent.

Since \( \mathbf{Q}(t) \mathbf{Q}(t)^T = 1 \) we can identify \( \mathbf{\Omega} \) as

\[ \dot{\mathbf{Q}}(t) \mathbf{Q}(t)^T + \mathbf{Q}(t) \dot{\mathbf{Q}}(t)^T = 0 \]  

(8.86)

i.e.

\[ \mathbf{\Omega} = -\mathbf{\Omega}^T \]  

(8.87)

Assume a second property related to \( \text{grad}\hat{\mathbf{x}} \), i.e.

\[ \mathbf{A}_2 = \mathbf{\dot{A}}_1 + \mathbf{A}_1 \mathbf{L} + \mathbf{L}^T \mathbf{A}_1 \]  

(8.88)

A transformation yields

\[ \mathbf{\dot{A}}_1^* = \mathbf{Q}(t) \mathbf{A}_1 \mathbf{Q}(t)^T + \mathbf{Q}(t) \mathbf{\dot{A}}_1 \mathbf{Q}(t)^T + \mathbf{Q}(t) \mathbf{A}_1 \dot{\mathbf{Q}}(t)^T \]  

(8.89)

With further arrangements one obtain

\[ \mathbf{A}_1^* \mathbf{L}^* = \mathbf{Q}(t) \mathbf{A}_1 \mathbf{Q}(t)^T \left( \mathbf{Q}(t) \mathbf{L} \mathbf{Q}(t)^T + \dot{\mathbf{Q}}(t) \mathbf{Q}(t)^T \right) \]  

(8.90)

\[ = \mathbf{Q}(t) \mathbf{A}_1 \mathbf{Q}(t)^T \mathbf{Q}(t) \mathbf{L} \mathbf{Q}(t)^T + \mathbf{Q}(t) \mathbf{A}_1 \mathbf{Q}(t)^T \dot{\mathbf{Q}}(t) \mathbf{Q}(t)^T \]  

\[ = \mathbf{Q}(t) \mathbf{A}_1 \mathbf{L} \mathbf{Q}(t)^T - \mathbf{Q}(t) \mathbf{A}_1 \dot{\mathbf{Q}}(t)^T \]  

(8.91)

Noting also that

\[ \mathbf{L}^T \mathbf{A}_1^* = \left( \mathbf{Q}(t) \mathbf{L}^T \mathbf{Q}(t)^T + \dot{\mathbf{Q}}(t) \mathbf{Q}(t)^T \right) \mathbf{Q}(t) \mathbf{A}_1 \mathbf{Q}(t)^T \]  

(8.91)

\[ = \mathbf{Q}(t) \mathbf{L}^T \mathbf{Q}(t)^T \mathbf{Q}(t) \mathbf{A}_1 \mathbf{Q}(t)^T + \dot{\mathbf{Q}}(t) \mathbf{Q}(t)^T \mathbf{Q}(t) \mathbf{A}_1 \mathbf{Q}(t)^T \]  

\[ = \mathbf{Q}(t) \mathbf{L}^T \mathbf{A}_1 \mathbf{Q}(t)^T - \dot{\mathbf{Q}}(t) \mathbf{A}_1 \mathbf{Q}(t)^T \]
This derivation leads us to the conclusion that

\[ A_2^* = \mathbf{A}_1^* + A_1^* \mathbf{L}^* + L^* \mathbf{A}_1^* \]  \hspace{1cm} (8.92)

i.e.

\[ A_2^* = Q(t) \mathbf{A}_1 Q(t)^T + Q(t) A_1 \mathbf{L} Q(t)^T + Q(t) \mathbf{L}^T A_1 Q(t)^T \]  \hspace{1cm} (8.93)

\[ = Q(t) \left( \mathbf{A}_1 + A_1 \mathbf{L} + \mathbf{L}^T A_1 \right) Q(t)^T \]  \hspace{1cm} (8.94)

That is, the property \( A_2 \) is frame indifferent. From above we have

\[ A_2^* = Q(t) A_2 Q(t)^T \]  \hspace{1cm} (8.94)

The second axiom of thermodynamics, however, may not necessarily be in accordance with this type of frame indifferent assumption.

8.8. Frame indifference of the convective stress tensor

Consider the rate assumption for the stress tensor as

\[ \dot{T} = f(T, D) \]  \hspace{1cm} (8.95)

A frame indifferent behavior must result in that a different frame denoted by (*)

\[ \dot{T}^* = f(T^*, D^*) \]  \hspace{1cm} (8.96)

The symmetric part of the velocity gradient and the stress tensor are transformed as

\[ \mathbf{D}^* = Q(t) \mathbf{D} Q(t)^T; \quad \mathbf{T}^* = Q(t) \mathbf{T} Q(t)^T \]  \hspace{1cm} (8.97)

It is noted that \( \dot{T}^* \) does not represent a isotropic function in space, i.e.

\[ \dot{T}^* = \dot{Q}(t) \mathbf{T} Q(t)^T + Q(t) \dot{\mathbf{T}} Q(t)^T + \dot{Q}(t) \mathbf{T} Q(t)^T \]  \hspace{1cm} (8.98)

Introduce the convective definition of the rate of the stress tensor as

\[ \dot{T} = \dot{T} - W^T \mathbf{T} + \mathbf{W} \dot{T}; \quad \dot{T}^* = \dot{T}^* - W^* \mathbf{T}^* + \mathbf{T}^* W^* \]  \hspace{1cm} (8.99)

where \( W = \frac{1}{2} (\mathbf{L} - \mathbf{L}^T) \). From above chapter it has been derived that

\[ \mathbf{W}^* = Q(t) \mathbf{W} Q(t)^T + \dot{Q}(t) \mathbf{Q}(t)^T = Q(t) \mathbf{W} Q(t)^T + \Omega \]  \hspace{1cm} (8.100)

where \( \Omega = -\Omega^T \).

The transformation rule is

\[ \dot{T}^* = Q(t) \dot{\mathbf{T}} Q(t)^T \]  \hspace{1cm} (8.101)

i.e.

\[ \dot{T}^* = \dot{T}^* - W^* \mathbf{T}^* + \mathbf{T}^* W^* \]  \hspace{1cm} (8.102)

\[ = \dot{Q}(t) \mathbf{T} Q(t)^T + Q(t) \dot{\mathbf{T}} Q(t)^T + \dot{Q}(t) \mathbf{T} Q(t)^T \]

\[ + \left( \mathbf{W} \dot{Q}(t)^T + \dot{Q}(t) \mathbf{Q}(t)^T \right) Q(t) \mathbf{T} Q(t)^T \]

\[ + Q(t) \dot{\mathbf{T}} Q(t)^T (\mathbf{W} Q(t)^T + \dot{Q}(t) \mathbf{Q}(t)^T) \]
Noting that \( Q(t)^T Q(t) = I \), reduces the above to

\[
\dot{T}^* = \dot{Q}(t) TQ(t)^T + Q(t) \dot{T}Q(t)^T + Q(t) T\dot{Q}(t)^T
+ Q(t) WTQ(t)^T + Q(t) TQ(t)^T \dot{Q}(t) Q(t)^T
\]

(8.103)

Using also that \( \dot{Q}(t) Q(t)^T = -Q(t) \dot{Q}(t)^T \) and again that \( Q(t)^T Q(t) = I \), one obtain

\[
\dot{T}^* = \dot{Q}(t) TQ(t)^T + Q(t) \dot{Q}(t)^T TQ(t) + Q(t) T\dot{Q}(t)^T
+ Q(t) TWQ(t)^T + Q(t) TQ(t)^T \dot{Q}(t) Q(t)^T
\]

(8.104)

That is

\[
\dot{T}^* = Q(t) \dot{T}Q(t)^T + Q(t) WTQ(t)^T + Q(t) TQ(t)^T
\]

(8.105)

The important conclusion is that when defining the material functions and the convective stress tensor as shown above the properties are frame indifferent.

8.9. Rate dependent vectors

Consider a situation were, for example, the heat flux vector is transformed as

\[
q^* = Q(t) \dot{q}
\]

(8.106)

and where the material time derivative of the same property becomes

\[
\ddot{q}^* = \dot{Q}(t) \dot{q} + Q(t) \ddot{q}
\]

(8.107)

That is, the property \( \dot{q} \) is not frame indifferent. Therefore it is tempting to assume the following convective rate dependent assumption, that is

\[
\dot{q} = \dot{q} - Wq; \ddot{q}^* = \dot{q}^* - W^* q^*
\]

(8.108)

The proper calculation gives

\[
\dot{q}^* = \dot{q}^* - W^* q^* = \dot{Q}(t) q + Q(t) \dot{q} - \left( Q(t) WQ(t)^T + \dot{Q}(t) Q(t)^T \right) Q(t) q
\]

(8.109)

\[
= \dot{Q}(t) q + Q(t) \dot{q} - Q(t) WQ(t)^T Q(t) q - \dot{Q}(t) Q(t)^T Q(t) q
\]

\[
= \dot{Q}(t) q + Q(t) \dot{q} - Q(t) Wq - \dot{Q}(t) q
\]

\[
= Q(t) (\dot{q} - Wq) = Q(t) \dot{q}
\]

Other types of assumption may be used. Consider for example the following
\[ T_r = f_r (q \otimes q) = f_r (q_r q_r^T) ; \quad q_r^* = Q_r q_r; \quad q_r'^* = q_r'^T Q_r^T \]  
\[ q_r'^* q_r'^T = Q_r q_r q_r^T Q_r^T ; \quad q_r'^\otimes q_r'^* = Q q \otimes q Q^T \]  
(8.110)
(8.111)

Or as time dependent vectors, such as

\[ \dot{q} \otimes \dot{q} = (\dot{q} - W_q) \otimes (\dot{q} - W_q) \]  
(8.112)

where

\[ \dot{T} = \ddot{T} - WT + TW + (\dot{q} - W_q) \otimes (\dot{q} - W_q) ; \]  
(8.113)

and

\[ \ddot{T}^* = \ddot{T}^* - (T^* - W^* T^* + T^* T^* + (q^* - W^* q^*) \otimes (q^* - W^* q^*) ) \]  
(8.114)

8.10. Material symmetry, material isotropy

The material isotropy which is to be discussed here should not be mixed up with the frame-indifference postulate. The important difference is that when studying the consequences of frame-indifference two observers are moving with a speed relatively to each others and therefrom observe the same physical event. When changing the frame the reference configuration is the same for both frames and the reference configuration is kept constant. When, on the other hand, studying material symmetry properties, such as isotropy, one which to study what happens with the material response function when having one single fixed coordinate system and let the material body rotate by 'testing' different reference configurations. If different directions of a hypothetical applied 'load' gives the same response in terms of, for example, stresses, the material is said to be isotropic. This special case can be studied by imagining having a fixed applied 'load' (and a fixed direction of the load) on a material and then rotate the material body.

The stress determined with a certain reference configuration \( \chi \) is the expression

\[ T = f_\chi (D, \rho, g) \]  
(8.115)

When rotating the material and assigning the 'new' positions in the material with a new reference configuration \( \tilde{\chi} \) (still subjecting the material to the same physical properties \( D, \rho \) and \( g \) with the same direction and magnitude as in the reference configuration \( \chi \) the stress may not necessarily be the same. The stress obtained if rotating the material is denoted \( \ddot{T} \) and is given by the material function \( f_\chi \) in the reference configuration \( \chi \), as

\[ \ddot{T} = f_\chi(\tilde{D}, \tilde{\rho}, \tilde{g}) \]  
(8.116)

The objectivity or frame indifference, discussed in previous sections, stated that the actual (or measured) material response is independent of the coordinate system we choose, and also independent of the rate of change of the rotation \( \dot{Q}(t) \) and translation \( \dot{\ell}(t) \) describing the relative rate between to frames. Applying this theory, also, for a case where the material is subjected to a rotation interpreted by letting the material having different reference configurations for different rotations, one may write

\[ \ddot{T} = Q(t) T Q(t)^T \text{ (objectivity)} \]  
(8.117)
and for the symmetric part of the velocity gradient $D$, frame-indifference (or objectivity) gives

$$\dot{D} = Q(t) D Q(t)^T \text{ (objectivity)} \quad (8.118)$$

The temperature gradient transformation is

$$\ddot{Q} = g Q(t)^T \quad (8.119)$$

Using the objectivity principles (8.117), (8.118) and (8.119) the relation (8.116) can be expressed as

$$\ddot{T} = f_x (\dot{D}, \rho, \ddot{g}) = f_x (Q(t) D Q(t)^T, \rho, g Q(t)^T) \quad (8.120)$$

Due to (8.117) and (8.115), the expression for $\ddot{T}$ can also be expressed as

$$\ddot{T} = Q(t) f_x (D, \rho, g) Q(t)^T \quad (8.121)$$

Combining (8.120) and (8.121) yields

$$f_x (Q(t) D Q(t)^T, \rho, g Q(t)^T) = Q(t) f_x (D, \rho, g) Q(t)^T \quad (8.122)$$

The special symmetry condition to be considered here is isotropy which implies that

$$f_x (\dot{D}, \rho, \ddot{g}) = f_x (\dot{D}, \rho, \ddot{g}) \quad (8.123)$$

The physical interpretation of (8.123) is that the material response (in terms of stresses) is the same for different direction of the material for a given applied fixed 'load'.

Using (8.120) and (8.122) it is seen that the relation between $f_x$ and $f_x$ transforms like a objective tensor

$$f_x (\dot{D}, \rho, \ddot{g}) = Q(t) f_x (D, \rho, g) Q(t)^T \quad (8.124)$$

This follows also directly from (8.115), (8.116) and (8.117). The combined requirement from the frame-indifference, i.e. (8.120) and the supplementary, assumed, condition of material symmetry, one obtain

$$f_x (\dot{D}, \rho, \ddot{g}) = Q(t) f_x (D, \rho, g) Q(t)^T \quad (8.125)$$

or, equally

$$f_x (Q(t) D Q(t)^T, \rho, g Q(t)^T) = Q(t) f_x (D, \rho, g) Q(t)^T \quad (isotropy) \quad (8.126)$$

That is, the material response for a given load is independent of the orientation of the body.

It should be mentioned that it is often explicitly assumed that a fluid is isotropic.

### 8.11. Invariants to symmetric tensors

Symmetric tensors such as the stress tensor $T$ include components which can be combined with certain mathematical operations to yield a scalar number. Some special combinations of components in a tensor results in a scalar number which remains the same if the same mathematical operation is performed with components in a transformed tensor $T^\ast$. Such a special scalar number is called an invariant. Here a discussion will be performed were it will be shown how some of the most important invariants can be obtained.
Consider the traction vector $t$ which is obtained by the linear equation

$$t = Tn$$  \hspace{1cm} (8.127)

where $n$ is the out-ward directed normalized vector to the surface on which the traction act. The stress component normal to the studied surface can be obtained as $n^T t = n^T Tn = T_{nn}$, i.e.

$$T_{nn} = n^T t$$  \hspace{1cm} (8.128)

In the same manner the shear stress $T_{nm}$ is obtained by the projection

$$T_{nm} = m^T t$$  \hspace{1cm} (8.129)

A special case where $t$ is colinear with $n$, i.e. the case when the direction of $n$ and $t$ is the same the length of the vector $t$ can be related to $n$ by a scalar number $\lambda$, as

$$t = \lambda n$$  \hspace{1cm} (8.130)

From (8.128) one obtain

$$T_{nn} = n^T t = n^T \lambda n = \lambda$$  \hspace{1cm} (8.131)

since $n$ is a normalized vector.

Hence, the relation between the traction stress $t$ and the stress tensor $T$, i.e. the expression (8.127) and the relation for the magnitude of the traction stress $t$ in the direction normal to the studied surface, i.e. expression (8.130) gives the following requirement

$$\lambda n = Tn$$  \hspace{1cm} (8.132)

i.e.

$$(T - \lambda I) n = 0$$  \hspace{1cm} (8.133)

This is the eigenvalue problem or the characteristic equation for the stress tensor $T$.

If a nontrivial solution $n$ is to exist, one must require

$$\text{det} (T - \lambda I) = 0$$  \hspace{1cm} (8.134)

furthermore, it is possible to show that for symmetric tensors all eigenvalues are real numbers, i.e.

$$T \text{ symmetric} \Rightarrow \text{all eigenvalues are real}$$

Writing the stress tensor $T$ in a Cartesian coordinate system as

$$T = \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix}$$  \hspace{1cm} (8.135)

when the expression (8.134) can be explicitly obtained as

$$\text{det} \begin{bmatrix} T_{11} - \lambda & T_{12} & T_{13} \\ T_{21} & T_{22} - \lambda & T_{23} \\ T_{31} & T_{32} & T_{33} - \lambda \end{bmatrix} =$$

$$(T_{11} - \lambda) (T_{22} - \lambda) (T_{33} - \lambda) +$$

$$T_{12} T_{23} T_{31} + T_{13} T_{21} T_{32} -$$

$$(T_{11} - \lambda) T_{23} T_{32} - T_{12} T_{21} (T_{33} - \lambda) -$$

$$T_{13} (T_{22} - \lambda) T_{31}$$
Consider, for example, a stress state given as

\[
T = \begin{bmatrix}
1 & 0 & -4 \\
0 & 5 & 4 \\
-4 & 4 & 3
\end{bmatrix}
\]  

(8.137)

The eigenvalue to this special stress state is determined as

\[
\det \begin{bmatrix}
1-\lambda & 0 & -4 \\
0 & 5-\lambda & 4 \\
-4 & 4 & 3-\lambda
\end{bmatrix} = -\lambda^3 + 9\lambda^2 + 9\lambda - 81 = 0
\]  

(8.138)

Solving the obtained cubic equation one obtain the roots

\[
\lambda_1 = 9, \quad \lambda_2 = 3, \quad \lambda_3 = -3
\]  

(8.139)

which corresponds to the so-called principal stresses \( T_1 = \lambda_1, \quad T_2 = \lambda_2 \) and \( T_3 = \lambda_3 \) at a given direction \( \mathbf{n} \) which can be determined by insert the values \( \lambda_1, \lambda_2 \) and \( \lambda_3 \) into (8.133) and also using the fact that the length of the vector \( \mathbf{n} \) is equal to one.

The principal stresses is

\[
T^{*p} = \begin{bmatrix}
T_1 & 0 & 0 \\
0 & T_2 & 0 \\
0 & 0 & T_3
\end{bmatrix}
\]  

(8.140)

where \( T^{*p} \) is used to denote the principal stresses which coincide with the principal directions which can be determined from (8.133). For the special stress state for \( T \) in (8.137) the principal stress, hence, becomes

\[
T^{*p} = \begin{bmatrix}
9 & 0 & 0 \\
0 & 3 & 0 \\
0 & 0 & -3
\end{bmatrix}
\]  

(8.141)

It turns out that the numbers determined from the equation (8.138) i.e. the numbers 9, 9, 81 in this example, can be calculated in a very systematic manner for arbitrary stress states, consider the equation (8.134), i.e.

\[
\det \begin{bmatrix}
T_{11} - \lambda & T_{12} & T_{13} \\
T_{21} & T_{22} - \lambda & T_{23} \\
T_{31} & T_{32} & T_{33} - \lambda
\end{bmatrix} = -\lambda^3 + \beta_1 \lambda^2 - \beta_2 \lambda + \beta_3 = 0
\]  

(8.142)

where \( \beta_1, \beta_2 \) and \( \beta_3 \) are the numbers to be calculated in an alternative manner compared to the method shown in (8.136). By algebraic operations it is possible to show that \( \beta_1, \beta_2 \) and \( \beta_3 \) are given by

\[
\beta_1 = \text{tr} T
\]  

(8.143)

\[
\beta_2 = \frac{1}{3} (\text{tr} T)^2 - \frac{1}{3} T^2
\]  

(8.144)

\[
\beta_3 = \det (T)
\]  

(8.145)

This means that (8.142) or equally (8.136) can be expressed as

\[
-\lambda^3 + \text{tr} T \lambda^2 - \left( \frac{1}{3} (\text{tr} T)^2 - \frac{1}{3} T^2 \right) \lambda + \det (T) = 0
\]  

(8.146)
In the example studied where the stress state is given by (8.137) on obtain

\[ \beta_1 = \text{tr} T = 1 + 5 + 3 = 9 \]  
\[ \beta_2 = \frac{1}{2} (\text{tr} T)^2 - \frac{1}{2} T^2 = \frac{1}{2} (9)^2 - \frac{1}{2} (1 + 16 + 25 + 16 + 16 + 9) = -9 \]  
\[ \beta_3 = \det (T) = 1 (15 - 16) + (\xi) (-20) = -81 \]

That, is an alternative way of determining the constants in, for example (8.138), is obtained, from which the principal stresses can be calculated.

It is noted that the characteristic equation satisfies its own solution which means that insertion of the calculated principal stresses into (8.146) results in

\[ -T_1^3 + \text{tr} T T_1^2 - \left( \frac{1}{2} (\text{tr} T)^2 - \frac{1}{2} T^2 \right) T_1 + \det (T) = 0 \]  
\[ -9^3 + (9)^2 = -9 + (-81) = 0 \]

where, again, the example of the stress state given in (8.137) is studied. The principal stress component \( T_2 \) is in the same manner obtained as

\[ -T_2^3 + \text{tr} T T_2^2 - \left( \frac{1}{2} (\text{tr} T)^2 - \frac{1}{2} T^2 \right) T_2 + \det (T) = 0 \]  
\[ -3^3 + (9)^3 = (-9) + (-81) = 0 \]

To show the remarkable properties of the \( \beta_1, \beta_2 \) and \( \beta_3 \) values, consider a rigid body rotation around the \( x_3 \)-axis, of coordinate points in which the rotation is described \( Q(t) \), as

\[ Q(t) = \begin{bmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \]  
(8.152)

where \( \varphi \) is the angle between the \( x_1 \) and \( x_1' \)-axis and also between the \( x_2 \) and \( x_2' \)-axis.

The stress is then transformed according

\[ T^* = Q(t) T Q(t)^T \]  
(8.153)

when the two systems \( x \) and \( x^* \) are studied, see previous sections, i.e.: \( T^* = \begin{bmatrix} \cos \varphi & -\sin \varphi & 0 \\ \sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \) \( \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix} \) \( \begin{bmatrix} \cos \varphi & \sin \varphi & 0 \\ -\sin \varphi & \cos \varphi & 0 \\ 0 & 0 & 1 \end{bmatrix} \) \( \begin{bmatrix} 1/\sqrt{2} & -1/\sqrt{2} & 0 \\ 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \) \( \begin{bmatrix} 1 \ 0 \ -4 \\ 0 \ 5 \ 4 \\ -1/\sqrt{2} \ 1/\sqrt{2} \ 0 \end{bmatrix} \) \( \begin{bmatrix} 3 \ -2 \ -5.6569 \\ -2 \ 3 \ 0 \\ -5.6569 \ 0 \ 3 \end{bmatrix} \) \( \begin{bmatrix} 1 \ 0 \ -4 \\ 0 \ 5 \ 4 \\ -1/\sqrt{2} \ 1/\sqrt{2} \ 0 \end{bmatrix} \) \( \begin{bmatrix} 3 \ -2 \ -5.6569 \\ -2 \ 3 \ 0 \\ -5.6569 \ 0 \ 3 \end{bmatrix} \)

As, an example, the rotation \( \varphi = 45^\circ \) of the axis will be studied, this choice gives the stress state evaluated when recording the stress state given in (8.137) in a different angel (or in a different frame), one obtain

\[ T^* = \begin{bmatrix} 3 \ -2 \ -5.6569 \\ -2 \ 3 \ 0 \\ -5.6569 \ 0 \ 3 \end{bmatrix} \]  
(8.154)
It turns out that the $\beta_1$, $\beta_2$ and $\beta_3$ values remain unaffected by the rotation, in the example, while the components in the stress tensor is not, e.g. compare (8.137) and (8.155).

By calculating $\text{tr}T^*$, $T^*^2$ and $\text{det} (T^*)$ for the rotation in the example studied one obtain

$$\beta_1 = \text{tr}T^* = 9$$
$$\beta_2 = \frac{1}{2} (\text{tr}T^*)^2 - \frac{1}{2} T^*^2 = -9$$
$$\beta_3 = \text{det} (T^*) = -81$$

(8.156)
(8.157)
(8.158)

That is $\beta_1$, $\beta_2$ and $\beta_3$ values remains unchanged. Indeed, any arbitrary rotation can be tested and still the $\beta_1$, $\beta_2$ and $\beta_3$ remains the same. Due to this fact the values $\text{tr}T$, $\frac{1}{2} (\text{tr}T)^2 - \frac{1}{2} T^2$ and $\text{det} (T^*)$ are called stress invariants. It should also be noted that all symmetric tensors have the same properties when it comes to the invariants. As an example $\text{tr}D$, $\frac{1}{2} (\text{tr}D)^2 - \frac{1}{2} D^2$ and $\text{det} (D)$ will always remain unchanged by a transformation given by $D^* = Q(t) D Q(t)^T$.

8.12. Isotropic material functions and the representation theory

An isotropic material which response for a given load is independent of the orientation of the body, can be formulated as

$$f_x(Q(t) D Q(t)^T, \rho, gQ(t)^T) = Q(t) f_x(D, \rho, g) Q(t)^T \text{ (isotropy)}$$

(8.159)

where also the objectivity requirement holds, i.e.

$$D^* = Q D Q^T, \quad T^* = Q T Q^T$$

(8.160)

The isotropic condition will be written, as

$$T = f_m(D); \quad T^* = f_m(D^*);$$

(8.161)

which indicates that the material response function $f_m$ is independent of the orientation.

Imagine a case where only principal directions in $D$ are active, but nothing is known about the stress state, this case is illustrated as

$$D = \begin{bmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{bmatrix}; \quad T = \begin{bmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{bmatrix};$$

(8.162)

Let us assume that the $x^*$-system is obtained by a $180^\circ$ rotation about the $x_1$-axis, when the transformation $Q$, i.e. the rotation matrix, is given by

$$Q = Q^T = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

(8.163)

Using the transformation rule $T^* = QTQ^T$, yields the ‘new’ stress state and principal directions for the symmetric part of the velocity gradient, as

$$T^* = \begin{bmatrix} T_{11} & -T_{12} & -T_{13} \\ -T_{21} & T_{22} & T_{23} \\ -T_{31} & T_{32} & T_{33} \end{bmatrix}; \quad D^* = \begin{bmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{bmatrix};$$

(8.164)
One obtain $D^* = D$ and it follows from the angular momentum that $T^*$ is symmetric. Consequently, one obtain $D^* = D$ and it follows from (8.161) that also $T^* = T$. Hence one must have $T_{22} = T_{33} = 0$ and also $T_{21} = T_{31} = 0$, which is obvious when (8.162) and (8.164) is compared together with (8.161).

Assume next that the $x^*$-system is obtained by a 180° rotation about the $x_2$-axis, when the transformation $Q$, i.e. the rotation matrix, is given by

$$Q = Q^T = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$ (8.165)

and using the same argument as above, it follows that $T_{23} = 0$ (and also, $T_{32} = 0$).

Consequently, it has been shown that if $D$ is diagonal, so is $T$. This means that the assumption of material isotropy means that the principal directions for $D$ and $T$ coincide.

Studying the material response function (8.161a) in a coordinate system colinear with the principal direction of $D$, only the principal directions of $T$ need to be considered

$$T_1 = h_1 (D_1, D_2, D_3); \quad T_2 = h_2 (D_1, D_2, D_3); \quad T_3 = h_3 (D_1, D_2, D_3)$$ (8.166)

where $h_1$, $h_2$ and $h_3$ are some functions related to a certain material.

$$T_1 = h_1 + \frac{\partial h_1}{\partial D_1} D_1 + \frac{1}{2} \frac{\partial^2 h_1}{\partial D_1^2} D_1^2 + \frac{1}{6} \frac{\partial^3 h_1}{\partial D_1^3} D_1^3 + \ldots$$ (8.167)

this is, for simplicity, rewritten as

$$T_1 = b_1 + b_2 D_1 + b_3 D_1^2 + b_4 D_1^3 + \ldots$$ (8.168)

The eigenvalue problem for the symmetric part of the velocity gradient is similar to the eigenvalue problem for the stress, therefore one can write

$$-D_1^2 + \beta_1 D_1 - \beta_2 D_1 + \beta_3 = 0$$ (8.169)

where $\beta_1$, $\beta_2$ and $\beta_3$ are invariants.

Expression (8.169) can by purely mathematical arguments be rearranged as

$$D_1^{3+p} = \beta_1 D_1^{2+p} - \beta_2 D_1^{1+p} + \beta_3 D_1^p$$ (8.170)

where $p$ is non-negative integers. For example, consider expression (8.168) written as

$$T_1 = b_1 + b_2 D_1 + b_3 D_1^2 + b_4 D_1^3 + b_5 D_1^4 + (\ldots)$$ (8.171)

Using (8.170) with $p = 0$, gives

$$D_1^2 = \beta_1 D_1^2 - \beta_2 D_1^1 + \beta_3$$ (8.172)

and with $p = 1$, one obtain

$$D_1^4 = \beta_1 D_1^4 - \beta_2 D_1^2 + \beta_3 D_1$$ (8.173)
Inserting, the expression for \( D_1^4 \) given from (8.173) into (8.171), yields
\[
T_1 = b_1 + b_2 D_1 + b_3 D_1^2 + b_4 D_1^3 + b_5 (\beta_1 D_1^3 - \beta_2 D_1^2 + \beta_3 D_1) \tag{8.174}
\]
then in the same manner, replacement of \( D_1^2 \) given from (8.172) into (8.174), yields
\[
T_1 = b_1 + b_2 D_1 + b_3 D_1^2 + b_4 (\beta_1 D_1^2 - \beta_2 D_1 + \beta_3) + b_5 (\beta_1 (\beta_1 D_1^2 - \beta_2 D_1 + \beta_3) - \beta_2 D_1^2 + \beta_3 D_1) \tag{8.175}
\]
That is, terms of a higher order than \( D_1^2 \) can always be eliminated by repeated use of (8.170). It is therefore concluded that the most general relation between \( T_1 \) and \( D_1 \) is
\[
T_1 = q_1 + r_1 D_1 + s_1 D_1^2
\]
Likewise, making a Taylor expansion of the function \( h_2 \) in (8.166b) about \( D_2 = 0 \) and for \( h_3 \) about \( D_3 = 0 \) in (8.166c), one obtain
\[
T_2 = p_2 + r_2 D_2 + s_2 D_2^2 \tag{8.176}
\]
\[
T_3 = p_3 + r_3 D_3 + s_3 D_3^2
\]
Therefore it is possible to write \( T = f(D) \), as
\[
T = P + RD + SD^2 \tag{8.177}
\]
or in matrix format, as
\[
\begin{bmatrix}
  p_1 & 0 & 0 \\
  0 & p_2 & 0 \\
  0 & 0 & p_3
\end{bmatrix}
\begin{bmatrix}
  r_1 & 0 & 0 \\
  0 & r_2 & 0 \\
  0 & 0 & r_3
\end{bmatrix}
\begin{bmatrix}
  s_1 & 0 & 0 \\
  0 & s_2 & 0 \\
  0 & 0 & s_3
\end{bmatrix}
\]
Consider
\[
T = f_m (D) ; \quad \text{where} \quad f_m (D) = P + RD + SD^2 \tag{8.179}
\]
The objectivity and material isotropy gives
\[
Q (t) f_m (D) Q (t)^T = f_m \left( Q (t) D Q (t)^T \right) \tag{8.180}
\]
By transforming this condition as
\[
Q (t)^T Q (t) f_m (D) Q (t)^T Q (t) = Q (t)^T f_m \left( Q (t) D Q (t)^T \right) Q (t) \tag{8.181}
\]
one obtain
\[
f_m (D) = Q (t)^T f_m \left( Q (t) D Q (t)^T \right) Q (t) \tag{8.182}
\]
Combining (8.179) and (8.182) gives
\[
P + RD + SD^2 = Q (t)^T f_m \left( Q (t) D Q (t)^T \right) Q (t) \tag{8.183}
\]
Rearranging this with aid of \( Q(t) \) one obtain

\[
 f_m \left( Q(t) D Q(t)^T \right) = P + R Q(t) D Q(t)^T + S Q(t) D^2 Q(t)^T
\]  

(8.184)

It is concluded that the following holds

\[
P + R D + S D^2 = Q(t)^T \left( P + R Q(t) D Q(t)^T + S Q(t) D^2 Q(t)^T \right) Q(t)
\]

(8.185)

i.e.

\[
\tilde{P} + \tilde{R} D + \tilde{S} D^2 = 0
\]

(8.186)

where

\[
\tilde{P} = P - Q(t)^T P Q(t); \quad \tilde{R} = R - Q(t)^T R Q(t); \quad \tilde{S} = S - Q(t)^T S Q(t)
\]

(8.187)

The properties \( P, R \) and \( S \) must behave objective i.e.

\[
P = Q(t)^T P Q(t); \quad R = Q(t)^T R Q(t); \quad S = Q(t)^T S Q(t)
\]

(8.188)

The only isotropic second-order tensor is \( k I \) where the factor \( k \) may depend on some invariant.

That is

\[
P = \alpha_1 I; \quad R = \alpha_2 I; \quad S = \alpha_3 I
\]

(8.189)

where \( \alpha_1, \alpha_2 \) and \( \alpha_3 \) may depend on the invariants of \( D \), e.g. \( trD \).

From (8.189) and (8.179) one conclude that for an isotropic material the stress must be related to \( D \) in the following manner

\[
T = \alpha_1 I + \alpha_2 D + \alpha_3 D^2
\]

(8.190)

which is a non-linear condition.

8.13. Principle of equipresence

The principle of equipresence states that all constitutive variables should depend one the same properties, as long as the other principles, such as the second axiom of thermodynamics, allows for such a dependency.

8.14. Restrictions imposed by the second axiom of thermodynamics

The second axiom of thermodynamics imposes restrictions on the choice of constitutive functions and is, perhaps, the most helpful principle when it comes to develop stringent continuum models. The second axiom of thermodynamics, or equally the entropy inequality will be used to develop equilibrium, non-equilibrium and near-equilibrium conditions for a mixture. The mixture will be restricted in the sense that only two phases are considered, a solid and a liquid phase, being built up by \( N \) number of constituents.
9. Constitutive functions

A case where two phases, i.e. a liquid phase \( l \) and a solid phase \( s \) will be considered. Both phases contain \( N \) constituents.

The Helmholtz free energies for the solid phase and the liquid phase are the assumptions

\[
A_s \left( T, \rho_s, C^l_s, E_s \right) ; \quad A_l \left( T, \rho_l, C^l_l, E_s \right)
\]  

(9.1)

The classical format of the pressure \( p_\alpha \) in the \( \alpha \)-phase and the definition of the Gibb's free energy tensor \( G_\alpha \) will be used, i.e.

\[
p_\alpha = \rho_\alpha \frac{\partial A_\alpha}{\partial \rho_\alpha}; \quad G_\alpha = A_\alpha I - \rho_\alpha^{-1} E_\alpha
\]  

(9.2)

The classical effective stress tensor \( t^s_\alpha \) for the solid phase and the so-called hydration stress tensor \( t^l_\alpha \) are defined by the Helmholtz free energies \( A_\alpha \) for the phases, as

\[
t^s_\alpha = \rho_s F_s \frac{\partial A_s}{\partial E_s} F_s^T; \quad t^l_\alpha = \rho_l F_s \frac{\partial A_l}{\partial E_s} F_s^T
\]  

(9.3)

Further, the chemical potential scalar \( \mu^l_\alpha \) will be defined by the derivative

\[
\mu^l_\alpha = \frac{\partial A_\alpha}{\partial E_\alpha}
\]  

(9.4)

The Green-Lagrange strain rate, i.e.

\[
E_s = \frac{1}{2} (F_s^T F_s - I)
\]  

(9.5)

will be adopted, e.g. see equation (2.69).

The material time derivative of \( A_t \left( T, \rho_l, C^l_l, E_s \right) \) can by differentiation be expressed as

\[
\frac{D_t A_t}{D t} = \frac{\partial A_t}{\partial T} \frac{D_t T}{D t} + \frac{\partial A_t}{\partial \rho_l} \frac{D_t \rho_l}{D t} + \sum_{j=1}^{N} \frac{\partial A_t}{\partial C^l_j} \frac{D_t C^l_j}{D t} + \text{tr} \left( \frac{\partial A_t}{\partial E_s} \frac{D_t E_s}{D t} \right)
\]  

(9.6)

where the Green-Lagrange strain rate is given as

\[
\frac{D_t E_s}{D t} = F_s^T \mathbf{d}_s F_s
\]  

(9.7)

which has been derived in equation (2.116).

Using next the identities give by equation (2.29), i.e.

\[
\frac{D_t \Gamma}{D t} - \frac{D \Gamma}{D t} = \mathbf{u}_s \cdot \text{grad} \Gamma; \quad \frac{D_t \Gamma}{D t} - \frac{D \Gamma}{D t} = \mathbf{u}_l \cdot \text{grad} \Gamma
\]  

(9.8)

That is the equations in (9.8) verifies that material time derivative of an arbitrary property \( \Gamma \) following the motion of the liquid and the motion of the liquid phase are related by

\[
\frac{D_t \Gamma}{D t} = \frac{D \Gamma}{D t} + (\mathbf{u}_l - \mathbf{u}_s) \cdot \text{grad} \Gamma
\]  

(9.9)
With the property $\Gamma$ identified as $\Gamma = \mathbf{E}_s$, the equation (9.9) becomes

$$
\frac{D_t \mathbf{E}_s}{D t} = \frac{D_t \mathbf{E}_s}{D t} + \text{grad} \mathbf{E}_s \cdot (\mathbf{u}_t - \mathbf{u}_s)
$$

(9.10)

The hydration stress tensor $t^i_j$ can by the definition (9.3) be written as

$$
\mathbf{F}_s^{-1} \frac{1}{\rho_t} t^i_j = \mathbf{F}_s^{-1} \mathbf{F}_s \frac{\partial A_t}{\partial \mathbf{E}_s} \mathbf{F}_s^T = \frac{\partial A_t}{\partial \mathbf{E}_s} \mathbf{F}_s^T
$$

(9.11)

when multiplied with deformation gradient $\mathbf{F}_s^{-1}$ and noting that the relation $\mathbf{F}_s \mathbf{F}_s^{-1} = \mathbf{F}_s = \mathbf{I}$ holds, i.e. see equation (2.32).

The last term present in (9.6) can be formulated as

$$
\frac{\partial A_t}{\partial \mathbf{E}_s} \frac{D_t \mathbf{E}_s}{D t} = \frac{\partial A_t}{\partial \mathbf{E}_s} \mathbf{F}_s^T \mathbf{d}_s \mathbf{F}_s = \mathbf{F}_s^{-1} \frac{1}{\rho_t} t^i_j \mathbf{d}_s \mathbf{F}_s = \frac{1}{\rho_t} t^i_j \mathbf{d}_s
$$

(9.12)

by using the relations (9.7), (9.11) and $\mathbf{F}_s^{-1} \mathbf{F}_s = \mathbf{I}$.

The relation (9.10) multiplied with $\frac{\partial A_t}{\partial \mathbf{E}_s}$ becomes

$$
\frac{\partial A_t}{\partial \mathbf{E}_s} \frac{D_t \mathbf{E}_s}{D t} = \frac{\partial A_t}{\partial \mathbf{E}_s} \frac{D_t \mathbf{E}_s}{D t} + \left( \frac{\partial A_t}{\partial \mathbf{E}_s} \text{grad} \mathbf{E}_s \right) \cdot (\mathbf{u}_t - \mathbf{u}_s)
$$

(9.13)

Taking the trace of this expression and using (9.12) yields

$$
\text{tr} \left( \frac{\partial A_t}{\partial \mathbf{E}_s} \frac{D_t \mathbf{E}_s}{D t} \right) = \frac{1}{\rho_t} \text{tr} (t^i_j \mathbf{d}_s) + \text{tr} \left( \frac{\partial A_t}{\partial \mathbf{E}_s} \text{grad} \mathbf{E}_s \right) \cdot (\mathbf{u}_t - \mathbf{u}_s)
$$

(9.14)

That is, the material time derivative for $A_t$ in (9.6) can by (9.14) be written as

$$
\frac{D_t A_t}{D t} = \frac{\partial A_t}{\partial T} \frac{D_t T}{D t} + \frac{\partial A_t}{\partial \rho_t} \frac{D_t \rho_t}{D t} + \sum_{j=1}^{N-1} \frac{\partial A_t}{\partial C^j_s} \frac{D_t C^j_s}{D t} + \frac{1}{\rho_t} \text{tr} (t^i_j \mathbf{d}_s) + \text{tr} \left( \frac{\partial A_t}{\partial \mathbf{E}_s} \text{grad} \mathbf{E}_s \right) \cdot (\mathbf{u}_t - \mathbf{u}_s)
$$

(9.15)

The material time derivative for $A_s$ ($T, \rho_s, C^j_s, \mathbf{E}_s$) can by differentiation be formulated

$$
\frac{D_t A_s}{D t} = \frac{\partial A_s}{\partial T} \frac{D_t T}{D t} + \frac{\partial A_s}{\partial \rho_s} \frac{D_t \rho_s}{D t} + \sum_{j=1}^{N-1} \frac{\partial A_s}{\partial C^j_s} \frac{D_t C^j_s}{D t} + \text{tr} \left( \frac{\partial A_s}{\partial \mathbf{E}_s} \frac{D_t \mathbf{E}_s}{D t} \right)
$$

(9.16)

where it is noted that the last term in (9.16) can be written as

$$
\frac{\partial A_s}{\partial \mathbf{E}_s} \frac{D_t \mathbf{E}_s}{D t} = \frac{\partial A_s}{\partial \mathbf{E}_s} \mathbf{F}_s^T \mathbf{d}_s \mathbf{F}_s = \mathbf{F}_s^{-1} \frac{1}{\rho_s} t^i_j \mathbf{d}_s \mathbf{F}_s = \frac{1}{\rho_s} t^i_j \mathbf{d}_s
$$

(9.17)
where the same procedure used in receiving (9.12) was adopted. That is, (9.16) can also be formulated as

$$\frac{D_s A_s}{Dt} = \frac{\partial A_s}{\partial T} \frac{D_T}{Dt} + \frac{\partial A_s}{\partial \rho_s} \frac{D\rho_s}{DT} + \sum_{j=1}^{N-1} \frac{\partial A_s}{\partial C_s^j} \frac{D C_s^j}{Dt}$$

$$+ \frac{1}{\rho_s} \text{tr} (t_s^2 d_s)$$

(9.18)

With the thermodynamic definitions for the pressure in the two phases, i.e. \( p_o = \rho_o^2 \frac{\partial A_o}{\partial p_o} \), the proper function for \( D_t A_t / Dt \), corresponding to the constitutive function (9.3b) is

$$\frac{D_t A_t}{Dt} = \frac{\partial A_t}{\partial T} \frac{D_T}{Dt} + \frac{p_o}{\rho_o^2} \frac{D \rho_o}{DT} + \sum_{j=1}^{N-1} \frac{\partial A_t}{\partial E_t} \frac{D E_t}{Dt}$$

$$+ \frac{1}{\rho_t} \text{tr} (t_t^2 d_s) + \text{tr} \left( \frac{\partial A_t}{\partial E_t} \text{grad} E_t \right) \cdot (u_t - u_s)$$

(9.19)

And the function for \( D_s A_s / Dt \), corresponding to the constitutive function (9.3a) is

$$\frac{D_s A_s}{Dt} = \frac{\partial A_s}{\partial T} \frac{D_T}{Dt} + \frac{p_s}{\rho_s^2} \frac{D \rho_s}{DT} + \sum_{j=1}^{N-1} \frac{\partial A_s}{\partial C_s^j} \frac{D C_s^j}{Dt}$$

$$+ \frac{1}{\rho_s} \text{tr} (t_s^2 d_s)$$

(9.20)

The functions (9.19) and (9.20) will be used when examining the entropy inequality as expressed in equation (7.59).

10. Classical properties of the chemical potential

In classical Gibbsian thermodynamics, the chemical potential is defined to be the change of the total extensive Helmholtz potential, \( A \), with respect to the number of molecules of constituent \( j \), \( n_j \), keeping temperature, volume, and the number of molecules of all other constituents fixed, i.e. \( \partial A / \partial n_j \bigg|_{T,V,n} \). The following properties hold in this classical format.

1. It is a scalar quantity representing the amount of chemical energy required to insert/remove a molecule of constituent \( j \) (by definition).
2. At equilibrium, the chemical potential of a single constituent in different phases is the same.
3. The chemical potential is the driving force for diffusive flow. In particular, at equilibrium the gradient of the chemical potential is zero.

Note that the above properties do not imply that at equilibrium the chemical potentials of two different constituents are the same. It is especially important that property 3 holds, as it is the property used to indirectly measure the chemical potential.

Later the difference of the tensorial chemical potential, introduced by Bowen, and the classical scalar chemical potential will be pointed out.
11. Adding a virtual force in the inequality

A method where one add terms to the entropy inequality which is equal to zero will be adopted. The mass balance equation for the phase \( \alpha \), i.e. equation (3.9), the mass balance for the \( j \)th constituent within phase \( \alpha \), i.e. equation (3.35), and the condition for the diffusion velocities for constituents, i.e. equation (2.17), will be used. The virtual force adopted is

\[
\Lambda_f = 0 = \sum_{\alpha=l,s} \lambda_\alpha \left( \frac{D_\alpha (\varepsilon_\alpha \rho_\alpha)}{Dt} + \varepsilon_\alpha \rho_\alpha \text{div} (v_\alpha) - \dot{\varepsilon}_\alpha \right) \\
+ \sum_{\alpha=l,s} \sum_{j=1}^{N-1} \lambda_j \left( \varepsilon_\alpha \rho_\alpha \frac{D_j (C_j)}{Dt} + \text{div} (\varepsilon_\alpha \rho_\alpha^j u_\alpha^j) - \dot{\varepsilon}_\alpha^j - \dot{\varepsilon}_\alpha + C_j \dot{\varepsilon}_\alpha \right) \\
+ \sum_{\alpha=l,s} \varepsilon_\alpha \frac{\Gamma^N}{N} \sum_{j=1}^{N} \text{grad} (\rho_j^j u_\alpha^j)
\]

where \( \lambda_\alpha \), \( \lambda_j \), and \( \Gamma^N \) are the so-called Lagrange multipliers.

The terms in (11.1) will be re-written to fit the inequality. Consider the partial differentiation of the first term of the first row of equation (11.1), i.e.

\[
\frac{D_\alpha (\varepsilon_\alpha \rho_\alpha)}{Dt} = \varepsilon_\alpha \frac{D_\alpha (\rho_\alpha)}{Dt} + \rho_\alpha \frac{D_\alpha (\varepsilon_\alpha)}{Dt}
\]

The equation (2.29) are used for the solid and liquid phase as

\[
\frac{D_s \Gamma}{Dt} - \frac{D_l \Gamma}{Dt} = u_s \cdot \text{grad} \Gamma; \quad \frac{D_s \Gamma}{Dt} - \frac{D_l \Gamma}{Dt} = u_l \cdot \text{grad} \Gamma
\]

Setting \( \Gamma = \varepsilon_l \) these equations combine to yield

\[
\rho_l \frac{D_l \varepsilon_l}{Dt} = \rho_l \frac{D_s \varepsilon_l}{Dt} + \rho_l (u_l - u_s) \cdot \text{grad} \varepsilon_l
\]

where the whole expression has been multiplied with \( \rho_l \). The first term of the first row of equation (11.1) involving the derivative of \( \varepsilon_\alpha \) can be written

\[
\sum_{\alpha=l,s} \lambda_\alpha \rho_\alpha \frac{D_\alpha (\varepsilon_\alpha)}{Dt} = \lambda_l \rho_l \frac{D_s \varepsilon_l}{Dt} + \lambda_s \rho_s \frac{D_s \varepsilon_s}{Dt}
\]

Combining (11.4) and (11.5) gives

\[
\sum_{\alpha=l,s} \lambda_\alpha \rho_\alpha \frac{D_\alpha (\varepsilon_\alpha)}{Dt} = \lambda_l \rho_l \frac{D_s \varepsilon_l}{Dt} + \lambda_l \rho_l (u_l - u_s) \cdot \text{grad} \varepsilon_l + \lambda_s \rho_s \frac{D_s \varepsilon_s}{Dt}
\]

Note also that the volume fractions for the two considered phases are related as: \( \varepsilon_s + \varepsilon_l = 1 \), hence, the material derivatives following the motion of the solid phase must be related as

\[
\frac{D_s \varepsilon_s}{Dt} = -\frac{D_s \varepsilon_l}{Dt}
\]
The expressions (11.6) and (11.7) combines to yield

\[ \sum_{\alpha=1,s} \rho_\alpha \frac{D \alpha (\varepsilon_\alpha)}{Dt} = \rho_1 \frac{D \varepsilon_1}{Dt} + \rho_s (\mathbf{u}_s - \mathbf{u}_s) \cdot \text{grad} \varepsilon_1 - \rho_s \frac{D \varepsilon_1}{Dt} \]  

(11.8)

Consider next the term div(\(\mathbf{v}_\alpha\)) in the first row of (11.1). This term can be re-written with the identities

\[ \text{div}(\mathbf{v}_\alpha) = \text{tr}(\text{grad} \mathbf{v}_\alpha) = \text{tr} \mathbf{d}_\alpha \]  

(11.9)

where the velocity gradient \(\mathbf{d}_\alpha\) is defined as \(\mathbf{d}_\alpha = \text{grad} \mathbf{v}_\alpha\). That is the sum involving div(\(\mathbf{v}_\alpha\)) in the first row of (11.1) can, therefore, be written as

\[ \sum_{\alpha=1,s} \lambda_\alpha \varepsilon_\alpha \rho_\alpha \text{div}(\mathbf{v}_\alpha) = \sum_{\alpha=1,s} \lambda_\alpha \text{tr}(\text{grad} \mathbf{v}_\alpha (\varepsilon_\alpha \rho_\alpha I)) \]  

(11.10)

The last row in (11.1) can be re-written with the identity

\[ \varepsilon_\alpha \text{tr} \left( \Gamma_\alpha^N \sum_{j=1}^N \text{grad} (\rho_\alpha^j \mathbf{u}_\alpha^j) \right) = \varepsilon_\alpha \text{tr} \left( \sum_{j=1}^N \rho_\alpha^j \text{grad} (\mathbf{u}_\alpha^j) \Gamma_\alpha^N \right) \]  

(11.11)

The term \(\lambda_\alpha \text{div}(\varepsilon_\alpha \rho_\alpha^j \mathbf{u}_\alpha^j)\) in (11.1) can by using partial derivatives be written as

\[ \lambda_\alpha \text{div}(\varepsilon_\alpha \rho_\alpha^j \mathbf{u}_\alpha^j) = \lambda_\alpha \varepsilon_\alpha \rho_\alpha^j \text{div}(\mathbf{u}_\alpha^j) + \lambda_\alpha \varepsilon_\alpha \rho_\alpha^j \text{grad}(\varepsilon_\alpha \rho_\alpha^j) \]  

(11.12)

Further, the first term on the right hand side of (11.12) can be replaced by the identity

\[ \lambda_\alpha \varepsilon_\alpha \rho_\alpha^j \text{div}(\mathbf{u}_\alpha^j) = \lambda_\alpha \text{tr}(\text{grad} \mathbf{u}_\alpha^j (\varepsilon_\alpha \rho_\alpha^j I)) \]  

(11.13)

i.e.

\[ \lambda_\alpha \text{div}(\varepsilon_\alpha \rho_\alpha^j \mathbf{u}_\alpha^j) = \lambda_\alpha \text{tr}(\text{grad} \mathbf{u}_\alpha^j (\varepsilon_\alpha \rho_\alpha^j I)) + \lambda_\alpha \varepsilon_\alpha \rho_\alpha^j \cdot \text{grad}(\varepsilon_\alpha \rho_\alpha^j) \]  

(11.14)

The identities (11.8), (11.10), (11.11) and (11.14) are used in the virtual force equation (11.1) to obtain the alternative version
\[ \Lambda_I = 0 = \sum_{\alpha = l, s} \lambda_\alpha \left( \varepsilon_\alpha \frac{D_\alpha (\rho_\alpha)}{Dt} + \text{tr} \left( d_\alpha (\varepsilon_\alpha \rho_\alpha I) \right) - \dot{e}_\alpha \right) \]  

This equation will be added to the entropy inequality given by (7.59), which is possible since the expression (11.1) always is identical to zero.

12. The entropy inequality for the two phase case

Before proceeding with the method of deriving constitutive equations for the studied two phase system containing \( N \) number of constituents in each phase, an important assumption will be made. It will be assumed that the momentum supply terms \( T_l \) and \( T_s \), i.e. the momentum supply to the liquid and solid phase, respectively, is related as

\[ \dot{T}_l = -\dot{T}_s \]  

It must be carefully noted that this relation do not steam from the derived conditions for the exchange terms in the mixture. The condition in (12.1) should rather be seen as a super imposed assumption.

Due to the assumption (12.1) the terms in the entropy inequality (7.59) involving \( u_\alpha \), simply, becomes

\[ \sum_{\alpha = l, s} u_\alpha \cdot \dot{T}_\alpha = (u_l - u_s) \cdot \dot{T}_l \]  

By combining the entropy inequality (7.59) with the virtual force equation (11.15) and also using the assumption (12.2) and the definition (7.63) one obtain the following condition
\[ \Lambda = -\sum_{\alpha=l,s} \varepsilon_{\alpha} \rho_{\alpha} \eta_{\alpha} \frac{D_{\alpha} T}{Dt} \\
-\varepsilon_{l} \rho_{l} \left( \frac{\partial A_{l}}{\partial T} \frac{Dt}{Dt} + \frac{p_{l} D_{l} \rho_{l}}{\rho_{l}^2} + \sum_{j=1}^{N-1} \frac{\mu_{j} D_{l} C_{l}^{j}}{Dt} \right) \\
-\varepsilon_{l} \rho_{l} \left( \frac{1}{\rho_{l}} \text{tr} \left( t_{l}^{j} d_{s} \right) + \text{tr} \left( \frac{\partial A_{l}}{\partial E_{s}} \text{grad} E_{s} \right) \cdot (u_{l} - u_{s}) \right) \\
+ \frac{D_{l} \varepsilon_{l}}{Dt} \left( (\lambda_{l} \rho_{l} - \lambda_{s} \rho_{s}) + (u_{l} - u_{s}) \cdot \rho_{l} \text{grad} \varepsilon_{l} \right) \\
- (u_{l} - u_{s}) \cdot \hat{T}_{l} \\
-\varepsilon_{s} \rho_{s} \left( \frac{\partial A_{s} D_{s} T}{\partial T} \frac{Dt}{Dt} + \frac{p_{s} D_{s} \rho_{s}}{\rho_{s}^2} + \sum_{j=1}^{N-1} \frac{\mu_{j} D_{s} C_{s}^{j}}{Dt} + \frac{1}{\rho_{s}} \text{tr} \left( t_{s}^{j} d_{s} \right) \right) \\
+ \text{tr} \varepsilon_{s} d_{s} \left( t_{s} + \sum_{j=1}^{N} \rho_{s} t_{s}^{j} \otimes u_{s}^{j} + \lambda_{s} \rho_{s} I \right) \\
+ \text{tr} \varepsilon_{s} d_{s} \left( t_{s} + \sum_{j=1}^{N} \rho_{s} t_{s}^{j} \otimes u_{s}^{j} + \lambda_{s} \rho_{s} I \right) \\
+ \sum_{\alpha=l,s} \varepsilon_{\alpha} \sum_{j=1}^{N} \text{tr} \left( \text{grad} u_{\alpha}^{j} \right) \left( t_{\alpha}^{j} + \lambda_{\alpha}^{j} \rho_{\alpha}^{j} I - \rho_{\alpha}^{j} A_{\alpha}^{j} I + \rho_{\alpha}^{j} C_{\alpha}^{j} \right) \\
+ \sum_{\alpha=l,s} \sum_{j=1}^{N} u_{\alpha}^{j} \cdot \left( - \hat{T}_{\alpha}^{j} + \gamma_{\alpha}^{j} \right) - \text{grad} \left( \varepsilon_{\alpha} \rho_{\alpha}^{j} A_{\alpha}^{j} \right) \\
+ \sum_{\alpha=l,s} \sum_{j=1}^{N} u_{\alpha}^{j} \cdot \left( \lambda_{\alpha}^{j} \text{grad} \left( \varepsilon_{\alpha} \rho_{\alpha}^{j} \right) + \Gamma_{\alpha}^{N} \text{grad} \left( \rho_{\alpha}^{j} \right) \right) \\
- \sum_{\alpha=l,s} \sum_{j=1}^{N} u_{\alpha}^{j} \cdot \left( \varepsilon_{\alpha}^{j} + \varepsilon_{\alpha}^{j} \right) \frac{1}{2} u_{\alpha}^{j} + \sum_{\alpha=l,s} \sum_{j=1}^{N-1} \lambda_{\alpha}^{j} \left( - \varepsilon_{\alpha}^{j} - \varepsilon_{\alpha}^{j} + C_{\alpha}^{j} \varepsilon_{\alpha} \right) \\
- \text{grad} \left( T \right) \sum_{\alpha=l,s} \left( q_{\alpha} + \sum_{j=1}^{N} \varepsilon_{\alpha}^{j} u_{\alpha}^{j} - \sum_{j=1}^{N} \rho_{\alpha}^{j} u_{\alpha}^{j} \left( A_{\alpha}^{j} - \frac{1}{2} \rho_{\alpha}^{j} u_{\alpha}^{2j} \right) \right) \\
+ \sum_{\alpha=l,s} \lambda_{\alpha} \left( \frac{D_{\alpha} \left( \rho_{\alpha} \right)}{Dt} - \dot{\varepsilon}_{\alpha} \right) - \sum_{\alpha=l,s} \varepsilon_{\alpha} A_{\alpha} \\
+ \sum_{\alpha=l,s} \sum_{j=1}^{N-1} \lambda_{\alpha}^{j} \left( \varepsilon_{\alpha} \rho_{\alpha} C_{\alpha}^{j} \right) \frac{D_{\alpha} \left( C_{\alpha}^{j} \right)}{Dt} \geq 0 \]
This inequality will be re-arrange in order to fit the purpose of validate different constitutive functions and in order to derive equilibrium and non-equilibrium conditions. By collecting terms associated with the material derivatives $D\alpha\left(\rho\alpha\right)/Dt$, $D\alpha\left(C_{\alpha}\right)/Dt$, $D\alpha T/Dt$ and $D\alpha\varepsilon_{l}/Dt$ and with the terms $\text{tr}\varepsilon_{l}d_{l}$, $\text{tr}\varepsilon_{s}d_{s}$, $(u_{l} - u_{s})$, $\text{grad}u_{l}^{i}$, $u_{l}^{i}$, $\varepsilon_{l}^{i}$, $\partial_{l}^{i}$, $\varepsilon_{l}$ and $\text{grad}(T)$ in (12.3), one obtain...
\[ \Lambda = \sum_{\alpha=1,s} \frac{D_\alpha \rho_\alpha}{Dt} \left( \lambda_\alpha \varepsilon_\alpha - \varepsilon_\alpha \frac{p_\alpha}{\rho_\alpha} \right) \]

\[ + \sum_{\alpha=1,s} \sum_{j=1}^{N-1} \frac{D_\alpha C_{\alpha j}^f}{Dt} \left( \varepsilon_\alpha \rho_\alpha \lambda_{\alpha j}^f - \varepsilon_\alpha \rho_\alpha \tilde{p}_\alpha^f \right) \]

\[ - \sum_{\alpha=1,s} \varepsilon_\alpha \rho_\alpha \frac{D_\alpha T}{Dt} \left( \eta_\alpha + \frac{\partial A_\alpha}{\partial T} \right) \]

\[ + \text{tr} \varepsilon_i \mathbf{d}_i \left( t_i + \sum_{j=1}^{N} \rho_i^j \mathbf{u}_i^j \otimes \mathbf{u}_i^j + \lambda_1 \rho_1 \mathbf{I} \right) \]

\[ + \text{tr} \varepsilon_s \mathbf{d}_s \left( t_s + \sum_{j=1}^{N} \rho_s^j \mathbf{u}_s^j \otimes \mathbf{u}_s^j + \lambda_s \rho_s \mathbf{I} - \varepsilon_s t_s^j - t_s^j \right) \]

\[ + (\mathbf{u}_i - \mathbf{u}_s) \cdot \left( \rho_i \text{grad} \varepsilon_i - \varepsilon_i \rho_i \text{tr} \left( \frac{\partial A_i}{\partial \mathbf{E}_s} \text{grad} \mathbf{E}_s \right) - \mathbf{T}_i \right) \]

\[ + \frac{D_s \varepsilon_i}{Dt} (\lambda_1 \rho_1 - \lambda_s \rho_s) \]

\[ + \sum_{\alpha=1,s} \varepsilon_\alpha \sum_{j=1}^{N} \text{tr} \left( \text{grad} \mathbf{u}_\alpha^j \right) \left( \varepsilon_\alpha \rho_\alpha^j \mathbf{I} - \rho_\alpha^j A_\alpha^j \mathbf{I} + \rho_\alpha^j \mathbf{F}_\alpha^N \right) \]

\[ + \sum_{\alpha=1,s} \sum_{j=1}^{N} \mathbf{u}_\alpha^j \cdot \left( - \left( \mathbf{T}_\alpha^j + \mathbf{u}_\alpha^j \right) - \text{grad} (\varepsilon_\alpha \rho_\alpha^j A_\alpha^j) \right) \]

\[ + \sum_{\alpha=1,s} \sum_{j=1}^{N} \mathbf{u}_\alpha^j \cdot \left( \lambda_\alpha \text{grad} (\varepsilon_\alpha \rho_\alpha^j) + \varepsilon_\alpha \mathbf{F}_\alpha^N \text{grad} (\rho_\alpha^j) \right) \]

\[ - \sum_{\alpha=1,s} \sum_{j=1}^{N} \mathbf{u}_\alpha^j \cdot \left( \varepsilon_i^j + \varepsilon_s^j \right) \frac{1}{2} \mathbf{u}_\alpha^j \]

\[ - \sum_{j=1}^{N-1} \varepsilon_\alpha^j \left( \lambda_\alpha^j - \lambda_\alpha^j \right) - \sum_{j=1}^{N-1} \varepsilon_s^j \left( \lambda_\alpha^j - \lambda_\alpha^j \right) \]

\[ - \varepsilon_i \left( \lambda_i - \lambda_s + \sum_{j=1}^{N-1} \left( C_{\alpha j}^f \lambda_{\alpha j}^f - C_{\alpha j}^f \lambda_{\alpha j}^f \right) + A_i - A_s \right) \]

\[ - \frac{\text{grad} (T)}{T} \sum_{\alpha=1,s} \left( q_\alpha + \sum_{j=1}^{N} t_{\alpha j}^m \mathbf{u}_\alpha^j - \sum_{j=1}^{N} \rho_\alpha^j \mathbf{u}_\alpha^j (A_\alpha^j - \frac{1}{2} \rho_\alpha^j \mathbf{u}_\alpha^j) \right) \geq 0 \]

This expression is suited for evaluating equilibrium and non-equilibrium results. This will be the subject for the next sections.
12.1. General non-equilibrium Results

The special form of the entropy inequality (12.4) must hold under general variations of state variables. This results in that some properties must be related to each other in a special way. Here it will be shown how such relations can be developed under the conditions that the Helmholtz free energies of the solid and liquid phase are given by the material functions \( A_s(T, \rho_s, C_s^j, E_s) \) and \( A_l(T, \rho_l, C_l^j, E_l) \). The so-called Lagrange multipliers introduced into the virtual force equation (11.15) will also be defined by the procedure to be described.

Let the following properties be arbitrary defining a non-equilibrium state

\[
\frac{D_\alpha T}{Dt} \quad \frac{D_\alpha \rho_\alpha}{Dt} \quad \frac{D_\alpha C_{\alpha}^j}{Dt} \quad \delta_\alpha \quad \text{grad} \mathbf{u}_\alpha^j
\]  

(12.5)

The part of the inequality (12.4) involving the term \( D_\alpha T/DT \) is

\[
\Lambda_{D_\alpha T} = - \sum_{\alpha=i,s} \frac{D_\alpha T}{Dt} \varepsilon_{\alpha\alpha} \rho_\alpha \left( \frac{\partial A_\alpha}{\partial T} + \eta_\alpha \right) \geq 0
\]

(12.6)

That is, if \( D_\alpha T/DT \) is arbitrary, according to the general non-equilibrium state defined in (12.5), the inequality (12.4) gives that \( \partial A_\alpha/\partial T \) and \( \eta_\alpha \) for the two considered phases must be related, as

\[
\sum_{\alpha=i,s} \varepsilon_{\alpha\alpha} \rho_\alpha \left( \frac{\partial A_\alpha}{\partial T} + \eta_\alpha \right) = 0
\]

(12.7)

The part of the inequality (12.4) involving the term material time derivative of \( \rho_\alpha \) is

\[
\Lambda_{D_\alpha \rho_\alpha} = \sum_{\alpha=i,s} \frac{D_\alpha \rho_\alpha}{Dt} \left( \varepsilon_{\alpha\alpha} \lambda_\alpha - \varepsilon_{\alpha\alpha} \frac{p_\alpha}{\rho_\alpha} \right) \geq 0
\]

(12.8)

In a general non-equilibrium state \( D_\alpha \rho_\alpha/DT \) is arbitrary, hence the Lagrange multiplier \( \lambda_\alpha \) must be defined, as

\[
\lambda_\alpha = \frac{p_\alpha}{\rho_\alpha}
\]

(12.9)

The term in (12.4) involving \( D_\alpha C_{\alpha}^j/DT \) is

\[
\Lambda_{D_\alpha C_{\alpha}^j} = \sum_{\alpha=i,s} \sum_{j=1}^{N-1} \frac{D_\alpha C_{\alpha}^j}{Dt} \left( \varepsilon_{\alpha\rho_\alpha} \lambda_\alpha^j - \varepsilon_{\alpha\rho_\alpha} \tilde{\nu}_\alpha^j \right) \geq 0
\]

(12.10)

For arbitrary choices of \( D_\alpha C_{\alpha}^j/DT \) the Lagrange multiplier \( \lambda_\alpha^j \) is given, as

\[
\lambda_\alpha^j = \tilde{\nu}_\alpha^j
\]

(11.11)

The part of the inequality (12.4) including the (symmetric) velocity gradient \( \delta_\alpha \) for the liquid phase, is

\[
\Lambda_{\delta_\alpha} = \text{tr} \varepsilon_{\alpha} \delta_\alpha \left( \mathbf{t}_\alpha + \sum_{j=1}^{N} \rho_\alpha^j \mathbf{u}_\alpha^j \otimes \mathbf{u}_\alpha^j + \lambda_\alpha \rho_\alpha \mathbf{I} \right) \geq 0
\]

(12.12)
which by aid of (12.9), i.e. \( \lambda_t = \rho_t / \rho_s \), can be expressed in terms of the hydrostatic pressure \( p_t \) instead of the mass density \( \rho_t \), i.e.

\[
\Lambda_{d_t} = \text{tr} \varepsilon_t d_t \left( t_t + \sum_{j=1}^{N} \rho_t^j u_t^j \otimes u_t^j + p_t I \right) \geq 0 \quad (12.13)
\]

That is, defining a non-equilibrium state in which \( d_t \) is arbitrary, gives the definition for the stress tensor for the liquid phase \( t_t \), as

\[
t_t = -p_t I - \sum_{j=1}^{N} \rho_t^j u_t^j \otimes u_t^j \quad (12.14)
\]

The term in the inequality including the (symmetric) velocity gradient \( d_s \) is

\[
\Lambda_{d_s} = \text{tr} \varepsilon_s d_s \left( t_s + \sum_{j=1}^{N} \rho_s^j u_s^j \otimes u_s^j + \lambda_s \rho_s I - \frac{\varepsilon_s}{\varepsilon_s} t_s^* - t_s^* \right) \geq 0 \quad (12.15)
\]

Using (12.9) with \( \alpha = s \), i.e. \( \lambda_s = p_s / \rho_s \). The expression (12.15) can be used to define the stress tensor for the solid \( t_s \), for arbitrary \( d_s \), as

\[
t_s = -p_s I + \frac{\varepsilon_s}{\varepsilon_s} t_s^* + t_s^* - \sum_{j=1}^{N} \rho_s^j u_s^j \otimes u_s^j \quad (12.16)
\]

The term in the inequality (12.4) including \( \text{grad} u^j_d \) is

\[
\Lambda_{\text{grad} u^j_d} = \sum_{\alpha=1,s} \varepsilon_\alpha \sum_{j=1}^{N} \text{tr} \left( \left( \text{grad} u^j_d \right) \left( t^j_\alpha + \lambda^j_\alpha \rho^j_\alpha I - \rho^j_\alpha A^j_\alpha I + \rho^j_\alpha \Gamma^N_\alpha \right) \right) \quad (12.17)
\]

For arbitrary choices of \( \text{grad} u^j_d \) one obtain the definition of the stress tensor for the \( j \)th constituent in phase \( \alpha \), \( t^j_\alpha \), as

\[
t^j_\alpha = \rho^j_\alpha A^j_\alpha I - \rho^j_\alpha \mu^j_\alpha I - \rho^j_\alpha \Gamma^N_\alpha \quad (12.18)
\]

where the condition \( \lambda^j_\alpha = \tilde{\mu}^j_\alpha \), i.e. (12.11), is used. Consider the stress tensor for the \( N \)th constituent which is

\[
t^N_\alpha = \rho^N_\alpha A^N_\alpha I - \rho^N_\alpha \mu^N_\alpha I - \rho^N_\alpha \Gamma^N_\alpha \quad (12.19)
\]

By identifying the Lagrange multiplier \( \Gamma^N_\alpha \) as the chemical potential tensor \( \tilde{\mu}^N_\alpha \) and also relating the chemical potential for the \( j \)th constituent in \( \alpha \)-phase, \( \tilde{\mu}^j_\alpha \), as relative the \( N \)th constituent, i.e.

\[
\Gamma^N_\alpha \equiv \mu^N_\alpha ; \quad \tilde{\mu}^N_\alpha = \mu^N_\alpha - \mu^N_\alpha \quad (12.20)
\]

From (12.20) it is concluded that \( \tilde{\mu}^N_\alpha I = 0 \), which means that the Lagrange multiplier \( \Gamma^N_\alpha \) can be identified as

\[
\Gamma^N_\alpha = A^N_\alpha I - \frac{1}{\rho^N_\alpha} t^N_\alpha \quad (12.21)
\]
where (12.19) is used.

From the choice of identifying $\Gamma^N_\alpha$ and $\hat{\rho}_\alpha^j I$, as described in (12.20), the definition of the stress tensor for the $j$th constituent in phase $\alpha$, $t_\alpha^j$, can be formulated, as

$$t_\alpha^j = \rho_\alpha^j A_\alpha^j I - \rho_\alpha^j (\mu_\alpha^j - \mu_\alpha^N) - \rho_\alpha^j \mu_\alpha^N$$  \hspace{1cm} (12.22)

According to (12.22) the chemical potential tensor $\mu_\alpha^j$ becomes

$$\mu_\alpha^j = A_\alpha^j I - \frac{1}{\rho_\alpha^j} t_\alpha^j$$  \hspace{1cm} (12.23)

which is the chemical potential tensor as defined by Bowen.

Consider next the definition (12.23) multiplied with $C_\alpha^j$ and summed over all $N$ constituents in phase $\alpha$, i.e.

$$\sum_{j=1}^N C_\alpha^j \mu_\alpha^j = \sum_{j=1}^N C_\alpha^j A_\alpha^j I - \sum_{j=1}^N \frac{C_\alpha^j t_\alpha^j}{\rho_\alpha^j}$$  \hspace{1cm} (12.24)

Using the definition (7.39), i.e. $\sum_{j=1}^N C_\alpha^j A_\alpha^j = A_\alpha$ and the definition for the stress tensor for the $\alpha$-phase, i.e. equation (4.23) in which the terms involving second order diffusion velocities are neglected, one obtain

$$\sum_{j=1}^N C_\alpha^j \mu_\alpha^j = A_\alpha I - \frac{1}{\rho_\alpha} t_\alpha = G_\alpha$$  \hspace{1cm} (12.25)

which is the definition of the Gibbs free energy tensor, e.g. see equation (9.2b).

### 12.2. The non-relative chemical potential

Consider the following derived expressions or definitions

$$t_\alpha = \sum_{j=1}^N t_\alpha^j - \sum_{j=1}^N (\rho_\alpha^j u_\alpha^j \otimes u_\alpha^j)$$  \hspace{1cm} (12.26)

$$t_\alpha^j = \rho_\alpha^j A_\alpha^j I - \hat{\rho}_\alpha^j \rho_\alpha^j I - \rho_\alpha^j \Gamma^N_\alpha$$  \hspace{1cm} (12.27)

$$t_\alpha = -p_\alpha I - \sum_{j=1}^N \rho_\alpha^j u_\alpha^j \otimes u_\alpha^j$$  \hspace{1cm} (12.28)

$$t_\alpha = -p_\alpha I + \frac{\varepsilon_I}{\varepsilon_\alpha} t_\alpha^j + t_\sigma^j - \sum_{j=1}^N \rho_\alpha^j u_\alpha^j \otimes u_\alpha^j$$  \hspace{1cm} (12.29)

$$\Gamma^N_\alpha = A_\alpha^N I - \frac{1}{\rho_\alpha^N} t_\alpha^N$$  \hspace{1cm} (12.30)

which is (4.23), (12.19), (12.14), (12.16) and (12.21) repeated. Consider the elimination of $\sum_{j=1}^N t_\alpha^j$, $t_\alpha$ and $\Gamma^N_\alpha$ from the above expression. Combining (12.26) and (12.27) gives
\[ t_\alpha = \sum_{j=1}^{N} \left( \rho_{\alpha}^j A_{\alpha}^j I - \bar{\mu}_{\alpha}^j \rho_{\alpha}^j I - \rho_{\alpha}^j A_{\alpha}^N I + \frac{\rho_{\alpha}^j}{\rho_{\alpha}} t_{\alpha}^N \right) \]  
\[ - \sum_{j=1}^{N} \left( \rho_{\alpha}^j u_{\alpha}^j \otimes u_{\alpha}^j \right) \]  
(12.31)

Further, by combining (12.31) and (12.30), one obtain

\[ t_\alpha = \sum_{j=1}^{N} \left( \rho_{\alpha}^j A_{\alpha}^j I - \bar{\mu}_{\alpha}^j \rho_{\alpha}^j I - \rho_{\alpha}^j A_{\alpha}^N I + \frac{\rho_{\alpha}^j}{\rho_{\alpha}} t_{\alpha}^N \right) \]  
\[ - \sum_{j=1}^{N} \left( \rho_{\alpha}^j u_{\alpha}^j \otimes u_{\alpha}^j \right) \]  
(12.32)

For the liquid phase, equations (12.32) and (12.28) give the expression

\[- \frac{\rho_{l}^j}{\rho_{l}} t_{l}^N = \sum_{j=1}^{N} \left( \rho_{l}^j A_{l}^j I - \bar{\mu}_{l}^j \rho_{l}^j I - \rho_{l}^j A_{l}^N I \right) + p_{l} I \]  
(12.33)

Using the definition (7.39), i.e. \( \rho_{l} A_{l} = \sum_{j=1}^{N} \rho_{l}^j A_{l}^j \), and dividing the whole expression (12.33) with \( \rho_{l} \), one obtain

\[- \frac{C_{l}^j}{\rho_{l}} t_{l}^N = \left( A_{l} - \sum_{j=1}^{N} \bar{\mu}_{l}^j C_{l}^j - A_{l}^N + \frac{p_{l}}{\rho_{l}} \right) I \]  
(12.34)

where (2.13) has been used, i.e. \( C_{l}^j = \rho_{l}^j / \rho_{l} \).

The corresponding relation to (12.34) for the solid phase \( s \), is obtained by combining (12.32) and (12.29), i.e.

\[- p_{s} I + \frac{\epsilon_{l}}{\epsilon_{s}} t_{s}^l + t_{s}^s = \sum_{j=1}^{N} \left( \rho_{s}^j A_{s}^j I - \bar{\mu}_{s}^j \rho_{s}^j I - \rho_{s}^j A_{s}^N I + \frac{p_{s}}{\rho_{s}} t_{s}^N \right) \]  
(12.35)

Using the definition (7.39), i.e. \( \rho_{s} A_{s} = \sum_{j=1}^{N} \rho_{s}^j A_{s}^j \), and (2.13), i.e. \( C_{s}^j = \rho_{s}^j / \rho_{s} \), dividing the whole expression with \( \rho_{s} \), one obtain the expression

\[- \frac{C_{s}^j}{\rho_{s}} t_{s}^N + \frac{1}{\rho_{s}} \left( \frac{\epsilon_{l}}{\epsilon_{s}} t_{s}^l + t_{s}^s \right) = \left( A_{s} - \sum_{j=1}^{N} \bar{\mu}_{s}^j C_{s}^j - A_{s}^N + \frac{p_{s}}{\rho_{s}} \right) I \]  
(12.36)

The the left-hand-sides of expressions (12.34) and (12.36) tells us that equations (12.34) and (12.36) are scalar multipliers of the identity \( I \). With this as a motivation, define the scalar chemical potentials

\[ \mu_{l}^j I = A_{l}^j I - \frac{1}{\rho_{l}^j} t_{l}^j \]  
(12.37)
and

\[ \mu_j^i I = A_j^i I - \frac{1}{\rho^i} t_j^i + \frac{1}{\rho^i} \left( \varepsilon_j \left( t_j^i + t_j^s \right) \right) \]  

(12.38)

where the notations \( \mu_j^i \) and \( \mu_j^s \) has been used instead of \( \tilde{\mu}_j^i \) and \( \tilde{\mu}_j^s \) to distinguish it from Bowen's tensorial chemical potential. Multiplying (12.37) and (12.38) with \( C_j^i \) and summing on \( j \) gives the relation analogous to (12.24) is obtained. For the liquid phase one obtain

\[ \sum_{j=1}^{N} C_j^i \mu_j^i = \sum_{j=1}^{N} C_j^i A_j^i I - \sum_{j=1}^{N} \frac{C_j^i}{\rho^i} t_j^i \]  

(12.39)

which by the definitions \( \rho_\alpha A_\alpha = \sum_{j=1}^{N} \rho_\alpha A_j^i \), \( \sum_{j=1}^{N} \rho_\alpha = \rho_\alpha \), and \( C_j^i = \rho_j^i / \rho_\alpha \), the expression (12.39) can be written as

\[ \sum_{j=1}^{N} C_j^i \mu_j^i = A_i - \frac{1}{\rho_l} \sum_{j=1}^{N} t_j^i \]  

(12.40)

the following definitions concerning the property \( t_j^i \) will be made

\[ t_j^i = -p_j^i I, \quad \text{and} \quad \sum_{j=1}^{N} t_j^i = -p_l I \]  

(12.41)

which partly, also, can be seen as a consequence of \( \mu_j^i \) being a scalar property. By combining (12.40) and (12.41) it is concluded that

\[ \sum_{j=1}^{N} C_j^i \mu_j^i = A_i - \frac{p_l}{\rho_l} \]  

(12.42)

If expression (12.42) for the scalar chemical potential for the liquid phase \( \mu_j^i \), should be valid also for the solid phase, the somewhat general relation

\[ \sum_{j=1}^{N} C_j^i \mu_j^i = A_i + \frac{p_s}{\rho_s} = G_\alpha \]  

(12.43)

which is the classical Gibbsian thermodynamical definition, i.e. compare with the tensorial definition (9.2b), should hold. In this case the definition of the pressure of the constituents in solid phase \( p_j^i \) must take a different form than the classical definitions shown in (12.41). To show this consider (12.38) multiplied with \( C_j^i \) and summed on \( j \), i.e.

\[ \sum_{j=1}^{N} C_j^i \mu_j^i I = \sum_{j=1}^{N} C_j^i A_j^i I - \sum_{j=1}^{N} \frac{C_j^i}{\rho^i} t_j^i + \sum_{j=1}^{N} \frac{C_j^i}{\rho_s} \left( \varepsilon_j \left( t_j^i + t_j^s \right) \right) \]  

(12.44)

Using the same definitions used to receive (12.40), i.e. \( \rho_\alpha A_\alpha = \sum_{j=1}^{N} \rho_\alpha A_j^i \), \( \sum_{j=1}^{N} \rho_\alpha = \rho_\alpha \), and \( C_j^i = \rho_j^i / \rho_\alpha \), one obtain

\[ \sum_{j=1}^{N} C_j^i \mu_j^i I = A_i I - \frac{1}{\rho_s} \left( \sum_{j=1}^{N} t_j^i - \frac{C_j^i}{\varepsilon_s} t_j^i - t_j^s \right) \]  

(12.45)
That is, by ignoring the second order diffusion velocities in the definition (4.23), and defining the pressure of the constituents in solid phase \( p_s \), as

\[
-p_s I = t_s - \frac{\epsilon_i}{\varepsilon_s} t_s^i - t_s^c
\]  
(12.46)

the classical result (12.43) is valid. Further, due the expression (12.44) and (12.46), it seems natural to define the partial pressure \( p_s^i \), as

\[
-p_s^i I = t_s^i - C_s^i \left( \frac{\epsilon_i}{\varepsilon_s} t_s^i - t_s^c \right)
\]  
(12.47)

By comparing expressions (12.41) and (12.47) with its corresponding definitions (12.37) and (12.38) it is directly concluded that

\[
\mu_s^i = A_s^i + \frac{p_s^i}{\rho_s^i}; \quad \alpha = l, s
\]  
(12.48)

where \( C_s^i / \rho_s^i = 1 / \rho_s \) was used when combining (12.47) and (12.38) for identifying the validity of (12.48) for the solid phase. Not that (12.48) shows consistency with (12.43).

By comparing the two definitions of the scalar chemical potentials, i.e. (12.37) and (12.38), with Bowen’s tensorial chemical potential one arrive at the following relationships

\[
\mu_s^i I = \mu_s^i
\]  
(12.49)

\[
\mu_s^i I - \mu_s^i = \frac{1}{\rho_s} \left( \frac{\epsilon_i}{\varepsilon_s} t_s^i + t_s^c \right)
\]  
(12.50)

It is also noted that when the definition \( \tilde{\mu}_s^i = \partial A_s^i / \partial C_s^i \), i.e. (9.4), and expression (12.20b) is combined with (12.49) or (12.50), one obtain

\[
\tilde{\mu}_s^i I \equiv \frac{\partial A_s^i}{\partial C_s^i} I \equiv \mu_s^i - \mu_s^N = (\mu_s^i - \mu_s^N) I
\]  
(12.51)

where it is noted that the term \( 1 / \rho_s (\epsilon_i / \varepsilon_s t_s^i + t_s^c) \) vanish when (12.50) is combined with (9.4) and (12.20b).

### 12.3. Equilibrium Restrictions

Before considering the equilibrium restrictions imposed by the entropy inequality, it is necessary to re-write the term in entropy inequality associated with \( u_i^s, j = 1, ..., N \), in terms of independent variables \( u_i^j, j = 1, ..., N - 1 \). To do so, consider the terms in inequality (12.4) associated with \( u_i^s \), written as

\[
\sum_{j=1}^{N} u_i^s \cdot w_j^s = \sum_{j=1}^{N} u_i^s \cdot w_j^s + u_i^N \cdot w_i^N
\]  
(12.52)

where \( w_i^s \) is a vector representing the coefficient of \( u_i^s \) in (12.4). From (2.17), it follows that

\[
\sum_{j=1}^{N} C_i^j u_i^s = 0; \quad \sum_{j=1}^{N-1} C_i^j u_i^j = - C_i^N u_i^N
\]  
(12.53)
where the definition $C^j_\alpha = \rho^j_\alpha / \rho_\alpha$ is used. Therefore the expression for $u^N_\alpha$ becomes

$$u^N_\alpha = - \sum_{j=1}^{N-1} \frac{C^j_\alpha}{C^N_\alpha} u^j_\alpha$$

(12.54)

Combining (12.52) and (12.54), yields

$$\sum_{j=1}^{N} u^j_\alpha \cdot w^j_\alpha = \sum_{j=1}^{N-1} u^j_\alpha \cdot w^j_\alpha - \sum_{j=1}^{N-1} \frac{C^j_\alpha}{C^N_\alpha} u^j_\alpha \cdot w^N_\alpha$$

(12.55)

$$\sum_{j=1}^{N-1} u^j_\alpha \cdot \left( w^j_\alpha - \frac{C^j_\alpha}{C^N_\alpha} w^N_\alpha \right)$$

where it is noted that $C^j_\alpha / C^N_\alpha$ also can be written as

$$\frac{C^j_\alpha}{C^N_\alpha} = \frac{\rho^j_\alpha}{\rho^N_\alpha}$$

(12.56)

since $C^j_\alpha = \rho^j_\alpha / \rho_\alpha$. Noting that the Lagrange multiplier $\lambda^j_\alpha$, according to (12.11) is identified as $\lambda^j_\alpha = \bar{\mu}^j_\alpha$, the vector $w^j_\alpha$ representing the coefficient of $u^j_\alpha$ in (12.4), can be identified as

$$w^j_\alpha = - \left( T^j_\alpha + \varphi^j_\alpha \right) - \text{grad} (\varepsilon_\alpha \rho^j_\alpha A^j_\alpha) + \bar{\mu}^j_\alpha \text{grad} (\rho^j_\alpha)$$

+ $\varepsilon_\alpha \varepsilon^N_\alpha \text{grad} (\rho^N_\alpha)$

(12.57)

Using (12.21), i.e. $\Gamma^N_\alpha = A^N_\alpha I - t^N_\alpha / \rho^N_\alpha$, the sum of $w^j_\alpha$ can be expressed as

$$\sum_{j=1}^{N-1} w^j_\alpha = \sum_{j=1}^{N-1} \left( T^j_\alpha + \varphi^j_\alpha \right) - \sum_{j=1}^{N-1} \text{grad} (\varepsilon_\alpha \rho^j_\alpha A^j_\alpha)$$

(12.58)

$$+ \sum_{j=1}^{N-1} \bar{\mu}^j_\alpha \text{grad} (\varepsilon_\alpha \rho^j_\alpha)$$

$$+ \sum_{j=1}^{N-1} \varepsilon_\alpha A^N_\alpha I \text{grad} (\rho^j_\alpha)$$

$$- \sum_{j=1}^{N-1} \varepsilon_\alpha \left( \frac{1}{\rho^j_\alpha} t^N_\alpha \right) \text{grad} (\rho^N_\alpha)$$

Partial differentiation of $\text{div} (\varepsilon_\alpha \rho^j_\alpha \bar{\mu}^j_\alpha I)$ gives

$$\sum_{j=1}^{N-1} \text{div} (\varepsilon_\alpha \rho^j_\alpha \varepsilon^j_\alpha) = \sum_{j=1}^{N-1} \bar{\mu}^j_\alpha \text{grad} (\varepsilon_\alpha \rho^j_\alpha) + \varepsilon_\alpha \rho^j_\alpha \text{grad} (\bar{\mu}^j_\alpha)$$

(12.59)
That is, the term $\mu^j_{\alpha} \text{grad}(\varepsilon_{\alpha} \rho^j_{\alpha})$ in (12.58), can be written as

$$
\sum_{j=1}^{N-1} \mu^j_{\alpha} \text{grad}(\varepsilon_{\alpha} \rho^j_{\alpha}) = \sum_{j=1}^{N-1} \text{div}(\varepsilon_{\alpha} \rho^j_{\alpha} \mu^j_{\alpha} I) - \varepsilon_{\alpha} \rho^j_{\alpha} \text{grad}(\mu^j_{\alpha})
$$

(12.60)

The equations (12.58) and (12.60) combined gives

$$
\sum_{j=1}^{N-1} w^j_{\alpha} = - \sum_{j=1}^{N-1} \left( \mathbf{T}^j_{\alpha} + \mathbf{G}^j_{\alpha} \right) - \sum_{j=1}^{N-1} \text{grad}(\varepsilon_{\alpha} \rho^j_{\alpha} A^j_{\alpha})
$$

$$
+ \sum_{j=1}^{N-1} \text{div}(\varepsilon_{\alpha} \rho^j_{\alpha} \mu^j_{\alpha} I) - \varepsilon_{\alpha} \rho^j_{\alpha} \text{grad}(\mu^j_{\alpha})
$$

$$
+ \sum_{j=1}^{N-1} \varepsilon_{\alpha} (A^j_{\alpha} I) \text{grad}(\rho^j_{\alpha})
$$

$$
- \sum_{j=1}^{N-1} \varepsilon_{\alpha} \left( \frac{1}{\rho^j_{\alpha}} \mathbf{t}^{N}_{\alpha} \right) \text{grad}(\rho^j_{\alpha})
$$

(12.61)

From (2.14) it is concluded that the concentrations $C^j_{\alpha}$, $j = 1, \ldots, N - 1$, are related as

$$
\sum_{j=1}^{N} C^j_{\alpha} = 1; \quad \sum_{j=1}^{N-1} C^j_{\alpha} = 1 - C^{N}_{\alpha}
$$

(12.62)

That is, the term $C^j_{\alpha}/C^{N}_{\alpha}$ in (12.55) can be written as

$$
\sum_{j=1}^{N-1} \frac{C^j_{\alpha}}{C^{N}_{\alpha}} = \frac{1}{C^{N}_{\alpha}} - 1
$$

(12.63)

The term $\sum_{j=1}^{N-1} C^j_{\alpha}/C^{N}_{\alpha} w^N_{\alpha}$ needed for evaluation of expression (12.55) can be written as

$$
\sum_{j=1}^{N-1} \frac{C^j_{\alpha}}{C^{N}_{\alpha}} w^N_{\alpha} = - \sum_{j=1}^{N-1} \frac{P^j_{\alpha}}{P^{N}_{\alpha}} \left( \tilde{T}^N_{\alpha} + \tilde{G}^N_{\alpha} \right) - \sum_{j=1}^{N-1} \frac{P^j_{\alpha}}{P^{N}_{\alpha}} \text{grad}(\varepsilon_{\alpha} \rho^j_{\alpha} A^N_{\alpha})
$$

$$
+ \sum_{j=1}^{N-1} \frac{P^j_{\alpha}}{P^{N}_{\alpha}} \varepsilon_{\alpha} (A^j_{\alpha} I) \text{grad}(\rho^N_{\alpha})
$$

$$
- \sum_{j=1}^{N-1} \frac{P^j_{\alpha}}{P^{N}_{\alpha}} \varepsilon_{\alpha} \left( \frac{1}{\rho^N_{\alpha}} \mathbf{t}^{N}_{\alpha} \right) \text{grad}(\rho^N_{\alpha})
$$

(12.64)

where $\mu^N_{\alpha} = 0$ is used which is a consequence of equation (12.20).

The term $\rho^j_{\alpha}/\rho^{N}_{\alpha} \text{grad}(\varepsilon_{\alpha} \rho^j_{\alpha} A^N_{\alpha})$ in (12.64) can be re-written with the identity

$$
\frac{\rho^j_{\alpha}}{\rho^{N}_{\alpha}} \text{grad}(\varepsilon_{\alpha} \rho^j_{\alpha} A^N_{\alpha}) = \frac{\rho^j_{\alpha}}{\rho^{N}_{\alpha}} \varepsilon_{\alpha} (A^j_{\alpha} I) \text{grad}(\rho^N_{\alpha}) + \rho^j_{\alpha} \text{grad}(\varepsilon_{\alpha} A^N_{\alpha})
$$

(12.65)
Further, by using $\rho^N_{\alpha} = \rho^i_{\alpha} C^N_{\alpha}/C^i_{\alpha}$, i.e. equation (12.56), the last term on the right-hand side in (12.64) can be written as

$$-rac{\rho^i_{\alpha}}{\rho^N_{\alpha}} \varepsilon_{\alpha} \left( \frac{1}{\rho^N_{\alpha}} t^N_{\alpha} \right) \text{grad} (\rho^N_{\alpha}) = -\frac{(\rho^i_{\alpha})^2}{\rho^N_{\alpha}} \varepsilon_{\alpha} \left( \frac{1}{\rho^N_{\alpha}} t^N_{\alpha} \right) \text{grad} \left( \frac{C^N_{\alpha}}{C^i_{\alpha}} \right)$$

(12.66)

Combining (12.65) and (12.64), yields

$$\sum_{j=1}^{N-1} \frac{C^j_{\alpha}}{C^N_{\alpha}} w^N_{\alpha} = -\sum_{j=1}^{N-1} \frac{C^j_{\alpha}}{C^N_{\alpha}} \left( \tilde{T}^N_{\alpha} + \tilde{r}^N_{\alpha} \right) - \sum_{j=1}^{N-1} \rho^j_{\alpha} \text{grad} (\varepsilon_{\alpha} A^N_{\alpha})$$

(12.67)

$$-\sum_{j=1}^{N-1} \frac{C^j_{\alpha}}{C^N_{\alpha}} \varepsilon_{\alpha} \frac{t^N_{\alpha}}{\rho^N_{\alpha}} \text{grad} (\rho^N_{\alpha})$$

where $C^i_{\alpha}/C^N_{\alpha} = \rho^i_{\alpha}/\rho^N_{\alpha}$ is used. Note also that the following identity holds

$$\sum_{j=1}^{N-1} \varepsilon_{\alpha} A^N_{\alpha} \text{grad} (\rho^j_{\alpha}) + \sum_{j=1}^{N-1} \rho^j_{\alpha} \text{grad} (\varepsilon_{\alpha} A^N_{\alpha}) = \sum_{j=1}^{N-1} \text{div} (\varepsilon_{\alpha} \rho^j_{\alpha} A^N_{\alpha} \mathbf{1})$$

(12.68)

By combining (12.61) and (12.67), yields

$$\sum_{j=1}^{N-1} \rho^j_{\alpha} w^j_{\alpha} - \sum_{j=1}^{N-1} \frac{C^j_{\alpha}}{C^N_{\alpha}} w^N_{\alpha} = -\sum_{j=1}^{N-1} \left( \tilde{T}^j_{\alpha} + \tilde{r}^j_{\alpha} \right) - \sum_{j=1}^{N-1} \text{grad} (\varepsilon_{\alpha} \rho^j_{\alpha} A^N_{\alpha})$$

(12.69)

$$+ \sum_{j=1}^{N-1} \text{div} (\varepsilon_{\alpha} \rho^j_{\alpha} \rho^N_{\alpha} \mathbf{1}) - \varepsilon_{\alpha} \rho^j_{\alpha} \text{grad} (\rho^j_{\alpha})$$

$$+ \sum_{j=1}^{N-1} \varepsilon_{\alpha} (A^N_{\alpha} \mathbf{1}) \text{grad} (\rho^j_{\alpha})$$

$$- \sum_{j=1}^{N-1} \varepsilon_{\alpha} \left( \frac{1}{\rho^N_{\alpha}} t^N_{\alpha} \right) \text{grad} (\rho^j_{\alpha})$$

$$+ \sum_{j=1}^{N-1} \frac{C^j_{\alpha}}{C^N_{\alpha}} \left( \tilde{T}^N_{\alpha} + \tilde{r}^N_{\alpha} \right) + \sum_{j=1}^{N-1} \rho^j_{\alpha} \text{grad} (\varepsilon_{\alpha} A^N_{\alpha})$$

$$+ \sum_{j=1}^{N-1} \frac{C^j_{\alpha}}{C^N_{\alpha}} \varepsilon_{\alpha} \frac{t^N_{\alpha}}{\rho^N_{\alpha}} \text{grad} (\rho^N_{\alpha})$$

Consider the terms involving $t^N_{\alpha}$ in (12.69) denoted $w^j_{\alpha} A^N_{\alpha}$, as

$$\sum_{j=1}^{N-1} w^j_{\alpha} A^N_{\alpha} = \sum_{j=1}^{N-1} \frac{C^j_{\alpha}}{C^N_{\alpha}} w^N_{\alpha} = \sum_{j=1}^{N-1} \varepsilon_{\alpha} \frac{t^N_{\alpha}}{\rho^N_{\alpha}} \text{grad} (\rho^N_{\alpha}) - \sum_{j=1}^{N-1} \varepsilon_{\alpha} \left( \frac{1}{\rho^N_{\alpha}} t^N_{\alpha} \right) \text{grad} (\rho^j_{\alpha})$$

(12.70)
That is, expression (12.70) can be written

\[
\sum_{j=1}^{N-1} w_{\alpha j}^N = \left( \varepsilon_\alpha t_\alpha^N \right) C_i^j \sum_{j=1}^{N-1} \left( \frac{C_i^j}{C_{\alpha}} \text{grad} \left( \frac{\rho_\alpha^N}{\rho_\alpha^j} \right) - \text{grad} \left( \rho_\alpha^j \right) \right)
\]  

(12.71)

Using \( \rho_\alpha^N = C_{\alpha} \rho_\alpha^j / C_i^j \), i.e., equation (12.56), the expression (12.71) can be brought to the form

\[
\sum_{j=1}^{N-1} w_{\alpha j}^N = \left( \varepsilon_\alpha t_\alpha^N \right) \sum_{j=1}^{N-1} \left( \frac{C_i^j}{C_{\alpha}} \text{grad} \left( \frac{\rho_\alpha^N}{\rho_\alpha^j} \right) - \text{grad} \left( \rho_\alpha^j \right) \right)
\]  

(12.72)

Differentiation of the first term on the right hand side of (12.72), gives

\[
\frac{C_i^j}{C_{\alpha}} \text{grad} \left( \frac{\rho_\alpha^N}{\rho_\alpha^j} \right)^{-1} = \frac{1}{C_{\alpha}^N} \text{grad} \left( \frac{\rho_\alpha^N}{\rho_\alpha^j} \right) - \frac{C_i^j \rho_\alpha^N}{C_{\alpha}^N} \left( \frac{\rho_\alpha^j}{C_{\alpha}^j} \right)^2 \text{grad} \left( C_{\alpha}^j \right)
\]  

(12.73)

i.e.,

\[
\frac{C_i^j}{C_{\alpha}} \text{grad} \left( \frac{\rho_\alpha^N}{\rho_\alpha^j} \right)^{-1} = \frac{1}{C_{\alpha}^N} \text{grad} \left( \frac{\rho_\alpha^N}{\rho_\alpha^j} \right) - \frac{\rho_\alpha^j}{C_{\alpha}^j} \text{grad} \left( C_{\alpha}^j \right)
\]  

(12.74)

By differentiation of the first term on the right hand side of (12.74), one obtains

\[
\frac{C_i^j}{C_{\alpha}} \text{grad} \left( \frac{\rho_\alpha^N}{\rho_\alpha^j} \right)^{-1} = \text{grad} \left( \rho_\alpha^j \right) + \frac{\rho_\alpha^j}{C_{\alpha}^j} \text{grad} \left( C_{\alpha}^j \right)
\]  

(12.75)

\[-\frac{\rho_\alpha^j}{C_{\alpha}^j} \text{grad} \left( C_{\alpha}^j \right)
\]

Combining (12.75) and (12.72), gives

\[
\sum_{j=1}^{N-1} w_{\alpha j}^N = \left( \varepsilon_\alpha t_\alpha^N \right) \sum_{j=1}^{N-1} \left( \frac{C_i^j}{C_{\alpha}^N} \text{grad} \left( \frac{\rho_\alpha^N}{\rho_\alpha^j} \right) - \frac{1}{C_{\alpha}^N} \text{grad} \left( C_{\alpha}^j \right) \right)
\]  

(12.76)

where (12.56), i.e. \( \rho_\alpha^N = C_{\alpha} \rho_\alpha^j / C_i^j \) is used. Note, also, that the identity

\[
\frac{C_i^j}{C_{\alpha}^N} \text{grad} \left( \frac{\rho_\alpha^N}{\rho_\alpha^j} \right) - \frac{1}{C_{\alpha}^N} \text{grad} \left( C_{\alpha}^j \right) = -\text{grad} \left( \frac{C_i^j}{C_{\alpha}^N} \right)
\]  

(12.77)

holds, i.e. the expression (12.76) can be written

\[
\sum_{j=1}^{N-1} w_{\alpha j}^N = \left( \varepsilon_\alpha t_\alpha^N \right) \sum_{j=1}^{N-1} \left( -\text{grad} \left( \frac{C_i^j}{C_{\alpha}^N} \right) \right)
\]  

(12.78)
Using (12.78), valid for the terms associated with terms involving $t^N_\alpha$ in (12.69), one obtain

$$
\sum_{j=1}^{N} \mathbf{u}_\alpha^j \cdot \mathbf{w}_\alpha^j = \sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \left( \text{grad} \left( \varepsilon_\alpha \rho_\alpha^j A^j_\alpha \right) - \left( \mathbf{T}_\alpha^j + \mathbf{I}_\alpha^j \right) \right) \quad (12.79)
$$

$$
+ \sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \text{div} \left( \varepsilon_\alpha \rho_\alpha^j A^j_\alpha \mathbf{I} \right)
$$

$$
+ \sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \left( \text{div} \left( \varepsilon_\alpha \rho_\alpha^j \mathbf{p}_\alpha^j \mathbf{I} \right) - \varepsilon_\alpha \rho_\alpha^j \text{grad} \left( \mathbf{p}_\alpha^j \right) \right)
$$

$$
+ \sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \left( \frac{C^j_\alpha}{C^N_\alpha} \left( \mathbf{T}_\alpha^N + \mathbf{r}_\alpha^N \right) \right)
$$

$$
- \sum_{j=1}^{N-1} \mathbf{u}_\alpha^j \cdot \varepsilon_\alpha t^N_\alpha \text{grad} \left( \frac{C^j_\alpha}{C^N_\alpha} \right).
$$

where also the identity (12.68) is used.

Consider next the momentum balance equation for the $j$th constituent in $\alpha$-phase.

$$
\varepsilon_\alpha \rho_\alpha^j \frac{D^j_\alpha}{Dt} \left( \mathbf{v}_\alpha^j \right) = \text{div} \left( \varepsilon_\alpha \mathbf{t}_\alpha^j \right) + \varepsilon_\alpha \rho_\alpha^j \mathbf{g}_\alpha^j + \mathbf{T}_\alpha^j + \mathbf{r}_\alpha^j \quad (12.80)
$$

At the equilibrium situation considered the acceleration $\frac{D^j_\alpha}{Dt} \mathbf{v}_\alpha^j / Dt$ is zero and that the gravity is, further assumed to be small, i.e. $\varepsilon_\alpha \rho_\alpha^j \mathbf{g}_\alpha^j = 0$. That is at equilibrium the following condition is assumed valid

$$
- \left( \mathbf{T}_\alpha^j + \mathbf{r}_\alpha^j \right) = \text{div} \left( \varepsilon_\alpha \mathbf{t}_\alpha^j \right) \quad (12.81)
$$

The two last rows in (12.79) will be denoted $w^j_\alpha \mathbf{T}_\alpha^N$ and is given as

$$
w^j_\alpha \mathbf{T}_\alpha^N = \frac{C^j_\alpha}{C^N_\alpha} \left( \mathbf{T}_\alpha^N + \mathbf{r}_\alpha^N \right) - \varepsilon_\alpha t^N_\alpha \text{grad} \left( \frac{C^j_\alpha}{C^N_\alpha} \right) \quad (12.82)
$$

where (12.72) has been used with $j = N$. The expression (12.82) can be re-written be the identity

$$
- \frac{C^j_\alpha}{C^N_\alpha} \text{div} \left( \varepsilon_\alpha t^N_\alpha \right) - \varepsilon_\alpha t^N_\alpha \text{grad} \left( \frac{C^j_\alpha}{C^N_\alpha} \right) = -\text{div} \left( \varepsilon_\alpha t^N_\alpha \frac{D^j_\alpha}{\rho_\alpha^j} \right) \quad (12.83)
$$

where $\rho^N_\alpha / \rho_\alpha^j = C^N_\alpha / C^j_\alpha$ is used. hence the expression for $\sum_{j=1}^{N} \mathbf{u}_\alpha^j \cdot \mathbf{w}_\alpha^j$ becomes using (12.79),
(12.81), (12.82) and (12.83)

\[
\sum_{j=1}^{N} u_{\alpha j} \cdot w_{\alpha j} = \sum_{j=1}^{N-1} u_{\alpha j} \cdot \left( -\text{div} \left( \varepsilon_{\alpha} \rho_{\alpha} A_{\alpha j} I \right) + \text{div} \left( \varepsilon_{\alpha} \varepsilon_{\alpha j} \right) \right) + \sum_{j=1}^{N-1} \varepsilon_{\alpha} \rho_{\alpha} A_{\alpha j} \cdot \text{div} \left( \varepsilon_{\alpha} \rho_{\alpha} A_{\alpha j} I \right) + \sum_{j=1}^{N-1} \varepsilon_{\alpha} \rho_{\alpha} \varepsilon_{\alpha j} \cdot \text{div} \left( \varepsilon_{\alpha} \rho_{\alpha} A_{\alpha j} I \right) - \sum_{j=1}^{N-1} \varepsilon_{\alpha} \rho_{\alpha} A_{\alpha j} \cdot \text{div} \left( \varepsilon_{\alpha} \rho_{\alpha} A_{\alpha j} I \right) \right).
\]

The equilibrium condition for \( w_{\alpha j} \) can be evaluated from this expression since the diffusion velocities \( u_{\alpha j} \), \( j = 1, \ldots, N-1 \) are independent variables.

The equilibrium condition to be studied is defined when the following properties vanish

\[
\frac{D_{\alpha} e_{i}}{D t} ; (u_{i} - u_{s}) ; u_{\alpha j} ; \varepsilon_{\alpha j} ; \varepsilon_{\alpha i} ; \varepsilon_{\alpha} ; \text{grad} T
\]

For the \( u_{\alpha j} \), \( j = 1, \ldots, N-1 \) independent variables in (12.84) it is concluded that

\[
\text{div} \varepsilon_{\alpha} \rho_{\alpha} \left( \bar{p}_{\alpha} I - \left( A_{\alpha j} - A_{\alpha j}^{N} \right) I + \left( \frac{t_{\alpha}^{j}}{\rho_{\alpha}} - \frac{t_{\alpha}^{N}}{\rho_{\alpha}} \right) \right) = \varepsilon_{\alpha} \rho_{\alpha} \text{grad} \left( \bar{p}_{\alpha} \right)
\]

is an equilibrium result when \( u_{\alpha j} \) vanish in the inequality (12.4).

The term involving \( D_{\alpha} e_{i}/D t \) in the inequality (12.4) is

\[
\Lambda_{\alpha} = \frac{D_{\alpha} e_{i}}{D t} \left( \lambda_{\alpha} \rho_{\alpha} - \lambda_{s} \rho_{s} \right) \geq 0
\]

If \( D_{\alpha} e_{i}/D t \) vanish at equilibrium, the following relation must hold

\[
\lambda_{\alpha} \rho_{\alpha} = \lambda_{s} \rho_{s}
\]

Using further the non-equilibrium result \( \lambda_{\alpha} = \rho_{\alpha}/\rho_{\alpha}, \text{ i.e. } (12.9) \), gives the condition

\[
\rho_{r} = \rho_{s}
\]

The terms associated with \((u_{i} - u_{s})\) in the inequality (12.9) is

\[
\Lambda_{u_{i} - u_{s}} = (u_{i} - u_{s}) \cdot \left( \rho_{i} \text{grad} e_{i} - \varepsilon_{i} \rho_{i} \text{tr} \left( \frac{\partial A_{l}}{\partial E_{s}} \text{grad} E_{s} \right) - \bar{T}_{l} \right) \geq 0
\]

At equilibrium \((u_{i} - u_{s})\) must vanish, so that

\[
\bar{T}_{l} = \rho_{i} \text{grad} e_{i} - \varepsilon_{i} \rho_{i} \text{tr} \left( \frac{\partial A_{l}}{\partial E_{s}} \text{grad} E_{s} \right)
\]
holds.

The terms associated with \( \dot{c}_i^f \) in the inequality (12.4) is

\[
\Lambda_{\dot{c}_i^f} = \dot{c}_i^f \left( \lambda_i^f - \lambda_s^f \right) \geq 0
\]  

(12.92)

Noting that \( \lambda_i^f = \bar{\mu}_s^i \) holds at a non-equilibrium condition, e.g. see equation (12.11), and that \( \dot{c}_i^f \) vanish at equilibrium. The expression (12.92) gives the condition

\[
\bar{\mu}_s^f = \bar{\mu}_s^f
\]  

(12.93)

at equilibrium.

The term \( \sum_{j=1}^{N-1} \dot{c}_j^f \left( \lambda_j^f - \lambda_s^f \right) \) and \( \lambda_s^f = \bar{\mu}_s^f \) the \( \dot{c}_j^f \) vanish

The terms in the inequality (12.9) associated with \( \dot{c}_j^f \) is

\[
\Lambda_{\dot{c}_j^f} = \dot{c}_j^f \left( \lambda_j^f - \lambda_s^f \right) \geq 0
\]  

(12.94)

which gives an identical condition as illustrated in (12.93), i.e. \( \bar{\mu}_s^f = \bar{\mu}_s^f \). Since the chemical reactions \( \dot{c}_j^f \) only is connected to reactions within the two considered phases and not between phases, the expression (12.94) will be separated into two terms, as

\[
\Lambda_{\dot{c}_j^f} = \sum_{j=1}^{N-1} \dot{c}_j^f \left( \lambda_j^f - \lambda_s^f \right) = \sum_{j=1}^{N-1} \dot{c}_j^f \lambda_j^f - \sum_{j=1}^{N-1} \dot{c}_j^f \lambda_s^f \geq 0
\]  

(12.95)

which with \( \lambda_j^f = \bar{\mu}_j^f \) and \( \lambda_s^f = \bar{\mu}_s^f \) gives the conditions

\[
\sum_{j=1}^{N-1} \dot{c}_j^f \bar{\mu}_j^f \geq 0; \text{ and } \sum_{j=1}^{N-1} \dot{c}_j^f \bar{\mu}_s^f \geq 0
\]  

(12.96)

for the two different phases. Making the assumption that only reaction involving two constituent in phase \( \alpha \) can occur at a time level. Let \( \bar{\mu}_{\alpha}^j \) and \( \bar{\mu}_{\alpha}^i \) be the chemical potentials for the two reacting constituents in \( \alpha \)-phase, where \( i \neq j \). In such a case the relation between \( \dot{c}_j^f \) and \( \dot{c}_j^f \) is:

\[
\dot{c}_j^f = -\dot{c}_j^f.\text{ That is, when making the above restrictions (12.96) can be expressed as}
\]  

\[
\dot{c}_j^f \left( \bar{\mu}_j^f - \bar{\mu}_s^f \right) \geq 0; \text{ and } \dot{c}_j^f \left( \bar{\mu}_s^f - \bar{\mu}_s^f \right) \geq 0
\]  

(12.97)

The expression (12.97) gives the condition

\[
\bar{\mu}_j^f = \bar{\mu}_s^f; \text{ and } \bar{\mu}_s^f = \bar{\mu}_s^f
\]  

(12.98)

at equilibrium, i.e. when \( \dot{c}_j^f \) and \( \dot{c}_j^f \) vanish. If considering reactions which involves more than two constituents within the phase, the conditions in (12.98) are noted not to be valid.

Consider next the condition in the inequality (12.4) in the case when \( \dot{c}_i \) vanish, i.e.

\[
\Lambda_{\dot{c}_i} = \frac{p_i}{\rho_i} - \frac{p_s}{\rho_s} + \sum_{j=1}^{N-1} \left( C_j^f \bar{\mu}_s^j - C_j^f \bar{\mu}_s^j \right) + \Lambda_{\dot{c}_i} \geq 0
\]  

(12.99)
where $\lambda_{\alpha} = p_{\alpha}/\rho_{\alpha}$, $\lambda_i^j = \tilde{\lambda}_i^j$ and $\lambda_i^j = \tilde{\lambda}_i^j$ are used.

The following definitions will be used

$$\Gamma_{\alpha}^N = A_{\alpha}^N I - \frac{1}{\rho_{\alpha}^N} t_{\alpha}^N, \quad \mu_{\alpha}^j = A_{\alpha}^j I - \frac{1}{\rho_{\alpha}} t_{\alpha}^j$$  \hspace{1cm} (12.100)$$

and

$$\mu_{\alpha}^N = \Gamma_{\alpha}^N, \quad \tilde{\mu}_{\alpha}^j = \mu_{\alpha}^j - \mu_{\alpha}^N$$ \hspace{1cm} (12.101)$$

which is (12.21), (12.23), (12.20a) and (12.20b), repeated. The third term in (12.99) can be rewritten as:

$$\sum_{j=1}^{N-1} C_i^j \tilde{\mu}_i^j I = \sum_{j=1}^{N-1} C_i^j \left( \mu_i^j - \mu_i^N \right) = \sum_{j=1}^{N-1} C_i^j \mu_i^j - \sum_{j=1}^{N-1} C_i^j \mu_i^N$$ \hspace{1cm} (12.102)$$

$$= \sum_{j=1}^{N} C_i^j \mu_i^j - C_i^N \mu_i^N - \sum_{j=1}^{N} C_i^j \mu_i^N + C_i^N \mu_i^N$$

Using the relation $\sum_{j=1}^{N} C_i^j = 1$, i.e. equation (2.14), the expression (12.102) becomes

$$\sum_{j=1}^{N-1} C_i^j \tilde{\mu}_i^j I = \sum_{j=1}^{N-1} C_i^j \mu_i^j - \mu_i^N$$ \hspace{1cm} (12.103)$$

That is, when $\tilde{e}_l$ vanish the expression (12.99) gives

$$\left( \frac{p_I}{\rho_I} + A_i \right) I - \sum_{j=1}^{N} C_i^j \mu_i^j = \left( \frac{p_s}{\rho_s} + A_s \right) I - \sum_{j=1}^{N} C_i^j \mu_i^j + \mu_i^N$$ \hspace{1cm} (12.104)$$

at equilibrium, where (12.99) and (12.104) are used.

A more physical intuitive interpretation of (12.91) can be obtained by considering the momentum equation for the $\alpha$-phase, which is given by (4.24), i.e.

$$\varepsilon_{\alpha} \rho_{\alpha} \frac{D_{\alpha} \left( v_\alpha \right)}{Dt} = \text{div} \left( \varepsilon_{\alpha} t_\alpha \right) + \varepsilon_{\alpha} \rho_{\alpha} E_{\alpha} + \tilde{T}_\alpha$$ \hspace{1cm} (12.105)$$

At equilibrium $D_{\alpha} v_\alpha /Dt = 0$, hence

$$\tilde{T}_l = -\text{div} \left( \varepsilon_{\alpha} t_{\alpha} \right) - \varepsilon_{\alpha} \rho_{\alpha} \varepsilon_{\alpha}$$ \hspace{1cm} (12.106)$$

is the equilibrium version for the liquid phase momentum equation. Combining (12.91) and (12.106) gives

$$-\text{div} \left( \varepsilon_{\alpha} t_{\alpha} \right) - \varepsilon_{\alpha} \rho_{\alpha} \varepsilon_{\alpha} = \rho_{\alpha} \text{grad} \varepsilon_{\alpha} - \varepsilon_{\alpha} \rho_{\alpha} \text{tr} \left( \frac{\partial A_{\alpha}}{\partial E_{\alpha}} \text{grad} E_{\alpha} \right)$$ \hspace{1cm} (12.107)$$

The definition of the stress tensor for the liquid phase, i.e. $t_l = -p_l I - \sum_{j=1}^{N} \rho_{\alpha}^j u_l^j \otimes u_l^j$, given from equation (4.23) and (12.14), is at equilibrium given as: $t_l = -p_l I$, which means that (12.107) can be expressed as

$$\text{div} \left( \varepsilon_{\alpha} p_{\alpha} \right) - \varepsilon_{\alpha} \rho_{\alpha} \varepsilon_{\alpha} = \rho_{\alpha} \text{grad} \varepsilon_{\alpha} - \varepsilon_{\alpha} \rho_{\alpha} \text{tr} \left( \frac{\partial A_{\alpha}}{\partial E_{\alpha}} \text{grad} E_{\alpha} \right)$$ \hspace{1cm} (12.108)$$
Noting, also, that the following identity holds
\[ \text{div} (\epsilon_l p_l I) = \epsilon_l \text{grad} p_l + \rho_l \text{grad} \epsilon_l \] (12.109)
That is, by combining (12.108) and (12.109) one obtain
\[ \text{grad} p_l - \rho_l \mathbf{g}_l = -\rho_l \text{tr} \left( \frac{\partial A_l}{\partial E_s} \text{grad} E_s \right) \] (12.110)
which is an alternative version of (12.91).
The condition for the terms involving the property grad\( T \) is
\[ \Lambda_{\text{grad} T} = \frac{\text{grad} T}{T} \sum_{\alpha=1}^{N} \left( q_{\alpha} + \sum_{j=1}^{N} t_{\alpha}^{j} u_{\alpha}^{j} - \sum_{j=1}^{N} \rho_{\alpha}^{j} u_{\alpha}^{j} (A_{\alpha}^{j} - \frac{1}{2} \rho_{\alpha}^{j} u_{\alpha}^{j}) \right) \geq 0 \] (12.111)
The properties grad\( T \) and \( u_{\alpha}^{j} \) vanish at equilibrium, therefore (12.111) gives that
\[ q_{\alpha} + q_{\alpha} = 0 \] (12.112)
is an condition defined by (12.85) and (12.4).

12.4. Comparison with classical equilibrium results
Consider again the equilibrium result (12.110), i.e.
\[ \text{grad} p_l - \rho_l \mathbf{g}_l = -\rho_l \text{tr} \left( \frac{\partial A_l}{\partial E_s} \text{grad} E_s \right) \] (12.113)
which shows that the fluid in consideration is in contrast with the classical equilibrium result, i.e.: grad\( p_l = \rho_l \mathbf{g}_l \). A normal fluid satisfying grad\( p_l = \rho_l \mathbf{g}_l \) is called a bulk fluid and the fluid described by the equilibrium condition (12.113) can be referred to as a vincial fluid.
Consider, next, a combination of the equations (12.18), i.e.
\[ t_{\alpha}^{j} = \rho_{\alpha}^{j} A_{\alpha}^{j} - \mu_{\alpha}^{j} \rho_{\alpha}^{j} I - \rho_{\alpha}^{j} \Gamma_{\alpha}^{N} \] (12.114)
and (12.86), i.e.
\[ \text{div} \epsilon_{\alpha} \rho_{\alpha}^{j} \left( \mu_{\alpha}^{j} I - (A_{\alpha}^{j} - A_{\alpha}^{N}) I + \left( \frac{t_{\alpha}^{j}}{\rho_{\alpha}^{j}} - \frac{t_{\alpha}^{N}}{\rho_{\alpha}^{N}} \right) \right) = \epsilon_{\alpha} \rho_{\alpha}^{j} \text{grad} (\mu_{\alpha}^{j}) \] (12.115)
which yields
\[ \text{div} \epsilon_{\alpha} \rho_{\alpha}^{j} \left( A_{\alpha}^{N} I - \Gamma_{\alpha}^{N} - \frac{t_{\alpha}^{N}}{\rho_{\alpha}^{N}} \right) = \epsilon_{\alpha} \rho_{\alpha}^{j} \text{grad} (\mu_{\alpha}^{j}) \] (12.116)
Using the definition \( \Gamma_{\alpha}^{N} = A_{\alpha}^{N} I - t_{\alpha}^{N} / \rho_{\alpha}^{N} \), i.e. (12.21), the equilibrium condition (12.116) reduces to
\[ \text{grad} (\mu_{\alpha}^{j}) = \text{div} (\mu_{\alpha}^{j} - \mu_{\alpha}^{N}) = \text{grad} (\mu_{\alpha}^{j} - \mu_{\alpha}^{N}) = 0 \] (12.117)
where (12.20b) and (12.51) are used. This resembles the classical Gibbsian result stating that at equilibrium, the chemical potential is constant, but it is expressed only in terms of the relative chemical potential.

Consider now the non-relative definitions of the chemical potentials corresponding to the relative chemical potentials in (12.93) and (12.117). The derived expressions (12.25), (12.14), (12.16), (12.104) and (12.93) will be used, which are given as

$$\sum_{j=1}^{N} C_{\alpha}^{j} \mu_{\alpha}^{j} = A_{\alpha} I - \frac{1}{\rho_{\alpha}} t_{\alpha} = G_{\alpha}$$  \hspace{1cm} (12.118)

$$t_{i} = -p_{i} I - \sum_{j=1}^{N} \rho_{j}^{i} u_{j}^{i} \otimes u_{j}^{i}$$  \hspace{1cm} (12.119)

$$t_{s} = -p_{s} I + \frac{\epsilon_{s}}{\epsilon_{s}} t_{s}^{i} + t_{s}^{e} - \sum_{j=1}^{N} \rho_{s}^{j} u_{s}^{j} \otimes u_{s}^{j}$$  \hspace{1cm} (12.120)

$$\left(\frac{p_{i}}{\rho_{i}} + A_{i}\right) I - \sum_{j=1}^{N} C_{j}^{i} \mu_{j}^{i} \mu_{j}^{N} = \left(\frac{p_{s}}{\rho_{s}} + A_{s}\right) I - \sum_{j=1}^{N} C_{j}^{i} \mu_{j}^{i} \mu_{j}^{N}$$ \hspace{1cm} (12.121)

$$\tilde{\mu}_{i}^{j} = \tilde{\mu}_{s}^{j}$$  \hspace{1cm} (12.122)

where it should be noted that (12.121) and (12.122) are equilibrium results.

For the liquid phase combine (12.118) and (12.119) in order to eliminate the stress tensor $t_{i}$, i.e.

$$\sum_{j=1}^{N} C_{j}^{i} \mu_{j}^{i} = A_{i} I + \frac{1}{\rho_{i}} \left( p_{i} I + \sum_{j=1}^{N} \rho_{j}^{i} u_{j}^{i} \otimes u_{j}^{i} \right)$$  \hspace{1cm} (12.123)

Eliminating stress tensor $t_{s}$ in solid phase combine (12.118) and (12.120) to obtain

$$\sum_{j=1}^{N} C_{j}^{i} \mu_{j}^{i} = A_{s} I + \frac{1}{\rho_{s}} \left( p_{s} I - \frac{\epsilon_{s}}{\epsilon_{s}} t_{s}^{i} - t_{s}^{e} + \sum_{j=1}^{N} \rho_{s}^{j} u_{s}^{j} \otimes u_{s}^{j} \right)$$  \hspace{1cm} (12.124)

Combining (12.123) and (12.124) with the equilibrium condition (12.121), gives

$$-\frac{1}{\rho_{i}} \left( \sum_{j=1}^{N} \rho_{j}^{i} u_{j}^{i} \otimes u_{j}^{i} \right) + \mu_{i}^{N} = \frac{1}{\rho_{s}} \left( \frac{\epsilon_{s}}{\epsilon_{s}} t_{s}^{i} + t_{s}^{e} - \sum_{j=1}^{N} \rho_{s}^{j} u_{s}^{j} \otimes u_{s}^{j} \right) + \mu_{s}^{N}$$  \hspace{1cm} (12.125)

Note, further, that at equilibrium the diffusion velocities $u_{j}^{i}$ and $u_{s}^{j}$ vanish, and that $\tilde{\mu}_{i}^{j} I = \mu_{i}^{j} - \mu_{i}^{N}$, i.e. (12.101b) together with (12.122), gives

$$\tilde{\mu}_{i}^{j} I = \mu_{i}^{j} - \mu_{i}^{N} = \tilde{\mu}_{s}^{j} I = \mu_{s}^{j} - \mu_{s}^{N}$$  \hspace{1cm} (12.126)
That is, \( \mu_1^N - \mu_2^N = \mu_1^N - \mu_2^N \). Hence, by (12.125) and (12.126) it is concluded that

\[
\mu_1^N - \mu_2^N = \frac{1}{\rho_s} \left( \frac{\varepsilon_l}{\varepsilon_s} t_s^1 + t_s^2 \right) \quad (12.127)
\]

The equivalent expression for the scalar chemical potential can be obtained by considering

\[
\mu_i^\rho = \mu_2^\rho \quad (12.128)
\]

\[
\mu_2^\rho - \mu_3^\rho = \frac{1}{\rho_s} \left( \frac{\varepsilon_l}{\varepsilon_s} t_s^1 + t_s^2 \right) \quad (12.129)
\]

i.e. (12.49) and (12.50), combined with (12.127), to obtain

\[
\mu_i^\rho = \mu_2^\rho \quad (12.130)
\]

which is the classical Gibbsian result stating that the chemical potentials of a single species in two phases are equal at equilibrium. It is, however, concluded from (12.127) that the tensorial potential does not recover the classical result when the solid phase is stressed.

The absolute form of (12.117) can be derived by considering the constitutive function for \( A_l \), which is \( A_l (T, \rho_l, C_l^J, E_s) \), see (9.1). The gradient of \( A_l (T, \rho_l, C_l^J, E_s) \) is by the chain rule, give as

\[
\text{grad} A_l = \frac{\partial A_l}{\partial T} \text{grad} T + \frac{\partial A_l}{\partial \rho_l} \text{grad} \rho_l + \sum_{j=1}^{N-1} \frac{\partial A_l}{\partial C_l^J} \text{grad} C_l^J + \text{tr} \left( \frac{\partial A_l}{\partial E_s} \text{grad} E_s \right) \quad (12.131)
\]

where the third term on the right-hand side of (12.131) only is summed on \( j = 1, ..., N-1 \), due to the summation from 1 to \( N \) not is independent since \( \sum_{j=1}^{N} C_l^J = 1 \). Considering, further (12.51) with \( j = N \), i.e.

\[
\bar{\mu}_i^{N-1} = \frac{\partial A_l}{\partial C_l^N} \Rightarrow \bar{\mu}_i^{N-1} = \left( \mu_i^{N-1} - \mu_i^{N} \right) \bar{I} = 0 \quad (12.132)
\]

which justifies that (12.131) can be written as

\[
\text{grad} A_l = \frac{\partial A_l}{\partial T} \text{grad} T + \frac{\partial A_l}{\partial \rho_l} \text{grad} \rho_l + \sum_{j=1}^{N} \mu_i^J \text{grad} C_l^J + \text{tr} \left( \frac{\partial A_l}{\partial E_s} \text{grad} E_s \right) \quad (12.133)
\]

Observing that the relative chemical potential \( \mu_i^J \) and the pressure in the liquid phase \( p_l \) are given by the definitions (9.2a) and (9.4), i.e. \( \mu_i^J = \partial A_l / \partial C_l^J \), and \( p_l = \rho_l^2 \partial A_l / \partial \rho_l \). Recall, also,
that under the equilibrium conditions studied the property \( \nabla T \), in (12.133), vanish. Hence, at equilibrium (12.133) can be written as

\[
\nabla A_t = \frac{p_t}{\rho_t} \nabla \rho_t + \sum_{j=1}^{N} \mu_j \nabla C_j + \text{tr} \left( \frac{\partial A_t}{\partial E_s} \nabla E_s \right)
\]  

(12.134)

Note also that (12.43) with \( \alpha = 1 \), i.e.

\[
A_t = \sum_{j=1}^{N} C_j \mu_j - \frac{p_t}{\rho_t}
\]  

(12.135)

can be used to obtain an expression for the gradient of \( A_t \), as

\[
\nabla A_t = - \nabla \left( \frac{p_t}{\rho_t} \right) + \sum_{j=1}^{N} \nabla \left( C_j \mu_j \right)
\]  

(12.136)

By using the identities

\[
- \nabla \left( \frac{p_t}{\rho_t} \right) = \frac{p_t}{\rho_t^2} \nabla \rho_t - \frac{1}{\rho_t} \nabla p_t
\]  

(12.137)

and

\[
\sum_{j=1}^{N} \nabla \left( C_j \mu_j \right) = \sum_{j=1}^{N} C_j \nabla \mu_j + \sum_{j=1}^{N} \mu_j \nabla C_j
\]  

(12.138)

the term \( \nabla A_t \) in (12.136) takes the for

\[
\nabla A_t = \frac{p_t}{\rho_t^2} \nabla \rho_t - \frac{1}{\rho_t} \nabla p_t
\]  

(12.139)

\[
+ \sum_{j=1}^{N} C_j \nabla \mu_j + \mu_j \sum_{j=1}^{N} \nabla C_j
\]

Combining (12.134) and (12.139) one obtain

\[
\text{tr} \left( \frac{\partial A_t}{\partial E_s} \nabla E_s \right) = - \frac{1}{\rho_t} \nabla p_t + \sum_{j=1}^{N} C_j \nabla \mu_j
\]  

(12.140)

Using, further, the equilibrium condition (12.110), i.e. \( \nabla p_t - \rho_t \mathbf{g} = - \rho_t \text{tr} (\partial A_t/\partial E_s \nabla E_s) \)

\[
\sum_{j=1}^{N} C_j \nabla \mu_j = \text{tr} \left( \frac{\partial A_t}{\partial E_s} \nabla E_s \right) + \frac{1}{\rho_t} \nabla p_t = \mathbf{g}
\]  

(12.141)

which is the Gibbs-Duhem relation for the liquid phase. In order to obtain a sharper result for (12.117) consider the scalar version of (12.117) multiplied with \( C_j \) and summed over all constituents, i.e.

\[
\sum_{j=1}^{N} C_j \nabla \left( \bar{\rho}_j \right) = \sum_{j=1}^{N} C_j \nabla \left( \mu_j - \mu_j^N \right) = 0
\]  

(12.142)
By combining (12.143) and (12.141), one obtain

\[ \nabla \mu_i^N = g_i \]  

(12.144)

Using this expression with (12.117), i.e. \( \nabla (\mu_i^j - \mu_i^N) = 0 \), gives

\[ \nabla (\mu_i^j) = g_i \]  

(12.145)

Further, by using \( \mu_i^j = \mu_i^j \), i.e. (12.130), and (12.145) results in

\[ \nabla (\mu_i^j) = \nabla (\mu_i^j) = g \]  

(12.146)

where the body force \( g \) is identified as the gravity which is assumed to be the same for all constituents and phases, i.e. \( g_i^j = g_n = g \). The equilibrium condition in (12.146) is a sharper result than (12.117) and shows consistency with the classic Gibbsian result stating that in absence of gravity the scalar chemical potential is constant at equilibrium. By combining the condition (12.146) with the relation between scalar and tensorial chemical potentials for the liquid phase: \( \mu_i^j I = \mu_i^j \), i.e. equation (12.49), and with the corresponding condition for the solid phase: \( \mu_i^2 I - \mu_i^2 = 1/\rho_s (t_s^i \varepsilon_i / \varepsilon_s + t_s^i) \), i.e. equation (12.50), one obtains

\[ \text{div} \mu_i^j = g \]  

(12.147)

\[ \text{div} \mu_i^j = g - \text{div} \left( \frac{1}{\rho_s} \left( \frac{\varepsilon_i}{\varepsilon_s} t_s^i + t_s^i \right) \right) \]  

(12.148)

The condition (12.146) confirms that in absence of gravity the tensorial chemical potential for the solid phase, as defined by (12.23), is not constant at equilibrium.

### 12.5. Near-equilibrium theory

To derive near-equilibrium results, the coefficients of the variables listed in (12.85) in entropy inequality (12.4), are linearized about the variables

\[ \frac{D \varepsilon_i^l}{D t}, \ (u_l - u_s) ; \ u_i^j ; \ \varepsilon_i^l ; \ \dot{\varepsilon}_i ; \ \hat{\varepsilon}_i^l ; \ \text{grad} T \]  

(12.149)

since they vanish at equilibrium. The approach of linearizing only about the one variable which gives a positive quadratic form in the entropy inequality. Consider \( z \) which is one of the variables which vanish at equilibrium and the function \( f \) is the coefficient of \( z \) within the entropy inequality. The linearization procedure is then given by

\[ f_{\text{new}} \approx f_{\text{eq}} + C z \]  

(12.150)
which is an approximation for the near equilibrium value of $f$, where $C$ is the linearization constant.

Consider, first, the condition when $\epsilon_l$ vanish at equilibrium, i.e.

\[ p_l = p_s \]  
(12.151)

The near-equilibrium result, hence becomes

\[ p_l - p_s = \mu_s \frac{D_s \epsilon_l}{Dt} \]  
(12.152)

where (12.149) is used with $f_{eq} = p_l - p_s$, $z = D_s \epsilon_l / Dt$ and $C = \mu_s$.

When $(u_l - u_s)$ vanish at equilibrium, one obtain (12.91), i.e.

\[ \hat{T}_l = \rho_1 \text{grad} \epsilon_l - \epsilon_l \rho_1 \text{tr} \left( \frac{\partial A_1}{\partial E_s} \text{grad} E_s \right) \]  
(12.153)

The near-equilibrium result is obtained by identifying $z$ and $C$ as: $z = (u_l - u_s)$ and $C = R_l$, i.e.

\[ \rho_1 \text{grad} \epsilon_l - \epsilon_l \rho_1 \text{tr} \left( \frac{\partial A_1}{\partial E_s} \text{grad} E_s \right) - \hat{T}_l = R_l (u_l - u_s) \]  
(12.154)

The linearized version of the equilibrium condition $\tilde{\mu}_l^j = \hat{\mu}_s^j$, i.e. equation (12.93), becomes

\[ \tilde{\mu}_l^j - \hat{\mu}_s^j = K^j \tilde{\epsilon}_o^j, \quad j = 1, \ldots, N - 1 \]  
(12.155)

where $K^j$ is the linearization constant.

When $\tilde{\epsilon}_o^j$ vanish at equilibrium, the conditions $\tilde{\mu}_l^j = \hat{\mu}_l^j$ and $\tilde{\mu}_s^j = \hat{\mu}_s^j$ was obtained, see equations (12.98a) and (12.98b), hence the linearization process gives

\[ \tilde{\mu}_l^j - \hat{\mu}_l^j = W_l^j \tilde{\epsilon}_l^j, \quad \text{and} \quad \tilde{\mu}_s^j - \hat{\mu}_s^j = W_s^j \tilde{\epsilon}_s^j \]  
(12.156)

where $W_l^j$ and $W_s^j$ are the linearization constants for the reaction between two constituents in the liquid phase and the solid phase, respectively. Note also that $j \neq i$.

In the above near-equilibrium results the term $f_{eq}$ is zero. This it not the case for the coefficients for $u_s^j$ which includes an equilibrium condition. For this case it is, therefore, necessary to do some further manipulations. Consider the property $w_\alpha^j$ which is the terms associated with $u_s^j$ in the entropy inequality (12.4), i.e.

\[ \sum_{j=1}^{N-1} w_\alpha^j = - \left( \hat{T}_\alpha^j + t_\alpha^j \right) - \text{grad} \left( \epsilon_\alpha \rho_\alpha^j A_\alpha^j \right) + \tilde{\mu}_\alpha^j \text{grad} \left( \epsilon_\alpha \rho_\alpha^j \right) \]  
(12.157)

where second order terms of the diffusion velocities are ignored and where (12.11) has been used, i.e. $\lambda_\alpha^j = \hat{\mu}_\alpha^j$. Using the definition of $\Gamma_\alpha^N$, i.e. equation (12.20a), and adding $\sum_{j=1}^{N} u_s^j \left( \rho_\alpha^j \tilde{\mu}_\alpha^N \text{grad} \epsilon_\alpha \right)$
which is zero by the constraint (2.17), one obtain

\[
\sum_{j=1}^{N} \mathbf{w}_a^j \cdot \mathbf{u}_a^j = \mathbf{u}_a^j \cdot \left( \mu_{\alpha} \nabla (\varepsilon_{\alpha} \rho_{\alpha}) - \mu_{\alpha} \nabla (\varepsilon_{\alpha} \rho_{\alpha}^N) - \nabla (\varepsilon_{\alpha} \rho_{\alpha}^d A_{\alpha}^d) \right) + \mathbf{u}_a^j \left( - \left( \mathbf{T}_a^j + \mathbf{e}_a^j \right) + \varepsilon_{\alpha} \mu_{\alpha} \nabla \rho_{\alpha}^b \right) + \varepsilon_{\alpha} \mu_{\alpha} \nabla \rho_{\alpha}^d \nabla \varepsilon_{\alpha} \tag{12.158}
\]

where the summation is from \( j = 1, \ldots, N \). Note that the identity

\[
\mu_{\alpha} \nabla (\varepsilon_{\alpha} \rho_{\alpha}^N) = \varepsilon_{\alpha} \mu_{\alpha} \nabla \rho_{\alpha}^b + \rho_{\alpha}^d \mu_{\alpha} \nabla \rho_{\alpha}^d \varepsilon_{\alpha} \tag{12.159}
\]

holds, i.e. (12.158) is reduced to

\[
\sum_{j=1}^{N} \mathbf{w}_a^j \cdot \mathbf{u}_a^j = \mathbf{u}_a^j \cdot \left( \mu_{\alpha} \nabla (\varepsilon_{\alpha} \rho_{\alpha}^N) - \nabla (\varepsilon_{\alpha} \rho_{\alpha}^d A_{\alpha}^d) - \left( \mathbf{T}_a^j + \mathbf{e}_a^j \right) \right) \tag{12.160}
\]

Consider, further, the momentum balance equation for the \( \alpha \)-phase, i.e. equation (4.9), and assuming that the inertial terms is negligible near equilibrium, i.e. (4.9) reduces to the form

\[
- \left( \mathbf{T}_a^j + \mathbf{e}_a^j \right) = \nabla \varepsilon_{\alpha} \mathbf{t}_{\alpha}^j + \varepsilon_{\alpha} \rho_{\alpha}^d \mathbf{g}_{\alpha}^j \tag{12.161}
\]

By combining (12.160) and (12.161) the result is

\[
\sum_{j=1}^{N} \mathbf{w}_a^j \cdot \mathbf{u}_a^j = \mathbf{u}_a^j \cdot \left( \mu_{\alpha} \nabla (\varepsilon_{\alpha} \rho_{\alpha}^N) - \nabla (\varepsilon_{\alpha} \rho_{\alpha}^d A_{\alpha}^d) + \nabla \varepsilon_{\alpha} \mathbf{t}_{\alpha}^j + \varepsilon_{\alpha} \rho_{\alpha}^d \mathbf{g}_{\alpha}^j \right) \tag{12.162}
\]

Hence, according to the linearization procedure illustrated in (12.150), one obtain

\[
\left( \mu_{\alpha} \nabla (\varepsilon_{\alpha} \rho_{\alpha}^N) - \nabla (\varepsilon_{\alpha} \rho_{\alpha}^d A_{\alpha}^d) \right)_{\text{neg}} = \left( \mu_{\alpha} \nabla (\varepsilon_{\alpha} \rho_{\alpha}^N) - \nabla (\varepsilon_{\alpha} \rho_{\alpha}^d A_{\alpha}^d) \right)_{\text{eq}} + \mathbf{R}_{\alpha}^j \mathbf{u}_a^j \tag{12.163}
\]

where \( z = \mathbf{u}_a^j \) and the linearization constant is given by \( \mathbf{R}_{\alpha}^j = \mathbf{u}_a^j \), where the matrix \( \mathbf{R}_{\alpha}^j \), must be positive definite.

The expression (12.163) can be rearranged further. Note that the chemical potential tensor \( \mu_{\alpha}^d \) is defined as

\[
\mu_{\alpha}^d = A_{\alpha}^d \mathbf{I} - \frac{1}{\rho_{\alpha}^d} \mathbf{t}_{\alpha}^j \tag{12.164}
\]

which is (12.23) repeated. By multiplying the definition (12.164) by \( \varepsilon_{\alpha} \rho_{\alpha}^d \) and taking the divergence of the whole expression one obtain

\[
\nabla (\varepsilon_{\alpha} \rho_{\alpha}^d A_{\alpha}^d) = \nabla (\varepsilon_{\alpha} \rho_{\alpha}^d \mu_{\alpha}^d) + \nabla (\varepsilon_{\alpha} \mathbf{t}_{\alpha}^j) \tag{12.165}
\]

The first term on the right-hand side of (12.165) can be re-written by the identity

\[
\nabla (\varepsilon_{\alpha} \rho_{\alpha}^d \mu_{\alpha}^d) = \varepsilon_{\alpha} \rho_{\alpha}^d \nabla (\mu_{\alpha}^d) + \mu_{\alpha}^d \nabla (\varepsilon_{\alpha} \rho_{\alpha}^d) \tag{12.166}
\]
Combining (12.165) and (12.166) gives

$$\mu^i_a \text{grad} (\varepsilon_a \rho^i_a) - \text{grad} (\varepsilon_a \rho^i_a \mathbf{A}_a^i) + \text{div} (\varepsilon_a \mathbf{t}_a^i) = -\varepsilon_a \rho^i_a \text{div} (\mu^i_a)$$  \hspace{1cm} (12.167)

where it is noted that \(\text{div}(\varepsilon_a \rho^i_a \mathbf{A}_a^i) = \text{grad}(\varepsilon_a \rho^i_a \mathbf{A}_a^i)\). The terms of the left-hand side of (12.167) is identical with the terms in the near-equilibrium equation (12.163), i.e. combining (12.163) and (12.167) gives the result

$$(-\varepsilon_a \rho^i_a \text{div} (\mu^i_a) + \varepsilon_a \rho^i_a \mathbf{g}^i)_{neq} = (-\varepsilon_a \rho^i_a \text{div} (\mu^i_a) + \varepsilon_a \rho^i_a \mathbf{g}^i)_{eq} + \mathbf{R}^j_i \mathbf{u}^j_i$$  \hspace{1cm} (12.168)

By considering the equilibrium result (12.147), for the liquid phase, i.e.

$$\text{div} \left( \mathbf{\mu}^j_i \right) = \mathbf{g}$$  \hspace{1cm} (12.169)

it is noted that the first term on the right-hand side of (12.168), with \(\alpha = l\), vanish. That is, by combining (12.168) and the equilibrium condition (12.169) and using \(\mathbf{g}^i = \mathbf{g}_\alpha = \mathbf{g}\), one obtain

$$\left( -\varepsilon_l \rho^i_l \text{div} (\mathbf{\mu}^i_l) + \varepsilon_l \rho^i_l \mathbf{g}^i \right)_{neq} = \mathbf{R}^j_i \mathbf{u}^j_i$$  \hspace{1cm} (12.170)

which is a generalized version of the classical Fick's law. The generalized Fick's law will in this case be written as

$$\mathbf{R}^j_i \mathbf{u}^j_i = -\varepsilon_l \rho^i_l \left( \text{div} \left( \mathbf{\mu}^i_l \right) - \mathbf{g} \right)$$  \hspace{1cm} (12.171)

The equilibrium condition corresponding to (12.169), for the solid phase, is given by

$$\text{div} \left( \mathbf{\mu}^j_s \right) = \mathbf{g} - \text{div} \left( \frac{1}{\rho_s} \left( \mathbf{t}_s + \frac{\varepsilon_t}{\varepsilon_s} \mathbf{t}_s \right) \right)$$  \hspace{1cm} (12.172)

which is equation (12.148) repeated. Combining (12.172) with (12.168) using \(\mathbf{g}^i = \mathbf{g}_\alpha = \mathbf{g}\) and setting \(\alpha = s\), gives

$$\left( -\varepsilon_s \rho^i_s \text{div} (\mathbf{\mu}^i_s) + \varepsilon_s \rho^i_s \mathbf{g}^i \right)_{neq} = \left( -\varepsilon_s \rho^i_s \left( \mathbf{g} - \text{div} \left( \frac{1}{\rho_s} \left( \mathbf{t}_s + \frac{\varepsilon_t}{\varepsilon_s} \mathbf{t}_s \right) \right) \right) + \varepsilon_s \rho^i_s \mathbf{g}^i \right)_{eq} + \mathbf{R}^j_i \mathbf{u}^j_i$$ \hspace{1cm} (12.173)

i.e.

$$\left( -\varepsilon_s \rho^i_s \text{div} (\mathbf{\mu}^i_s) + \varepsilon_s \rho^i_s \mathbf{g}^i \right)_{neq} = \varepsilon_s \rho^i_s \text{div} \left( \frac{1}{\rho_s} \left( \mathbf{t}_s + \frac{\varepsilon_t}{\varepsilon_s} \mathbf{t}_s \right) \right)_{eq} + \mathbf{R}^j_i \mathbf{u}^j_i$$  \hspace{1cm} (12.174)

Therefore, the near equilibrium theory gives that the diffusion velocity for the \(j\)th constituents in solid phase is

$$\mathbf{R}^j_i \mathbf{u}^j_i = -\varepsilon_s \rho^i_s \left( \text{div} (\mathbf{\mu}^i_s) - \mathbf{g} \right) - \varepsilon_s \rho^i_s \text{div} \left( \frac{1}{\rho_s} \left( \mathbf{t}_s + \frac{\varepsilon_t}{\varepsilon_s} \mathbf{t}_s \right) \right)$$  \hspace{1cm} (12.175)

which, also, is a generalized version of the classical Fick's law valid for diffusion of constituents in a stressed solid.
Next the interest will be turned to the derivation of a modified expression of the Darcy's law. Consider the equilibrium condition (12.110) with $g_i' = g_i = g$, i.e.

$$-\text{grad} p_l - \rho_l \text{tr} \left( \frac{\partial A_l}{\partial E_s} \text{grad} E_s \right) + \rho_l g = 0$$

(12.176)

which is an alternative version of (12.91). The equilibrium expression (12.91) is associated with the variable $\left(u_l - u_s\right)$ which vanish at equilibrium, see also the entropy inequality (12.4). Hence, by linearizing (12.176), according to (12.150) with $C = \left(u_l - u_s\right)$, one obtain

$$R_l \left(u_l - u_s\right) = -\text{grad} p_l - \rho_l \text{tr} \left( \frac{\partial A_l}{\partial E_s} \text{grad} E_s \right) + \rho_l g$$

(12.177)

In addition to the pressure gradient this generalized form of the Darcy's law includes a term accounting for flow of liquid in the solid pore structure induced by strains in the solid phase, the magnitude of this flow is, of course, given by the constitutive function for $A_l(T, \rho_l, C_l', E_s)$.

Finally, the Fourier’s law will be examined. Consider the equilibrium condition (12.112), i.e.

$$\mathbf{q}_s + \mathbf{q}_l = 0$$

(12.178)

The terms associated with this condition in the entropy inequality (12.4) is $\text{grad} T$, hence the linearization according to (12.150) becomes

$$\mathbf{q}_s + \mathbf{q}_l = \lambda \text{grad} T$$

(12.179)

which is the classical Fourier’s law, in which the constant $\lambda$ must be positive definite.

13. Internal variables

Internal variables are frequently used in different applications, such as in plasticity, creep and thermo-elastic models. The internal variables denoted $H_k$, $k = 1, \ldots, Z$, where $Z$ is the number of introduced variables, are introduced in the constitutive function for the Helmholtz free energy for the solid and liquid phase, as

$$A_s \left(T, \rho_s, C_s', E_s, H_k\right) ; \quad A_l \left(T, \rho_l, C_l', E_s, H_k\right)$$

(13.1)

With reference to the material time derivatives of $A_s$ in equation (9.20), and $A_l$ in (9.19), one must add the following $Z$ terms

$$\frac{D_s A_s}{D t} = \frac{\partial A_s}{\partial H_k} \frac{D_s H_k}{D t} + \ldots$$

(13.2)

and

$$\frac{D_l A_l}{D t} = \frac{\partial A_l}{\partial H_k} \frac{D_l H_k}{D t} + \ldots$$

(13.3)

Further, it is noted that the Helmholtz free energy for the two considered phases are included in the entropy inequality as, for example, presented in (7.59). The terms that must be added
in the inequality, due to the inclusion of $H_k$ in the constitutive functions for the Helmholtz free energy for the solid and liquid phase, are

$$\Lambda = \sum_{\alpha = l, s} \frac{\partial A_i}{\partial H_k} \frac{D_i H_k}{Dt} + ... \geq 0$$

That is, the nature of these terms must be examined and arranged so as they satisfy the above condition.

14. Different versions of the energy equation

In the method of using the Helmholtz free energy as a constitutive function it can be an advantage to re-write the energy equation in terms of the chemical potential tensor and the Helmholtz free energy or with the Gibb’s energy tensor and the Helmholtz free energy, instead of using the internal energy as used before. Consider the energy equation for the $j$th constituent in phase $\alpha$, i.e.

$$\varepsilon_\alpha \rho_\alpha \frac{D_j (E_{13})}{Dt} = \text{tr} \left( \varepsilon_\alpha T^T_j e^j \right) - \text{div} \left( \varepsilon_\alpha q_j^\alpha + \varepsilon_\alpha \rho_\alpha \tau_j^\alpha + \dot{Q}_\alpha + \dot{E}_\alpha \right)$$

which is (6.16) repeated. The energy equation for the inner part of the internal energy of the $\alpha$ phase is according to equation (6.47) given as

$$\varepsilon_\alpha \rho_\alpha \frac{D_j (E_{13})}{Dt} = \varepsilon_\alpha \text{tr} \sum_{j=1}^N \left( T^T_j e^j \right) - \text{div} \left( \varepsilon_\alpha k_\alpha + \dot{Q}_\alpha \right)$$

$$- \sum_{j=1}^N \left( \frac{1}{2} u_j^\alpha \left( e^j + c_j^\alpha - C_j^\alpha e_\alpha \right) \right)$$

where it is noted that $k_\alpha$ is defined as in equation (6.23), i.e.

$$k_\alpha = \sum_{j=1}^N \left( q_j^\alpha + \rho_j^\alpha E_j^\alpha \right)$$

$$= q_{1\alpha} + \sum_{j=1}^N T^T_j e^j$$

$$= q_{1\alpha} - \sum_{j=1}^N \rho_j^\alpha \left( -T^T_j / \rho_\alpha + \frac{1}{2} u_j^\alpha \right)$$

The defined relation (7.37) between $A_{1\alpha}$, $E_{1\alpha}$, $T$ and $\eta_{1\alpha}$ is

$$A_{1\alpha} = E_{1\alpha} - T n_{1\alpha}$$
Combining (14.3) and (14.4) gives

\[
\mathbf{k}_\alpha = \sum_{j=1}^{N} (q_{i\alpha}^j + \rho_{i\alpha}^j \mathbf{E}_{\alpha}^j \mathbf{u}_{\alpha}^j) \tag{14.5}
\]

\[
= \sum_{j=1}^{N} q_{i\alpha}^j + \sum_{j=1}^{N} \rho_{i\alpha}^j A_{i\alpha}^j \mathbf{u}_{\alpha}^j + \sum_{j=1}^{N} \rho_{i\alpha}^j T \eta_{i\alpha}^j \mathbf{u}_{\alpha}^j
\]

The entropy flux \( \mathbf{h}_\alpha \) for the \( j \)th constituent in phase \( \alpha \) is defined in (7.23), i.e.

\[
\mathbf{h}_\alpha^j = q_{i\alpha}^j + \rho_{i\alpha}^j \eta_{i\alpha}^j T \mathbf{u}_{\alpha}^j \tag{14.6}
\]

The entropy flux \( \mathbf{h}_\alpha \) for the phase \( \alpha \) is the sum of the equation (14.6) written as

\[
\mathbf{h}_\alpha = \sum_{j=1}^{N} q_{i\alpha}^j + \sum_{j=1}^{N} \rho_{i\alpha}^j \eta_{i\alpha}^j T \mathbf{u}_{\alpha}^j \tag{14.7}
\]

The Gibb's energy for the \( \alpha \) phase is given by the definition (9.2b), i.e.

\[
G_\alpha = A_\alpha t - \rho_{i\alpha}^j t_\alpha \tag{14.8}
\]

By using (14.4) and (6.19b) the inner part of the Helmholtz free energy can be related to the inner part of the internal energy density \( E_\alpha \), as

\[
A_{1\alpha} = \sum_{j=1}^{N} \rho_{i\alpha}^j A_{i\alpha}^j = E_{1\alpha} - T \eta_\alpha
\]

The material time derivative of (14.9) is

\[
\frac{D_\alpha (E_{1\alpha})}{Dt} = \frac{D_\alpha (A_{1\alpha})}{Dt} + T \frac{D_\alpha (\eta_\alpha)}{Dt} + \eta_\alpha \frac{D_\alpha (T)}{Dt} \tag{14.10}
\]

The term \( \text{div}(\varepsilon_\alpha \mathbf{k}_\alpha) \) can according to (14.4) be expressed as

\[
\text{div}(\varepsilon_\alpha \mathbf{k}_\alpha) = \text{div} \sum_{j=1}^{N} (\varepsilon_\alpha q_{i\alpha}^j)
\]

\[
+ \text{div} \sum_{j=1}^{N} (\varepsilon_\alpha \rho_{i\alpha}^j A_{i\alpha}^j \mathbf{u}_{\alpha}^j) + \text{div} \sum_{j=1}^{N} (\varepsilon_\alpha \rho_{i\alpha}^j T \eta_{i\alpha}^j \mathbf{u}_{\alpha}^j)
\]

The term \( \varepsilon_\alpha \sum_{j=1}^{N} \rho_{i\alpha}^j D_{j\alpha} (A_{i\alpha}^j) / Dt \) can using the relation:

\[
\varepsilon_\alpha \rho_{i\alpha}^j \frac{D_\alpha (\Gamma_{j\alpha})}{Dt} = \sum_{j=1}^{N} \left( \varepsilon_\alpha \rho_{i\alpha}^j \frac{D_{j\alpha} (\Gamma_{j\alpha})}{Dt} - \text{div} (\varepsilon_\alpha \rho_{i\alpha}^j A_{i\alpha}^j \mathbf{u}_{\alpha}^j) \right)
\]

\[
+ \sum_{j=1}^{N} \Gamma_{j\alpha}^j (\hat{e}_{i\alpha}^j + \hat{\epsilon}_{i\alpha}^j - \mathbf{C}_\alpha \mathbf{e}_{i\alpha})
\]

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that is, equation (4.18) with $\Gamma_\alpha = A^i_\alpha$, be written

$$\varepsilon_\alpha \rho_a \frac{D_a (A^{10})}{Dt} + \sum_{j=1}^{N} \text{div} (\varepsilon_\alpha \rho_a^j A^j_\alpha u^j_\alpha) = \varepsilon_\alpha \sum_{j=1}^{N} \rho_a^j \frac{D^j_\alpha (A^j_\alpha)}{Dt}$$

\[ + A^i_\alpha (\dot{\varepsilon}^i_\alpha + \ddot{\varepsilon}^i_\alpha - C^i_\alpha \dot{\varepsilon}_\alpha) \tag{14.13} \]

Hence, by combining (14.2), (14.10) and (14.11) one obtain the energy equation

$$\varepsilon_\alpha \rho_a \frac{D_a (A^{10})}{Dt} = -\varepsilon_\alpha \rho_a T \frac{D_a (\eta_\alpha)}{Dt} - \varepsilon_\alpha \rho_a \eta_\alpha \frac{D_a (T)}{Dt}$$

\[ + \varepsilon_a \alpha \sum_{j=1}^{N} (T^j_{\alpha} \dot{d}^j_\alpha) - \text{div} \sum_{j=1}^{N} (\varepsilon_a q^j_\alpha) \]

\[ - \text{div} \sum_{j=1}^{N} \varepsilon_\alpha \rho_a^j A^j_\alpha u^j_\alpha - \text{div} \sum_{j=1}^{N} \varepsilon_\alpha \rho_a^j T^n^j_\alpha u^j_\alpha \]

\[ + \varepsilon_a \rho_a r_\alpha + \dot{Q}_\alpha \]

\[ - \sum_{j=1}^{N} u^j_\alpha \cdot (\dot{T}^j_\alpha + \ddot{\varepsilon}^j_\alpha) \]

\[ - \sum_{j=1}^{N} (\frac{1}{2} u^2_\alpha (\dot{\varepsilon}^j_\alpha + \ddot{\varepsilon}^j_\alpha - C^j_\alpha \dot{\varepsilon}_\alpha)) \tag{14.14} \]

Using, further (14.11) in (14.14) the following result is yielded

$$\varepsilon_\alpha \sum_{j=1}^{N} \rho_a^j \frac{D^j_\alpha (A^j_\alpha)}{Dt} = -A^i_\alpha (\dot{\varepsilon}^i_\alpha + \ddot{\varepsilon}^i_\alpha - C^i_\alpha \dot{\varepsilon}_\alpha)$$

\[ -\varepsilon_\alpha \rho_a T \frac{D_a (\eta_\alpha)}{Dt} - \varepsilon_\alpha \rho_a \eta_\alpha \frac{D_a (T)}{Dt} \]

\[ + \varepsilon_a \alpha \sum_{j=1}^{N} (T^j_{\alpha} \dot{d}^j_\alpha) - \text{div} \sum_{j=1}^{N} (\varepsilon_a q^j_\alpha) \]

\[ - \text{div} \sum_{j=1}^{N} \varepsilon_\alpha \rho_a^j A^j_\alpha u^j_\alpha \]

\[ + \varepsilon_a \rho_a r_\alpha + \dot{Q}_\alpha \]

\[ - \sum_{j=1}^{N} u^j_\alpha \cdot (\dot{T}^j_\alpha + \ddot{\varepsilon}^j_\alpha) \]

\[ - \sum_{j=1}^{N} (\frac{1}{2} u^2_\alpha (\dot{\varepsilon}^j_\alpha + \ddot{\varepsilon}^j_\alpha - C^j_\alpha \dot{\varepsilon}_\alpha)) \]
It is noted that $\mathbf{h}_{i}^{a} = \mathbf{q}_{i}^{a} + \rho_{i}^{a} \eta_{i}^{a} \mathbf{T} \mathbf{u}_{i}^{a}$ by definition (14.6), therefore one can conclude that the terms including the divergence operator in (14.15) can be expressed solely in terms of the entropy flux $\mathbf{h}_{i}^{a}$, as

$$-\text{div} \sum_{j=1}^{N} (\varepsilon_{i}^{a} \mathbf{q}_{i}^{a}) - \text{div} \sum_{j=1}^{N} \varepsilon_{i}^{a} \rho^{a}_{j} T \eta^{a}_{j} \mathbf{u}_{i}^{a} = \text{div} \sum_{j=1}^{N} (\varepsilon_{i}^{a} \mathbf{h}_{i}^{a})$$

(14.16)

The proper equation for calculating the temperature $T$ in the energy equation, therefore, becomes

$$\varepsilon_{a} \rho_{a} \eta_{a} \frac{D_{a}(T)}{Dt} = -A_{a}^{i} (\hat{\varepsilon}_{a}^{i} + \hat{\sigma}_{a}^{i} - C_{a}^{i} \hat{\varepsilon}_{a})$$

(14.17)

$$-\varepsilon_{a} \rho_{a} T \frac{D_{a}(\eta_{a})}{Dt} - \varepsilon_{a} \sum_{j=1}^{N} \rho^{a}_{j} \frac{D_{a}^{j}(A_{a}^{j})}{Dt}$$

$$+ \varepsilon_{a} \frac{\text{tr}}{N} \sum_{j=1}^{N} (\mathbf{T}_{a}^{j} \mathbf{d}_{a}^{j}) - \text{div} \sum_{j=1}^{N} (\varepsilon_{a} \mathbf{h}_{i}^{a})$$

$$+ \varepsilon_{a} \rho_{a} T \alpha + \dot{Q}_{a}$$

$$- \sum_{j=1}^{N} \mathbf{u}_{a}^{j} \cdot (\mathbf{T}_{a}^{j} + \mathbf{z}_{a}^{j})$$

$$- \sum_{j=1}^{N} (\frac{1}{2} \mathbf{u}_{a}^{j} \mathbf{z}_{a}^{j} (\hat{\varepsilon}_{a}^{j} + \hat{\sigma}_{a}^{j} - C_{a}^{j} \hat{\varepsilon}_{a})$$

which is (14.15) and (14.16) combined.

Next, the energy equation expressed in terms of the chemical potential tensor will be derived. Consider the partial derivatives of $D_{a} (\rho^{a} A_{a}^{j}) / Dt$, i.e.

$$D_{a}^{j} (\varepsilon_{a} \rho_{a}^{j} A_{a}^{j}) = \varepsilon_{a} \rho_{a}^{j} \frac{D_{a} (A_{a}^{j})}{Dt} + A_{a}^{j} \frac{D_{a} (\varepsilon_{a} \rho_{a}^{j})}{Dt}$$

(14.18)

The mass balance for the for the $j$th constituent in phase $a$ is given by (3.39), i.e.

$$\frac{D_{a}^{j} (\varepsilon_{a} \rho_{a}^{j})}{Dt} = \hat{\varepsilon}_{a}^{j} + \hat{\sigma}_{a}^{j} - \varepsilon_{a} \rho_{a}^{j} \text{div} \mathbf{v}_{a}^{j}$$

(14.19)

Combining (14.18) and (14.19) gives

$$\frac{D_{a}^{j} (\varepsilon_{a} \rho_{a}^{j} A_{a}^{j})}{Dt} = \varepsilon_{a} \rho_{a}^{j} \frac{D_{a} (A_{a}^{j})}{Dt} + A_{a}^{j} (\hat{\varepsilon}_{a}^{j} + \hat{\sigma}_{a}^{j} - \varepsilon_{a} \rho_{a}^{j} \text{div} \mathbf{v}_{a}^{j})$$

(14.20)

The last term on the right-hand side of the above expression can be re-written by the identity

$$\varepsilon_{a} A_{a}^{j} \rho_{a}^{j} \text{div} \mathbf{v}_{a}^{j} = \varepsilon_{a} \rho_{a}^{j} A_{a}^{j} \text{tr} (\text{grad} \mathbf{v}_{a}^{j}) = \varepsilon_{a} \rho_{a}^{j} A_{a}^{j} \text{tr} (\mathbf{d}_{a}^{j})$$

(14.21)

where it is recalled that $\mathbf{d}_{a}^{j} = \text{grad} \mathbf{v}_{a}^{j}$. Hence (14.21) can be written as

$$\frac{D_{a}^{j} (\varepsilon_{a} \rho_{a}^{j} A_{a}^{j})}{Dt} = \varepsilon_{a} \rho_{a}^{j} \frac{D_{a} (A_{a}^{j})}{Dt} + A_{a}^{j} (\hat{\varepsilon}_{a}^{j} + \hat{\sigma}_{a}^{j})$$

(14.22)
Recall that the definition of the chemical potential tensor $\mu^j_\alpha$ for the $j$th constituent in $\alpha$ phase is given by (12.23), i.e.

$$\mu^j_\alpha = A^j_\alpha I - \frac{1}{\rho^j_\alpha} t^j_{\alpha}$$

(14.23)

This means that the term $\varepsilon_\alpha \rho^j_\alpha A^j_\alpha \text{tr}(d^j_\alpha)$ in (14.22) by the condition

$$\varepsilon_\alpha \rho^j_\alpha A^j_\alpha I = \varepsilon_\alpha \rho^j_\alpha \mu^j_\alpha + \varepsilon_\alpha t^j_{\alpha}$$

(14.24)

can be expressed in terms of $\mu^j_\alpha$ and $t^j_{\alpha}$. The condition (14.24) and equation (14.22), gives

$$\frac{D^j_\alpha (\varepsilon_\alpha \rho^j_\alpha A^j_\alpha I)}{D t} = \varepsilon_\alpha \rho^j_\alpha \frac{D^j_\alpha (A^j_\alpha I)}{D t} + A^j_\alpha (\ddot{\varepsilon}^j_\alpha + \dot{\varepsilon}^j_\alpha)$$

$$- \varepsilon_\alpha \rho^j_\alpha \text{tr}(\mu^j_\alpha d^j_\alpha) - \varepsilon_\alpha \text{tr}(t^j_{\alpha} d^j_\alpha)$$

(14.25)

By eliminating the sum of the $j = 1, \ldots, N$ number of terms $\varepsilon_\alpha \rho^j_\alpha D^j_\alpha (A^j_\alpha I)/D t$ in (14.17) using (14.25) one obtain

$$\varepsilon_\alpha \rho^j_\alpha \frac{D^j_\alpha (T^j_\alpha)}{D t} = -\varepsilon_\alpha \sum_{j=1}^{N} \text{tr}(\rho^j_\alpha \mu^j_\alpha d^j_\alpha) + \sum_{j=1}^{N} A^j_\alpha C^j_\alpha \dot{\varepsilon}^j_\alpha$$

(14.26)

$$- \sum_{j=1}^{N} \frac{D^j_\alpha (\varepsilon_\alpha \rho^j_\alpha A^j_\alpha I)}{D t} - \varepsilon_\alpha \rho^j_\alpha T^j_\alpha \frac{D^j_\alpha (n^j_\alpha)}{D t}$$

$$- \text{div} \sum_{j=1}^{N} (\varepsilon_\alpha h^j_\alpha)$$

$$+ \varepsilon_\alpha \rho^j_\alpha r^j_\alpha + \dot{Q^j}_\alpha$$

$$- \sum_{j=1}^{N} \mathbf{u}^j_\alpha \cdot (\mathbf{T}^j_\alpha + \varepsilon^j_\alpha)$$

$$- \sum_{j=1}^{N} \left( \frac{1}{2} \mathbf{u}^j_\alpha \cdot (\ddot{\varepsilon}^j_\alpha + \dot{\varepsilon}^j_\alpha - C^j_\alpha \dot{\varepsilon}^j_\alpha) \right)$$

which is the energy equation expressed with the chemical potential tensor $\mu^j_\alpha$.

15. Electric charge balance

In some cases one is forced to add variables to the normally introduced state variables used in continuum mechanical theories. An important case is phenomenon where electro-magnetic fields are of importance.

Consider the electric displacement vector $\mathbf{j}$ and the charge density $\mathbf{r}$ which must be balanced as

$$0 = -\oint_{\partial \Omega} \mathbf{j} \cdot ds + \int_{\Omega} \mathbf{r} \, dv$$

(15.1)
which is the postulate for the charge balance for a mixture of charged constituents. Using the divergence theorem on the first term on right-hand side of (15.1), i.e.

$$\oint_{\partial \Omega} \mathbf{j} \cdot d\mathbf{s} = \int_{\Omega} \text{div} \mathbf{j} \, d\mathbf{v}$$  \hspace{1cm} (15.2)

the local form of charge balance can be written as

$$-\text{div} \mathbf{j} = \gamma$$  \hspace{1cm} (15.3)

This expression will be used when considering diffusion and sorption of charged constituents in a porous medium.

16. Selected one dimensional examples

Assume incompressibility for the solid phase, i.e. $D_s \rho_s / Dt = 0$.

The deformed volume $dV^*$ can be related to the reference volume $dV$ in the reference configuration $x$ by considering the triple product of the side vectors $\partial x / \partial X$, as

$$dV^* = \left( \frac{\partial x}{\partial X_1} \times \frac{\partial x}{\partial X_2} \times \frac{\partial x}{\partial X_3} \right) dV = \det \left( \frac{\partial x}{\partial X} \right) dV$$  \hspace{1cm} (16.1)

where $J^F = \det (F)$ is the so-called Jacobian. Hence, the volume fraction in the deformed state $\varepsilon_s^*$ and in the reference configuration $\varepsilon_s$ can be related as

$$\varepsilon_s = \frac{\varepsilon_s^*}{J^F}$$  \hspace{1cm} (16.2)

The derivative $\partial \varepsilon_s / \partial P_s$, where $J^F = P_s$, will be needed which with $\varepsilon_s = \varepsilon_s^* P_s^{-1/2}$, becomes

$$\frac{\partial \varepsilon_s}{\partial (J^F)^2} = \frac{\partial \varepsilon_s}{\partial P_s} = -\frac{1}{2} \varepsilon_s^* P_s^{-3/2} = -\frac{1}{2} \varepsilon_s^* (J^F)^{-3}$$  \hspace{1cm} (16.3)

The relation (12.50) is

$$\mu_s^* I = \mu_s^* + \frac{1}{\rho_s} \left( \varepsilon_s^* \frac{t_s^e + \varepsilon_s^* t_s^l}{\varepsilon_s^*} \right)$$  \hspace{1cm} (16.4)

In order to compare $\mu_s^*$ and $\mu_s^*$ at equilibrium, consider the following definition of scalar difference of potentials

$$\Delta \mu_s^* \equiv \frac{1}{3} \varepsilon^s \mu_s^* - \mu_s^*$$  \hspace{1cm} (16.5)

Combining (16.4) and (16.5) gives

$$\Delta \mu_s^* = -\frac{1}{3 \rho_s} \left( \varepsilon^s t_s^e + \varepsilon_s^* \varepsilon^s t_s^l \right)$$  \hspace{1cm} (16.6)
Using the definitions for \( t_s^f \), \( t_s^e \) and \( E_s \), which are given by (9.3a), (9.3b) and (9.5), i.e.

\[
t_s^f = \rho_s F_s^T \frac{\partial A_s}{\partial E_s} F_s^T, \quad t_s^e = \rho_i F_s^T \frac{\partial A_i}{\partial E_s} F_s^T, \quad E_s = \frac{1}{2} (C_s - I)
\]

(16.7)

where \( C_s = F_s^T F_s \), one obtain

\[
\Delta \mu_s^f = - \frac{1}{3} \text{tr} \left( \frac{\partial A_s}{\partial E_s} C_s \right) - \frac{1}{3} \epsilon_i \rho_i \text{tr} \left( \frac{\partial A_i}{\partial E_s} C_s \right)
\]

(16.8)

\[
= - \frac{2}{3} \text{tr} \left( \frac{\partial A_s}{\partial C_s} C_s \right) - \frac{2}{3} \epsilon_i \rho_i \text{tr} \left( \frac{\partial A_i}{\partial C_s} C_s \right)
\]

where (16.7) and (16.8) has been used. The following identity will be of use

\[
\frac{1}{3} \text{tr} \left( \frac{\partial (J^F_s)^2}{\partial C_s} C_s \right) = (J^F_s)^2
\]

(16.9)

where \( J^F_s \) is the determinant of \( F_s \), see equation (2.37). The derivation of relation (16.9) can be performed by considering an arbitrary second order tensor \( A \) and its inverse \( A^{-1} \). Assuming that the determinant of \( A \) is different from zero, the following relation is obtained

\[
\frac{\partial J^A}{\partial A} = J^A A^{-1}
\]

(16.10)

where \( J^A = \det A \). By identifying \( A = C_s \) one obtain

\[
\frac{\partial J^C}{\partial C_s} = J^C C_s^{-1}
\]

(16.11)

where \( J^C = \det C \). By examining the definition of \( F_s = x_{k,K} \) and the determinant of \( F_s \), i.e. \( \det x_{k,K} \), where indices after comma indicate partial differentiation with respect to \( X_{(a)K} \) when they are majuscules, and with respect to \( x_k \) when they are minuscules, the following relation is obtained

\[
J^C_{(s)} = \det C_s = |x_{k,K} x_{k,K}| = |x_{k,K}|^2 = \left( J^F_{(s)} \right)^2
\]

(16.12)

where \( C_s = F_s^T F_s \), i.e. (2.70) has been used. That is, the Jacobi \( J^C_{(s)} \) is related to \( J^F_{(s)} \), as \( J^C_{(s)} = \left( J^F_{(s)} \right)^2 \). This means that the relation between \( C_s \) and \( C_s^{-1} \) can be expressed in terms of the Jacobi of the deformation gradient, i.e.

\[
\frac{\partial (J^F_s)^2}{\partial C_s} C_s^{-1} = (J^F_s)^2 C_s^{-1}
\]

(16.13)

which is (16.11) and (16.12) combined. By multiplying this equation with \( C_s \) and taking the trace of the whole expression, one obtain

\[
\text{tr} \left( \frac{\partial (J^F_s)^2}{\partial C_s} C_s \right) = \text{tr} \left( (J^F_s)^2 C_s^{-1} C_s \right) = 3 (J^F_s)^2
\]

(16.14)
where the identity \( C_\varepsilon^{-1} C_\varepsilon = 1 \), which follows directly from \( C_\varepsilon = F_\varepsilon^T F_\varepsilon \) and \( F_\varepsilon^{-1} F_\varepsilon = 1 \). That is

\[
\frac{1}{3} \text{tr} \left( \frac{\partial J^F_\varepsilon}{\partial C_\varepsilon} C_\varepsilon \right) = \left( J^F_\varepsilon \right)^2
\]

which is the equation stated in (16.9).

Using the chain rule and the identity (16.9) and the conditions (16.2) and (16.3) one can establish the following relations

\[
\frac{2}{3} \text{tr} \left( \frac{\partial A_\alpha}{\partial C_\varepsilon} C_\varepsilon \right) = \frac{2}{3} \left( \frac{\partial A_\alpha}{\partial \left( J^F_\varepsilon \right)^2} \right) \left( \frac{\partial J^F_\varepsilon}{\partial C_\varepsilon} \right) C_\varepsilon = 2 \left( J^F_\varepsilon \right)^2 \left( \frac{\partial A_\alpha}{\partial \left( J^F_\varepsilon \right)^2} \right) \left( \frac{\partial J^F_\varepsilon}{\partial \varepsilon_s} \right) \left( \frac{\partial \varepsilon_s}{\partial \varepsilon_\varepsilon} \right)
\]

where \( \varepsilon_\varepsilon + \varepsilon_s = 1 \) also has been used. Combining (16.8) with (16.16) yields

\[
\Delta \mu_\varepsilon = -\varepsilon_s \frac{\partial A_\alpha}{\partial \varepsilon_\varepsilon} - \frac{\varepsilon_\varepsilon \rho_\varepsilon}{\rho_\varepsilon} \frac{\partial A_\alpha}{\partial \varepsilon_s}
\]

which is a simplified one-dimensional relation ship between the tensorial and scalar chemical potentials. The terms on the right hand side of (16.17) represent the one-dimensional version of the effective stress tensor and the hydration stress tensor, respectively.

**Example 1: Classical State Fluid Column Problem.** Consider a static column filled with an incompressible (i.e. \( D \rho_\varepsilon / Dt = 0 \)) fluid. The fluid is assumed to be composed of a single constituent. In such a case one have \( G_\varepsilon = A_1 + p_\varepsilon / \rho_\varepsilon \) and \( \mu_\varepsilon = \mu_1 \) \( \left( p_\varepsilon / \rho_\varepsilon + A_1 \right) \), i.e. one have for this situation \( G_\varepsilon = \mu_1 \). In this example, therefore, the classical scalar chemical potential is identical to the Gibbs free energy scalar of the fluid. We gravi-chemical potential \( G_{fl} \) is defined in terms of \( G_\varepsilon \) as

\[
G_{fl}^\varepsilon = G_\varepsilon - \psi
\]

where \( \psi \) is the gravitational potential, i.e. \( \mathbf{g} = \text{grad} (\psi) \). The gravitational potential in (16.18) plays the same role as the effective and hydration stresses in (16.17). Orienting the one-dimensional coordinate system in the static column from top to bottom and referring this direction as the z-axis, setting \( \mathbf{g} = g \mathbf{i}_z \) where \( \mathbf{i}_z \) is the unit vector along the z-axis. Hence

\[
\psi = g z
\]

where at \( z = 0 \) the gravitational potential \( \psi \) is set to zero. This means that, in this case, the gravi-chemical and chemical potential (or equally, in this case, the Gibbs free energy) are
identical at the top of the column. From (16.18) and (16.19) it is concluded that

$$G_l - G^0_l = gz$$  \hspace{1cm} (16.20)

Since the considered single constituent fluid is assumed incompressible, the condition in (12.133), i.e.

$$\text{grad}A_l = \frac{\partial A_l}{\partial \rho_l} \text{grad} \rho_l + \sum_{j=1}^{N} \mu_j \text{grad} C_j^l$$  \hspace{1cm} (16.21)

$$+ \text{tr} \left( \frac{\partial A_l}{\partial \mathbf{E}_s} \text{grad} \mathbf{E}_s \right)$$

reduces to $\text{grad} A_l = 0$ at isothermal conditions. Thus, taking the gradient in (12.43), i.e. the gradient of

$$\sum_{j=1}^{N} C_j^l \mu_j^l A_l = A_l + \frac{p_l}{\rho_l} = G_l$$  \hspace{1cm} (16.22)

and using the equilibrium expression (12.141), i.e.

$$\sum_{j=1}^{N} C_j^l \text{grad} \mu_j^l = \text{tr} \left( \frac{\partial A_l}{\partial \mathbf{E}_s} \text{grad} \mathbf{E}_s \right) + \frac{1}{\rho_l} \text{grad} p_l = g_l$$  \hspace{1cm} (16.23)

yields

$$\text{grad} G_l = \frac{1}{\rho_l} \text{grad} p_l = g_l$$  \hspace{1cm} (16.24)

By combining (16.24) with (16.20) one obtain

$$\text{grad} G^0_l = 0$$  \hspace{1cm} (16.25)

The results in (16.20) and (16.25) shows that $G^0_l$ is constant throughout the length of the column while $G_l$ must increase linearly as the $z$ increases. Noting that the Gibbs free energy scalar $G_l$ and the scalar chemical potential is identical in this example, it is concluded that the chemical energy required to place a particle in the bottom of the column is greater than the chemical energy required at the top of due to the gravitational potential.

**Example 2: Terzaghi's Consolidation Problem.** In this example the influence of the effective stress tensor on $\Delta \mu^j$ will be studied. A one-dimensional version of the Terzaghi's consolidation problem for a non-swelling elastic medium will be considered. In the formulation presented so far this situation can easily be obtained by setting $t'_i = 0$. A isothermal conditions a porous elastic column is considered, bound by the sides and on the bottom by a rigid, adiabatic, impermeable wall. At the top, a load is applied and the bulk water is free to drain. The initial equilibrium configuration will be considered and each phase contains $N$ miscible components. By neglecting the dependency of $A_l$ on $\varepsilon_i$ in (16.17), one obtain

$$\Delta \mu^j = -\varepsilon_s \frac{\partial A_s}{\partial \varepsilon_i}$$  \hspace{1cm} (16.26)
A system with constant volume fraction \( \varepsilon_l \) and a case where the system initially is free from stress is considered. It is, further assumed that the porous medium is linearly elastic and the gravitational effects are neglected. The proper constitutive function of \( A_s \) is for this case

\[
A_s = \frac{C}{2} (\varepsilon_l - \bar{\varepsilon}_l)^2
\]  

(16.27)

where \( C \) is a material constant representing the compressibility of the solid matrix. Using (16.26), (16.27) and \( \varepsilon_l = -\bar{\varepsilon}_l \) one obtain

\[
\Delta \mu_s^e = \frac{1}{3} \text{tr} \mu_s^e - \mu_s^e = \frac{C}{2} \varepsilon_l \frac{\partial (\varepsilon_l^2 - 2\varepsilon_l \bar{\varepsilon}_l + \bar{\varepsilon}_l^2)}{\partial \varepsilon_l} \]  

(16.28)

\[-C \varepsilon_s (\varepsilon_l - \bar{\varepsilon}_l) \approx -C_l (\varepsilon_l - \bar{\varepsilon}_l)\]

where a linearization about equilibrium defined as \( \varepsilon_l = \bar{\varepsilon}_l \), has been performed, so that \( C_l = \varepsilon_s C \), where \( \varepsilon_s \) is the constant volume fraction of the solid matrix in the reference configuration. In addition it is possible to derive the linear relationship between the effective pressure \( p_s^e \) and the volume fraction \( \varepsilon_l \). The effective pressure is defined as \( p_s^e = \frac{1}{3} \text{tr} t_s^e \), hence, by (16.6) with \( t_s^1 = 0 \) and by (16.26) one obtain

\[
p_s^e = \frac{1}{3} \text{tr} t_s^e = -\varepsilon_s \rho_s \frac{\partial A_s}{\partial \varepsilon_l} = -C_l \rho_s (\varepsilon_l - \bar{\varepsilon}_l)
\]  

(16.29)

which is similar in form to the one heuristically proposed by Terzaghi.

The conclusion from this example is, among other things, that as the overburden pressure on the column is increased, \( \varepsilon_l \) decreases, and since \( \mu_s^e \) is constant at equilibrium when the effect of the gravity is small, according to the derived equilibrium condition \( \text{grad} \mu_s^e = g \), i.e. equation (12.146), then \( \text{tr} \mu_s^e \) increases. The fact that \( \text{tr} \mu_s^e \) increases during the described conditions can be confirmed by equation (16.28). Hence, the chemical energy required to insert a solid particle into the compressed system is greater than at the unstressed initial state.

**Example 3: Swelling Pressure Experiment.** In order to study the influence of the hydration stress tensor \( t_s^e \) on the chemical potential \( \Delta \mu_s^e \) defined in (16.5), the classical reverse osmosis swelling pressure experiment will be considered. A saturated mixture of clay and adsorbed incompressible fluid is separated from a bulk (non-adsorbed) fluid by a semi-permeable membrane which only allows fluid to pass. An overburden pressure is applied to the clay mixture and the shrinkage due to the loss of fluid is recorded. As in example 2, the gravity is assumed small as compared with the applied external pressure and each phase is assumed to be composed of the same N miscible components which concentration within a phase may be zero. It assumed that the clay minerals consists of flat plates and the clay medium is such that the flat plates are parallel so that the effective stress tensor \( t_s^e \) is negligible. Consequently, equation (16.17) is reduced to

\[
\Delta \mu_s^e = -\varepsilon_s \rho_s \frac{\partial A_s}{\partial \varepsilon_l}
\]  

(16.30)

that is \( A_s \) is assumed to be independent of \( \varepsilon_l \). As is seen from example 2, the equation (16.28) shows that \( \Delta \mu_s^e \) is proportional to the volume fraction \( \varepsilon_l \). In this example, however, it will be shown that \( \Delta \mu_s^e \) will appear as being inversely proportional to the volume fraction \( \varepsilon_l \). Assume that the macroscopic solid phase stress tensor in the clay mixture is negligible, i.e. \( t_s = 0 \) so
that all overburden pressure is supported by the adsorbed liquid. It is recalled that the total stress \( \mathbf{t} \) is given as: \( \mathbf{t} = \varepsilon_s \mathbf{t}_s + \varepsilon_t \mathbf{t}_t \). By using the assumptions \( \varepsilon_t = 0 \) and \( \mathbf{t}_s = 0 \), the equation for the solid phase stress tensor (12.15) together with the equilibrium condition \( p_l = p_s \), i.e. (12.89), reduces to

\[
p_l \mathbf{I} = \frac{\varepsilon_t}{\varepsilon_s} \mathbf{t}_t^s
\]  

(16.31)

which leads us to the conclusion that the pressure in the adsorbed fluid is balanced by the hydration forces. If this not was the case all the fluid would pass through the membrane with minimal applied pressure. Taking the trace of (12.15), using the definition (9.3), i.e. \( \mathbf{t}_t^s = \rho_l \mathbf{F}_s \frac{\partial A_l}{\partial \mathbf{E}_s} \mathbf{F}_s^T \), one obtain

\[
\text{tr} (p_l \mathbf{I}) = \text{tr} \left( \frac{\varepsilon_t}{\varepsilon_s} \mathbf{t}_t^s \right) = \text{tr} \left( \frac{\varepsilon_t \rho_l}{\varepsilon_s} \mathbf{F}_s \frac{\partial A_l}{\partial \mathbf{E}_s} \mathbf{F}_s^T \right)
\]  

(16.32)

using \( \mathbf{E}_s = \frac{1}{2} (\mathbf{C}_s - \mathbf{I}) \) and \( \mathbf{C}_s = \mathbf{F}_s^T \mathbf{F}_s \), one obtain the following relation between \( p_l \) and \( A_l \)

\[
\text{tr} (p_l \mathbf{I}) = \text{tr} \left( \frac{\varepsilon_t \rho_l}{\varepsilon_s} \mathbf{F}_s \frac{\partial A_l}{\partial \mathbf{E}_s} \mathbf{F}_s^T \right) = \text{tr} \left( \frac{\varepsilon_t \rho_l}{\varepsilon_s} \frac{\partial A_l}{\partial \mathbf{C}_s} \mathbf{C}_s^T \right)
\]  

(16.33)

From (16.16), one have that

\[
\frac{2}{3} \text{tr} \left( \frac{\partial A_\alpha}{\partial \mathbf{C}_s} \mathbf{C}_s \right) = \varepsilon_s \frac{\partial A_\alpha}{\partial \varepsilon_\ell}
\]  

(16.34)

Combining this expression with (16.33) the following is yielded

\[
\text{tr} (p_l \mathbf{I}) = \text{tr} \left( \frac{\varepsilon_t \rho_l}{\varepsilon_s} \frac{\partial A_l}{\partial \mathbf{C}_s} \mathbf{C}_s \right) = 3 \varepsilon_t \rho_l \frac{\partial A_\alpha}{\partial \varepsilon_\ell}
\]  

(16.35)

which also can be expressed as

\[
p_l = \varepsilon_l \rho_l \frac{\partial A_\alpha}{\partial \varepsilon_\ell} = \frac{1}{3} \frac{\varepsilon_t}{\varepsilon_s} \text{tr} (\mathbf{t}_t^s)
\]  

(16.36)

where (16.32) is used. Moreover, in this example, by design one have that the concentrations of all constituents in solid phase are constant. At equilibrium, which is the case studied, the condition in equation (12.146) is valid, i.e. \( \text{grad} \mu^l = \mathbf{g} \). With the assumption that \( \mathbf{g} \) is negligible \( \mu^l \) is constant in the spatial domain. Furthermore, in this case, the Gibbs free energy and chemical potential scalars are identical, hence, the relation

\[
\sum_{j=1}^N C^l_\alpha \mu^l_\alpha = A_\alpha + \frac{p_\alpha}{\rho_\alpha} = G_\alpha
\]  

(16.37)

which is (12.43) repeated, gives together with the condition that the concentrations of all constituents are constant, that the Gibbs free energy \( G_l \) must be constant, i.e.

\[
G_l = A_l + \frac{p_l}{\rho_l} = \text{const.}
\]  

(16.38)
Since, the adsorbed water was assumed incompressible, i.e. \( D_t \rho_I /Dt = 0 \), and since (16.38) can be written as

\[
\frac{\partial G_I}{\partial \varepsilon_I} = \frac{\partial A_I}{\partial \varepsilon_I} + \frac{1}{\rho_I} \frac{\partial \rho_I}{\partial \varepsilon_I} = 0
\]  

(16.39)

That is, one obtain the relation

\[
\frac{\partial A_I}{\partial \varepsilon_I} = -\frac{1}{\rho_I} \frac{\partial \rho_I}{\partial \varepsilon_I}
\]  

(16.40)

The equations (16.40) and (16.36) combined, gives

\[
\rho_I = -\varepsilon_I \frac{\partial \rho_I}{\partial \varepsilon_I}
\]  

(16.41)

Upon integration and using that when \( \varepsilon_I = 1 \), the pressure in the adsorbed fluid, \( p_I \), is equal to the bulk fluid pressure, \( p_f \), one obtain

\[
\int_{p_f}^{p_I} \frac{dp_I}{p_I} = \int_{1}^{\varepsilon_I} \frac{d\varepsilon_I}{\varepsilon_I}
\]  

(16.42)

or, equally

\[
\ln \left( \frac{p_I}{p_f} \right) = -\ln \varepsilon_I = \ln \left( \frac{1}{\varepsilon_I} \right)
\]  

(16.43)

This means that the pressure \( p_I \) and \( p_f \) are related by the volume fraction \( \varepsilon_I \) as

\[
p_I = \frac{p_f}{\varepsilon_I}
\]  

(16.44)

Combining (16.40) and (16.30) and eliminating \( p_I \) using (16.44) gives

\[
\frac{1}{3} \text{tr} \mu_s^j - \mu_s^j = \Delta \mu_s^j = -\frac{\rho_I}{\rho_s} = -\frac{p_f}{\varepsilon_I \rho_s}
\]  

(16.45)

It is observed that \( \Delta \mu_s^j \) is never zero due to the assumption that there is always some hydration force between the adsorbed liquid and solid phase. Contrary to the Terzaghi problem, this example shows that increasing the overburden pressure, which causes \( \varepsilon_I \) to decrease, results in a decrease in the magnitude of the term \( \text{tr} \mu_s^j \) when it is also assumed that \( \mu_s^j \) is constant at equilibrium when the effect of the gravity is small. Hence, according to the example it is easier to insert a solid particle into a compressed swelling media. This can be physically attributed to the stronger adsorption forces in the compressed system due to the closer proximity of the liquid and the solid phases.

An geometrical interpretation of the problem can be performed. Consider a separation of platelets, denoted by \( \lambda \), having a thickness \( \lambda_s \). The volume fraction \( \varepsilon_I \) can then be written

\[
\varepsilon_I = \frac{\lambda}{\lambda + \lambda_s}
\]  

(16.46)

The needed derivative \( \partial p_I /\partial \lambda \) can be expressed by the chain rule as
\[
\frac{\partial p_t}{\partial \lambda} = \frac{\partial \varepsilon_t}{\partial \lambda} \frac{\partial p_t}{\partial \varepsilon_t} = \frac{\lambda_s}{(\lambda + \lambda_s)^2} \frac{\partial p_t}{\partial \varepsilon_t} = -\frac{\lambda_s}{(\lambda + \lambda_s)^2} \frac{\partial p_t}{\partial \varepsilon_t}
\]

where (16.46) and (16.41) are used. The thickness of the platelets are, further, assumed to be constant. The separation between platelets can, hence, be expressed as

\[
\left(\frac{\lambda^2}{\lambda_s} + \lambda\right) \frac{\partial p_t}{\partial \lambda} = -p_t
\]

(16.47)

At high moisture contents the following approximation can be used

\[
\lambda \ll \frac{\lambda^2}{\lambda_s}
\]

(16.48)

That is

\[
\frac{\lambda^2}{\lambda_s} \frac{\partial p_t}{\partial \lambda} \approx -p_t
\]

(16.49)

The integrated version of (16.49), valid at high moisture contents, is

\[
\int_{p_f}^{p_t} \frac{\partial p_t}{\partial \lambda} = -\lambda s \int_0^\lambda \frac{\partial \lambda}{\lambda^2}
\]

(16.50)

where bulk fluid pressure, \(p_f\), is set to zero when the platelets are in contact with each others, i.e. when \(\lambda = 0\) or equally when no moisture is present in the system. Evaluation of the integrals in (16.50) gives

\[
\ln \left(\frac{p_t}{p_f}\right) = \frac{\lambda_s}{\lambda}, \quad \text{or} \quad p_t = p_f \exp \left(\frac{\lambda_s}{\lambda}\right)
\]

(16.51)

By using (16.45) one obtain the expression for \(\Delta \mu_i^j\), as

\[
\Delta \mu_i^j = -\frac{p_f}{\rho_s} \exp \left(\frac{\lambda_s}{\lambda}\right)
\]

(16.52)

which is an alternative expression of (16.45) incorporating a certain geometry of the platelets of the solid phases.

17. Conclusions

A review of the article; Macroscale Thermodynamics and the Chemical Potential for Swelling Porous Media, by Lynn Schreyer Bennethum, Márcio A. Murad and John H. Cushman, has been performed.
A novel definition of the macroscale chemical potential is introduced. Unlike Bowen’s tensorial chemical potential, this new chemical potential is a scalar which satisfies three properties consistent with the classical Gibssian chemical potential for a single phase medium.

The properties of the chemical potential satisfies the following three conditions: (1) it is a scalar, (2) at equilibrium, the chemical potential of a single constituent in different phases is the same, and (3) the chemical potential is the driving force for diffusive flow (generalized Fick’s law). These properties were obtained by exploiting the entropy inequality and using a generalized Gibbs-Duhem relation. It is noted that Lagrange multipliers were used to enforce the gradient of the relationship between the diffusive velocities. Near-equilibrium results were, further, obtained by linearizing coefficients which were not necessarily zero at equilibrium.

18. References

References

