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Introduction to biological mixture mechanics

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1. Introduction

1.1. Water: a medium in which biology thrieves

There is no biological tissue which is not a mixture. By mixture we mean a composition of different components – either miscible or immiscible – which move relative to one another. This relative motion is vital to every living organism. The human body is a structure that renews itself continually. In five years time every molecule of a human body is replaced. To allow this fast pace of repair, diffusion and convection of waste materials and nutrients are essential. A mayor component of biological tissues is water. The fast pace of renewal of tissues is possible thanks to many factors, one of which being the relative motion of solid, water and solutes within cells and tissues. The high water content ensures easy diffusion of solutes. The description of this motion is obtained by considering the behaviour of the total tissue as the sum of the behaviours of the individual components of which the tissue is constructed, extended with terms that describe the interaction between the different components. This is what we call mixture theory. The application of mixture is by no means restricted to biology. In engineering, several types of mixtures exist: only gasses, only fluids, gasses and fluids (e.g. multiple phase flows), or fluids and solids (flow through porous media). The theory of mixtures describes these types of systems. Because the theory of mixtures and its application to porous media have applications to subjects very different from biological tissues, these notes are relevant for geomechanics, polymer scientists, petroleum engineers and civil engineers as well.

1.2. The composition of biological tissues

The cell is the elementary building block of living organisms. The cells of multiple-celled organisms are arranged in tissues to make it possible for the organisms to function effectively. One can distinguish 4 types of tissue [Guyton and Hall, 1993]: neural tissue, epithelial tissue, muscle tissue, and connective and supportive tissue. In this book we will consider the mechanical function of a selection of tissues. All tissues show a multiple-component structure, consisting of a solid, in which at least one fluid is trapped. The fluid is generally distributed over functionally distinct compartments: intracellular, extracellular, lymphatic system, arterial system, venous system, capillary compartment. The fluid within each compartment has diffusing constituents whithin it, which play a key role in many physiological processes. As an example we illustrate this in the intervertebral disc (Fig. 1).

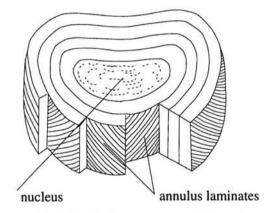


FIGURE 1. The intervertebral disc: laminar structure of the anulus enclosing the nucleus.

The solid mainly consists of collagen structures, elastin fibers and ionised large molecules, the proteoglycans. The fluid consists of water, in which several substances are disolved, from low-molecular ions, larger molecules (e.g. albumine). The proteoglycans are constructed of glycosaminoglycans, linear polysaccharides consisting of long strings of disaccharides (Fig. 2). Due to their size (molecular weight 1-3 million), the proteoglycans are tangled up in a fiberstructure. Furthermore they contain negatively charged hydroxyl-, carboxyl-, and sulphate groups, which makes them strongly hydrophylic. They are able to bind a water mass up to 50 times their own weight.

Depending on the properties of the solid component we speak of hard tissues or soft tissues. The hard tissues (bones, teeth) usually have small de-

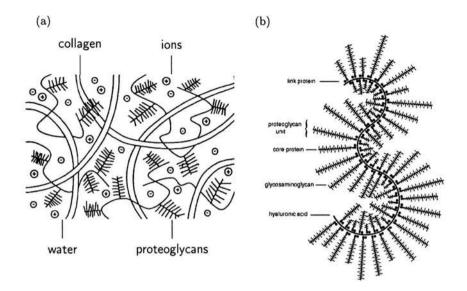


FIGURE 2. Schematic view of (a) the structure of tissue from the intervertebral disc and (b) the proteoglycan-molecule; from [1].

formations and show a linear relation between the stress and strain. Because of their elastic moduli generally higher than the bulk modulus of water, incompressible elasticity or poroelasticity does not apply to hard tissues. The compressibility of water, and even the intinsic compressibility of the solid play an important role in the overall mechanical response [2].

The soft tissues deform already fiercely under normal physiological circumstances. Strains of 10% up to 100% are easily obtained. The most important solid components in soft tissues are *elastin* and *collagen*. Elastin is a protein that has linear elastic behaviour up to strains of 60% with Young's modulus of about 1 MPa [4]. Collagen fibers consist of tropocollagen molecules. Such a tropocollagen molecule consists of a helix of three polypeptide chains.

Collagen is about 10^3 times as stiff as elastin. The Young's modulus is about 1000 MPa [4]. For small loads a network of unstretched, undulating collagen fibers between a network of stretched elastin fibers is found. This structure gives the tissue its low stiffness for small deformations. With increasing deformation more and more collagen fibers will be stretched, which causes an increase in the stiffness. Therefore the stress-strain relation is strongly *non-linear*, which for example can be seen from Fig. 3. A functional consequence is that the collagen network behaves like a protection against large

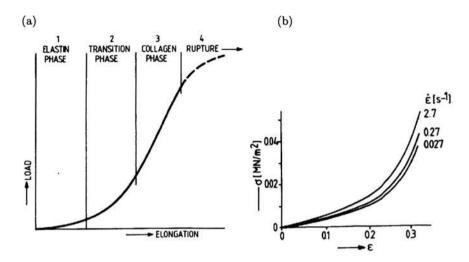


FIGURE 3. (a) a typical uniaxial force-length relation for soft biological tissues; (b) uniaxial stress-strain relation for aorta-tissue from a sinus of Valsalva for different strain rates; from [3].

deformations. The mentioned stiffnesses only apply for extension, because the elastin and collagen fibers buckle easily in compression. A compression load is initially transduced by the liquid component in the tissue.

Biological materials behave *anisotropically* at fiber level due to the fiber construction. This means that the mechanical properties are orientation dependent. Because the fibers are unevenly oriented, these tissues also respond anisotropically on a macroscopic level.

Visco-elasticity is typical for biological tissues. This visco-elasticity expresses itself for example in the strain rate dependence of the stress-strain relation (Fig. 3). For cyclic loading we find a hysteresis loop in the stress-strain diagram. The stress-strain curve during loading is higher than the unloading curve. Before we established that the non-linear anisotropic behaviour mainly can be ascribed to the solid component of the tissue. The viscous effect can not be localised that easily. It can be present intrinsically in the solid, but it can also be originating from the viscous liquid component. There is experimental evidence that most of the viscosity stems from micromotion of the fluid.

1.3. The mechano-electrochemical behaviour of biological tissues

Osmotic forces are probably equally important in tissues as viscosity and elasticity. Osmosis ensures that the fiber network of the tissue functions under

tensile prestressing and the fluid saturating the network is under pressure. This vital to the correct functioning of the tissue as aquous solution typically resist compression and fibers resist tension. To illustrate the typical mechano-electrochemical response of tissue, we consider a *swelling and consolidation experiment*. The composition of the tissue as shown in Fig. 2 causes a response as well as to mechanical (forces and displacements) as to chemical loads (variations of concentration). It is convenient to group the different components of the tissue to describe the response. We consider four components: the negatively charged solid component, consisting of fibers and fixed proteoglycans, the neutral liquid component, the positively charged cations and the negatively charged anions.

The experimental setup is shown in Fig. 4. The specimen is, precisely fitting, closed in between the walls of the container, piston and a porous filter. The filter makes it possible for the fluid to flow out of the specimen. The resistance to flow in the filter is much smaller than in the specimen. The specimen can be mechanically loaded, using the piston (pressure on the material). A chemical load is applied as a stepwise change in the salt concentration in the fluid flowing through the filter. The response of the tissue to the load is measured in terms of variation of the height of the specimen.

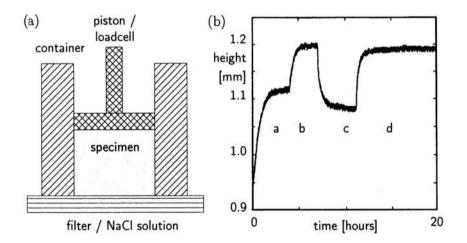


FIGURE 4. The swelling and consolidation experiment: a) the experimental setup; b) the measured variation in height of the specimen in a typical experiment, consisting of a conditioning phase a (salt concentration 0.6 M, piston pressure 0.08 MPa), a swelling phase b (0.2 M, 0.08 MPa), a consolidation phase c (0.2 M, 0.2 MPa), and a control phase d (0.2 M, 0.08 MPa); from [5].

The experiment starts with a conditioning phase (a), during which the specimen reaches an equilibrium for a known load. Next, the concentration of the ionic solution is decreased (b). This leads to swelling of the specimen. This is the result of a combination of osmotic, diffusion and convective effects. The concentration gradient between specimen and filter causes (i) an outflux of ions out of the specimen, and (ii) an influx of water into the specimen. Because the specimen has to be electrically neutral, an outflow of ions is limited and therefore a permanent inflow of fluid occurs. In this case we speak of *Donnan osmosis*. The swelling is caused by electrostatic effects. The finally attained condition represents an equilibrium between the swelling pressure in the fluid related to osmotic an electrical effects, and the stress in the solid component, related to the strains in the solid.

In phase (c) the pressure created by the piston is increased incrementally. If we consider both the fluid and solid as incompressible, the increased load is at first carried by the liquid component only. At the bottom of the specimen a large pressure gradient arises, which causes an outflux of fluid. An effect of this outflux is that the piston will lower. The deformation of the specimen causes a stress in the solid component that gradually will take over the load from the liquid.

Finally, in phase (d) the boundary conditions of phase (a) is re-established. The extent to which the equilibrium in phase (d) fits that of phase (a) is an indication for the quality of the experiment. Considering the amount of time the experiment requires this is highly recommandable.

The osmotic pressure causing the swelling here in this experiment by lowering the external concentration, is the procedure through which the body generates stiffness, even in soft tissues, and appears as a solid, while its main constituent is water. The smooth look of a young skin is a result of the pre-tension in the solid substance, as a consequence of the swelling pressure correlated with the presence of water binding molecule structures beneath the skin. The dissappearance of this smooth skin during our lives is to great extent connected to a decrease of the water binding ability of the tissues, as is the ageing of the human body in general. The amount of water decreases during our lives from 75% in a new born to 50% in our last years. Joint disorders are also a consequence of damage of the proteoglycan networks in the cartilage.

Beside biological tissues some engineering materials show the same swelling behaviour. Synthetic hydrogels swell in a similar manner. They are, among others, used for soft contact lenses, diapers, controlled drug delivery and to hold water in desert sands. In Fig. 5 the results are presented of a swelling and consolidation experiment, carried out upon a copolymerised synthetic foam. This material imitates some features of cartilaginous mater-

ial [1]. It is designed to do experiments in well controlled circumstances. The results of these experiments are used to validate some aspects of the theory of mixtures on biological tissues, as presented during this course.

The swelling behaviour of clays is important for the ceramics industry. In soil mechanics swelling clays are considered the worst manageable soil.

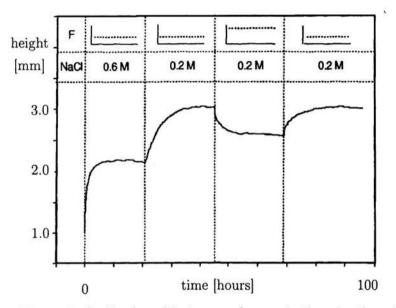


FIGURE 5. Swelling/consolidation test of an acrylacid-acrylamidecopolymergel processed in a polyurethane foam.

2. Mechanics and thermodynamics of 1-component mixtures

In this section 1-component mixtures represent simple continua, consisting of only one component in only one state of aggregation. The mechanical and thermodynamical behaviour of these substances will be discussed.

2.1. Kinematics and stress

2.1.1. Kinematics. Kinematics describes the displacement and deformation of continua. We identify an arbitrary point in the continuum with *material coordinates* $\{\xi_1, \xi_2, \xi_3\}$. We put these coordinates in a column ξ :

$$\underline{\xi} = \{\xi_1, \xi_2, \xi_3\}^{\mathrm{T}} \tag{2.1}$$

in which the superscript ^T represents the transposition. The momentary positioning vector x of a particle can be written as a function of the material coordinate ξ and the time t:

$$\boldsymbol{x} = \boldsymbol{\chi}(\boldsymbol{\xi}, t). \tag{2.2}$$

It is often convenient to identify the points in the continuum with their position x_0 in a state of reference, e.g. the state at time t_0 :

$$\boldsymbol{x}_0 = \boldsymbol{\chi}(\boldsymbol{\xi}, t_0). \tag{2.3}$$

We can therefore consider the momentary position x of a point as a function of the position in the state of reference:

$$\boldsymbol{x} = \boldsymbol{X}(\boldsymbol{x}_0, t). \tag{2.4}$$

If the positions of the points in the continuum can be followed, than also changes of these positions can be identified. These variations can reveal itself in changes of the distance between two points, or changes of the angles between line pieces. The size of these changes can be determined with the *deformation tensor*, which will be derived below.

Consider two neighbouring points with material coordinates ξ and $\xi + d\xi$, that are in the state of reference at positions x_0 and $x_0 + dx_0$. In the momentary state, these points are situated at the positions x en x + dx.

The projection of the difference vector dx_0 in the state of reference on the difference vector dx in the momentary state is the *deformation tensor* F:

$$d\boldsymbol{x} = \boldsymbol{F} \cdot d\boldsymbol{x}_0 \tag{2.5}$$

in which F can be determined using:

$$\boldsymbol{F} = (\boldsymbol{\nabla}_0 \boldsymbol{x})^{\mathrm{c}}.\tag{2.6}$$

In this formulation ∇_0 represents the gradient operator correlated to the state of reference, while the superscript ^c indicates the conjugated. Now, consider an infinitesimal cube of matter that has a volume dV_0 in the state of reference. The momentary volume dV, obtained after deformation F, is:

$$dV = \det(\mathbf{F}) \, dV_0. \tag{2.7}$$

Often, the volumetric variation factor is also used:

$$J = dV/dV_0 = \det(\mathbf{F}). \tag{2.8}$$

The deformation tensor F describes the variations in volume and shape as well as the rigid rotation of the material. We are mainly interested in the variations of volume and shape, because these cause the stresses in the material. To describe this pure deformation we can use the *right Cauchy-Green strain tensor* C, defined as:

$$\boldsymbol{C} = \boldsymbol{F}^{\mathsf{c}} \cdot \boldsymbol{F}. \tag{2.9}$$

The tensor C describes the elongation and shear. In the state of reference the right Cauchy-Green strain tensor C is equal to the unit tensor I. For a description of the constitutive behaviour of materials it is most convenient to use a strain tensor that is equal to the zero tensor, O, in the state of reference like the *Green-Lagrange strain tensor* E:

$$\boldsymbol{E} = \frac{1}{2} \left(\boldsymbol{C} - \boldsymbol{I} \right). \tag{2.10}$$

Let us now consider the changes in position and deformation in time. The *velocity* v of a material point is defined as the material time derivative of a momentary position vector of the point:

$$\boldsymbol{v} = \dot{\boldsymbol{x}} = \dot{\boldsymbol{\chi}}(\boldsymbol{\xi}, t) = \left. \frac{\partial \boldsymbol{\chi}(\boldsymbol{\xi}, t)}{\partial t} \right|_{\boldsymbol{\xi}}.$$
 (2.11)

This means that changes of the position are observed, while we are connected to one particle ($\bar{\xi}$ is constant). For the velocity $d\dot{x}$, with which a line element dx variates in size and direction, the momentary deformation rate, can be derived:

$$d\dot{\boldsymbol{x}} = \dot{\boldsymbol{F}} \cdot \boldsymbol{F}^{-1} \cdot d\boldsymbol{x} = (\boldsymbol{D} + \boldsymbol{\Omega}) \cdot d\boldsymbol{x}$$
(2.12)

in which the deformation rate tensor D and the rotational rate tensor Ω are defined as:

$$D = \frac{1}{2} \left\{ \dot{F} \cdot F^{-1} + (\dot{F} \cdot F^{-1})^{c} \right\} = \frac{1}{2} \left\{ (\nabla v)^{c} + (\nabla v) \right\}, \quad (2.13)$$

$$\boldsymbol{\Omega} = \frac{1}{2} \left\{ \dot{\boldsymbol{F}} \cdot \boldsymbol{F}^{-1} - (\dot{\boldsymbol{F}} \cdot \boldsymbol{F}^{-1})^{c} \right\} = \frac{1}{2} \left\{ (\boldsymbol{\nabla} \boldsymbol{v})^{c} - (\boldsymbol{\nabla} \boldsymbol{v}) \right\}$$
(2.14)

in which the identity $\dot{F} \cdot F^{-1} = (\nabla v)^c$ is used. For the velocity, with which the momentary volume of the material changes, applies:

$$\dot{J} = J \operatorname{tr}(\boldsymbol{D}). \tag{2.15}$$

The next expression can be deduced for the material time derivative of the Green-Lagrange strain tensor:

$$\dot{\boldsymbol{E}} = \boldsymbol{F}^{\mathsf{c}} \cdot \boldsymbol{D} \cdot \boldsymbol{F}. \tag{2.16}$$

2.1.2. Stress. The deformation, as described above, is usually caused by forces. These forces will often be applied on the surface of the continuum. It is common to relate the magnitude of the force to the size of the surface.

Now, consider an infinitesimal area with a normal vector n_0 and surface dA_0 . After applying a force df this area deforms according to a deformation tensor F, where the deformed area gets a normal vector n and a surface area dA. We define a stress vector t as force per unit surface area t = df/dA. The local state of stress in the material now is given by the Cauchy stress tensor σ , that projects the normal vector n upon the stress vector t in the momentary state:

$$\boldsymbol{t} = \boldsymbol{\sigma} \cdot \boldsymbol{n}. \tag{2.17}$$

This equation is a definition of the Cauchy stress tensor. The stress σ in general depends on the deformation of the material. For an incompressible material the stress is determined by the deformation (and its time and spatial derivatives) except for a constant hydrostatic contribution -pI, where p represents this hydrodynamic pressure. This can be shown by loading such a material on all sides by a single hydrostatic pressure. This load will not cause any deformation. The stress nevertheless has to increase to reach an equilibrium at the boundaries. In other words, a part of the stress in the material is independent of the state of deformation. It is convenient to subdivide the stress tensor σ in a hydrostatic part -pI and a deviatoric part σ^d :

$$\boldsymbol{\sigma} = -p \, \boldsymbol{I} + \boldsymbol{\sigma}^{\mathrm{d}}.\tag{2.18}$$

The constitutive relation of the stresses depend on the mechanical properties of the material. This constitutive relation has to be objective, which means that it is not allowed to change during rigid rotations. In a later chapter, we will show that when using the Green-Lagrange strain tensor as a strain quantity, it is convenient to use the *Piola-Kirchhoff stress tensor* P, as a stress quantity, based on objectivity. This stress tensor is defined as:

$$\boldsymbol{P} = \det(\boldsymbol{F}) \ \boldsymbol{F}^{-1} \cdot \boldsymbol{\sigma} \cdot \boldsymbol{F}^{-c}. \tag{2.19}$$

2.2. Conservation of mass, balance of momentum and balance of moment of momentum

2.2.1. Conservation of mass. We consider an arbitrary, but fixed part of space with volume V and outer surface A. The matter in this volume has a *density* ρ . Conservation of mass requires, that the variation of mass of this volume matches the mass flow per unit of time through the surface A,

$$\frac{\partial}{\partial t} \int_{V} \rho \, dV = -\int_{A} \rho \boldsymbol{v} \cdot \boldsymbol{n} \, dA \tag{2.20}$$

in which n is the outer normal unit vector. Applying Gauss' theorem and swapping of the time derivative and the integral gives

$$\int_{V} \left(\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \boldsymbol{v}) \right) \, dV = 0.$$
(2.21)

Because the volume V is arbitrary, the integrant has to be zero in every point in space. This results for the *local conservation of mass* into:

$$\frac{\partial \rho}{\partial t} + \boldsymbol{\nabla} \cdot (\rho \boldsymbol{v}) = 0 \tag{2.22}$$

or

$$\dot{\rho} + \rho \boldsymbol{\nabla} \cdot \boldsymbol{v} = 0 \tag{2.23}$$

in which the *material time derivative* is used:

$$\dot{\rho} = \frac{D\rho}{Dt} = \frac{\partial\rho}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla}\rho.$$
(2.24)

2.2.2. Balance of momentum. Again we consider an arbitrary, but fixed part of space with volume V and a surface A.

The impuls per unit volume is equal to ρv . Fully analogously to the previous derivation, we now consider transport of impuls ρv instead of mass ρ . The variation of momentum in a volume per unit of time is equal to:

$$\frac{\partial}{\partial t} \int_{V} \rho \boldsymbol{v} \, dV + \int_{A} (\rho \boldsymbol{v}) \boldsymbol{v} \cdot \boldsymbol{n} \, dA.$$
(2.25)

According to the balance of momentum this momentum variation is equal to the resulting force that works on the matter in V. Generally this force consists of a volume force q per unit of mass and a surface force t per unit of surface area. According to the balance of momentum we find:

$$\frac{\partial}{\partial t} \int_{V} \rho \boldsymbol{v} \, dV + \int_{A} (\rho \boldsymbol{v}) \boldsymbol{v} \cdot \boldsymbol{n} \, dA = \int_{V} \rho \boldsymbol{q} \, dV + \int_{A} \boldsymbol{t} \, dA.$$
(2.26)

The last term of this equation is written as:

$$\int_{A} \boldsymbol{t} \, dA = \int_{A} \boldsymbol{\sigma} \cdot \boldsymbol{n} \, dA = \int_{V} \boldsymbol{\nabla} \cdot \boldsymbol{\sigma}^{c} \, dV.$$
(2.27)

If we apply Gauss' theorem to the second term of (2.26) also, we obtain *local* balance of momentum, using (2.23):

$$\rho \dot{\boldsymbol{v}} = \boldsymbol{\nabla} \cdot \boldsymbol{\sigma}^{\mathrm{c}} + \rho \boldsymbol{q}. \tag{2.28}$$

2.2.3. Balance of moment of momentum. According to the balance of moment of momentum the variation of the moment of momentum in a volume V is equal to the transport of moment of momentum through the surface area A added to the moment of forces, that work on the volume. The moments of momentum are considered with respect to a fixed point O. This is written in integral form:

$$\frac{\partial}{\partial t} \int_{V} \boldsymbol{x} \cdot \rho \boldsymbol{v} \, dV = -\int_{A} (\boldsymbol{x} \cdot \rho \boldsymbol{v}) \boldsymbol{v} \cdot \boldsymbol{n} \, dA + \int_{V} \boldsymbol{x} \cdot \rho \boldsymbol{q} \, dV + \int_{A} \boldsymbol{x} \cdot \boldsymbol{t} \, dA.$$
(2.29)

This equation holds for *non-polar continua*, continua in which no spread moments are present. Through laborious deduction the *local balance of moment of momentum* is derived:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^{\mathbf{c}},\tag{2.30}$$

a simple result, which shows that σ is symmetric.

2.3. Thermodynamics

2.3.1. The first law of thermodynamics. The first law of thermodynamics is the *law of conservation of energy*. It says that the *heat dQ* added to a system can be used to increase an *internal energy U* of the system with an amount dU, to increase the *macroscopic kinetic energy K* of the system with an amount dK, and/or to increase the *work* done by the system with dW_s :

$$dQ = dU + dK + dW_{\rm s}.\tag{2.31}$$

If the first law is used for a continuum it is more convenient to consider the work $dW = -dW_s$ that is applied to the continuum. Furthermore we will consider the changes per unit of time, to write (2.31) as:

$$\dot{K} + \dot{U} = \dot{W} + \dot{Q}.$$
 (2.32)

We consider the part of space again with volume V and surface The *kinetic* energy K of the continuum is:

$$K = \int_{V} \frac{1}{2} \rho \boldsymbol{v} \cdot \boldsymbol{v} \, dV. \tag{2.33}$$

The variations in kinetic energy of the continuum per unit of time, \dot{K} , is:

$$\dot{K} = \frac{\partial}{\partial t} \int_{V} \frac{1}{2} \rho \boldsymbol{v} \cdot \boldsymbol{v} \, dV + \int_{A} (\frac{1}{2} \rho \boldsymbol{v} \cdot \boldsymbol{v}) \boldsymbol{v} \cdot \boldsymbol{n} \, dA.$$
(2.34)

The internal energy U of the matter in V, is:

$$U = \int_{V} \rho \tilde{U} \, dV \tag{2.35}$$

in which \tilde{U} indicates the *specific* internal energy, or the internal energy per unit mass. In this course we will indicate specific quantities with a tilde ($\tilde{}$) on top of every symbol. The variations of the internal energy per unit of time \dot{U} can be written as:

$$\dot{U} = \frac{\partial}{\partial t} \int_{V} \rho \tilde{U} \, dV + \int_{A} (\rho \tilde{U}) \boldsymbol{v} \cdot \boldsymbol{n} \, dA.$$
(2.36)

The applied load consists of a volume load q and a surface load t. The power that is provided by the load is:

$$\dot{W} = \int_{V} \rho \boldsymbol{q} \cdot \boldsymbol{v} \, dV + \int_{A} \boldsymbol{t} \cdot \boldsymbol{v} \, dA.$$
(2.37)

We will now specify the heat added to the system more accurately. We consider heat supply through internal *heat sources*, that produce an amount of heat \tilde{r} per unit of time per unit of mass and heat drainage through the surface caused by a *heat flux density vector* \boldsymbol{h} . The heat added per unit of time now yields:

$$\dot{Q} = \int_{V} \rho \tilde{r} \, dV - \int_{A} \boldsymbol{h} \cdot \boldsymbol{n} \, dA.$$
(2.38)

Application of the first law (2.32) now yields:

$$\frac{\partial}{\partial t} \int_{V} \rho(\tilde{U} + \frac{1}{2}\boldsymbol{v} \cdot \boldsymbol{v}) \, dV = -\int_{A} \rho\left(\tilde{U} + \frac{1}{2}\boldsymbol{v} \cdot \boldsymbol{v}\right) \boldsymbol{v} \cdot \boldsymbol{n} \, dA$$
$$+ \int_{V} \rho \boldsymbol{q} \cdot \boldsymbol{v} \, dV + \int_{A} \boldsymbol{t} \cdot \boldsymbol{v} \, dA$$
$$+ \int_{V} \rho \tilde{r} \, dV - \int_{A} \boldsymbol{h} \cdot \boldsymbol{n} \, dA. \qquad (2.39)$$

The local form of this law follows from Gauss' theorem. The last term of (2.37) is thereby transformed into:

$$\int_{A} \boldsymbol{t} \cdot \boldsymbol{v} \, dA = \int_{V} \boldsymbol{\nabla} \cdot (\boldsymbol{\sigma}^{c} \cdot \boldsymbol{v}) \, dV$$
$$= \int_{V} \{ (\boldsymbol{\nabla} \cdot \boldsymbol{\sigma}^{c}) \cdot \boldsymbol{v} + \boldsymbol{\sigma} : (\boldsymbol{\nabla} \boldsymbol{v})^{c} \} \, dV$$
$$= \int_{V} \{ (\boldsymbol{\nabla} \cdot \boldsymbol{\sigma}^{c}) \cdot \boldsymbol{v} + \boldsymbol{\sigma} : \boldsymbol{D} \} \, dV. \quad (2.40)$$

The last transition is justified, because the Cauchy stress tensor σ is symmetric. If we use the balance of mass (2.23) and the balance of momentum (2.28), we find the *local law for conservation of energy*:

$$\rho \tilde{U} = \rho \tilde{r} - \boldsymbol{\nabla} \cdot \boldsymbol{h} + \boldsymbol{\sigma} : \boldsymbol{D}.$$
(2.41)

Using (2.16) and (2.19) we obtain:

$$\rho \dot{\tilde{U}} = \rho \tilde{r} - \boldsymbol{\nabla} \cdot \boldsymbol{h} + \frac{1}{J} \boldsymbol{P} : \dot{\boldsymbol{E}}.$$
(2.42)

2.3.2. The second law of thermodynamics. Considering the original formulation of the second law, by Clausius in 1850, heat doesn't flow from a cold system to a warm system spontaneously. A more general formulation states that systems always show the tendency to transit from an ordered to an unordered state. The very existence of the second law is linked to the choice in continuum mechanics to describe a system of a limited number of independent variables. Because of this limitation, this macroscopic description of the system is inherently incomplete. In other words, there are many, many microstates which lead to the same macrostate. The precise definition of disorderliness or entropy (S) in statistical physica has little relevance to the subject of mixture theory has such and will therefore not be dealt with in detail. It suffies to say that the entropy of a system is related to the number of microstates, that leads to the same macrostate. A simple example illustrates this clearly. Consider a set of 5 red beads and 5 blue beads, which fit into a box with 5 spaces on the left and 5 spaces on the right. A microstate is defined by which colour is in which space. The macrostate is defined by a single variable: the number of red beads in the 5 spaces on the left. Macrostate *n* corresponds to $(\frac{5 \dots n+1}{(5-n)!})^2$ microstates:

macrostate	number of microstates
n = 5	1
n = 4	25
n = 3	100
n=2	100
n = 1	25
n = 0	1

TABLE 1. The number of microstates is a measure of the entropy of the macrostates.

When beads are moved around in the box, there is more chance to have the system moving towards state n = 2 or n = 3 than towards n = 0 or n = 5, simply because there are more ways to be in state n = 2 or n = 3than n = 0 or n = 5. This is what the second law of thermodynamics is all about. The second law is almost a tautology. The box naturally moves to the more entropy states n = 2 or n = 3. In the real problem of continuum mechanics we have billions of particles within each representative elementary volume, resulting in many more microstates for each macrostate. This makes it virtually impossible for entropy to move down. For a closed system we have,

$$dS \ge 0. \tag{2.43}$$

Entropy is the amount of knowledge of the system which is locking in the macroscopic description of the system in continuum mechanics terms. It is defined as a measure of the number of microstates which correspond to any microstate. The more microstates correspond to a macrostate, the less knowledge of the details of the system we gain from the macroscopic continuum knowledge, and therefore the higher the entropy. For an open system, the generated entropy is the change in entropy of the system minus the externally supplied entropy $\frac{dQ}{T}$:

$$dS - \frac{dQ}{T} \ge 0. \tag{2.44}$$

If the '='-sign in (2.44) counts, we speak of a *reversible* process, if the '>'-sign counts, the process is *irreversible*. Actually, (2.44) forms the thermodynamic definition of entropy. We will write (2.44) again for a part of space with volume V and surface area A. If we consider the variations per unit of time, we find, using (2.38):

$$\frac{\partial}{\partial t} \int_{V} \rho \tilde{S} \, dV + \int_{A} \rho \tilde{S} \boldsymbol{v} \cdot \boldsymbol{n} \, dA \ge \int_{V} \frac{\rho \tilde{r}}{T} \, dV - \int_{A} \frac{\boldsymbol{h}}{T} \cdot \boldsymbol{n} \, dA \tag{2.45}$$

in which the specific entropy \tilde{S} is defined as the entropy per unit mass.

TABLE 2. Balance laws for non-polar continua.

quantity	balance law
mass	$\dot{ ho} + ho \boldsymbol{\nabla} \cdot \boldsymbol{v} = 0$
momentum	$ ho \dot{oldsymbol{v}} = oldsymbol{ abla} \cdot oldsymbol{\sigma} + ho oldsymbol{q}$
moment of momentum	$\sigma = \sigma^{c}$
energy	$ ho\dot{ec{U}}= ho ilde{r}-oldsymbol{ abla}\cdotoldsymbol{h}+oldsymbol{\sigma}:D$
entropy	$ ho \dot{ ilde{S}} \geq rac{ ho ilde{r}}{T} - oldsymbol{ abla} \cdot \left(rac{oldsymbol{h}}{T} ight)$

For the local form follows:

$$\rho \dot{\tilde{S}} \ge \frac{\rho \tilde{r}}{T} - \boldsymbol{\nabla} \cdot \left(\frac{\boldsymbol{h}}{T}\right). \tag{2.46}$$

This form is also known as the Clausius-Duhem-equation.

2.4. Thermodynamic potentials

In this paragraph we will consider the amount of energy of a continua. The energy per unit mass, the specific energy, is also called the *thermodynamic potential*.

2.4.1. Ideal media. In the traditional application area of thermodynamics, gases are often considered. These gases are regarded as an *ideal medium*, which means, a medium in which the state of stress can be characterized with a *hydrostatic pressure p*. For the work done by the system dW_s applies:

$$dW_{\rm s} = p \, dV \tag{2.47}$$

in which dV is the change of volume of the medium. Furthermore, the macroscopic kinetic energy K is neglected, as to write the first law (2.31) as:

$$dQ = dU + p \, dV,\tag{2.48}$$

which converts for a reversible process into:

$$dU = T \, dS - p \, dV. \tag{2.49}$$

We can make a transition from the global to the local form again by working with specific quantities.

$$d\tilde{U} = T \, d\tilde{S} - p \, d\tilde{V} \tag{2.50}$$

in which $\tilde{V} = 1/\rho$ represents the volume per unit mass. If we now consider the specific internal energy \tilde{U} as a function of the independent variables \tilde{S} and \tilde{V} :

$$\tilde{U} = \tilde{U}(\tilde{S}, \tilde{V}) \tag{2.51}$$

and we determine the total differential of \tilde{U} ,

$$d\tilde{U} = \left(\frac{\partial \tilde{U}}{\partial \tilde{S}}\right)_{\tilde{V}} d\tilde{S} + \left(\frac{\partial \tilde{U}}{\partial \tilde{V}}\right)_{\tilde{S}} d\tilde{V}, \qquad (2.52)$$

we can derive from (2.50) and (2.52) that:

$$T = \left(\frac{\partial \tilde{U}}{\partial \tilde{S}}\right)_{\tilde{V}},\tag{2.53}$$

$$p = -\left(\frac{\partial \tilde{U}}{\partial \tilde{V}}\right)_{\tilde{S}}.$$
(2.54)

From Eq. (2.52) it turns out that the internal energy doesn't change for a thermodynamic process with which the specific entropy \tilde{S} and the specific volume \tilde{V} remain constant. Therefore it is convenient for such *isentropic*, *isochoric* processes to use the potential \tilde{U} . We call \tilde{S} and \tilde{V} the *characteristic* variables, corresponding to the potential \tilde{U} .

For *isentropic*, *isobaric* processes it is more convenient to use another potential, the specific enthalpy \tilde{H} , defined as:

$$\tilde{H} = \tilde{U} + p\tilde{V}.$$
(2.55)

In a reversible process we can write the total differential of \tilde{H} , using (2.50).

$$d\tilde{H} = Td\tilde{S} + \tilde{V}dp. \tag{2.56}$$

Obviously we can consider the enthalpy \tilde{H} as a function of the characteristic variables \tilde{S} and p: $\tilde{H} = \tilde{H}(\tilde{S}, p)$. It can also be derived that:

$$T = \left(\frac{\partial \tilde{H}}{\partial \tilde{S}}\right)_{p},\tag{2.57}$$

$$\tilde{V} = \left(\frac{\partial \tilde{H}}{\partial p}\right)_{\tilde{S}}.$$
(2.58)

For *isothermal, isochoric* processes we use the third thermodynamic potential, the *specific Helmholtz free energy*, defined as:

$$\tilde{F} = \tilde{U} - T\tilde{S},\tag{2.59}$$

for which we can derive that:

$$d\tilde{F} = d\tilde{U} - Td\tilde{S} - \tilde{S}dT = -\tilde{S}dT - pd\tilde{V}$$
(2.60)

and

$$\tilde{S} = -\left(\frac{\partial F}{\partial T}\right)_{\vec{V}},\tag{2.61}$$

$$p = -\left(\frac{\partial F}{\partial \tilde{V}}\right)_{T}$$
(2.62)

In some cases it is recommendable to assume a thermodynamic potential that has the temperature as well as the pressure as the characteristic quantities. This potential is called the *specific Gibbs free energy* $\tilde{G} = \tilde{G}(p,T)$, and is defined as:

$$\tilde{G} = \tilde{H} - T\tilde{S}.$$
(2.63)

For the variation $d\tilde{G}$ of \tilde{G} the next total differential applies:

$$d\tilde{G} = d\tilde{H} - Td\tilde{S} - \tilde{S}dT = \tilde{V}dp - \tilde{S}dT$$
(2.64)

in which (2.56) is used. Following the already known manner, we can derive that:

$$\tilde{V} = \left(\frac{\partial \tilde{G}}{\partial p}\right)_{T},\tag{2.65}$$

$$\tilde{S} = -\left(\frac{\partial \tilde{G}}{\partial T}\right)_{p}.$$
(2.66)

For isobaric, isothermal, reversible processes holds:

$$(d\bar{G})_{p,T,\text{rev}} = 0.$$
 (2.67)

For the *irreversible* case it can be derived that:

$$(d\tilde{G})_{p,T,\text{irrev}} < 0. \tag{2.68}$$

An arbitrary isobaric, isothermal process goes therefore in the direction of a decreasing Gibbs free energy until an equilibrium is reached, for which applies:

$$(d^2 \tilde{G})_{p,T,\text{evenwicht}} > 0. \tag{2.69}$$

We will use these properties of the Gibbs free energy later.

In the text above, two examples of a *free energy* have come up. From (2.59) and (2.63) it appears that such a free energy is defined by reducing

another measure of energy with $T\tilde{S}$. This term $T\tilde{S}$ represents that part of the specific energy, that cannot be released from the matter by some process of conversion, because of the second law. When we use the word 'energy' in daily life we mean free energy, energy that can readily be used. When we say 'energy' crisis, we mean free energy crisis. When we say 'law of conservation of energy' we mean, law of conservation of internal energy.

2.4.2. Non-ideal media. In general the state of stress in a continuum is not hydrostatic. In this paragraph we will describe state functions for a more general state of stress. According to the local balance of energy (2.42) and (2.46), the variations of the specific internal energy \tilde{U} in time are, for reversible processes:

$$\rho \dot{\tilde{U}} = \rho T \dot{\tilde{S}} + \frac{1}{J} \boldsymbol{P} : \dot{\boldsymbol{E}} - \frac{1}{T} \boldsymbol{h} \cdot \boldsymbol{\nabla} T.$$
(2.70)

We will now restrict ourselves to continua in which no temperature gradients are present. If we consider the variations independent of time, it follows, that:

$$d\tilde{U} = Td\tilde{S} + \frac{1}{\rho_0}\boldsymbol{P} : d\boldsymbol{E}.$$
(2.71)

If we match this expression with the corresponding expression for ideal media (2.50), we see that the transition to general media can be attained by the following substitution:

$$-p \, d\tilde{V} \longrightarrow \frac{1}{\rho_0} \boldsymbol{P} : d\boldsymbol{E}.$$
 (2.72)

Physically, both terms represent an infinitesimal amount of work, that is produced by the surface forces per unit of deformed volume. We see in (2.71) that the specific internal energy is a function of \tilde{S} and E:

$$\tilde{U} = \tilde{U}(\tilde{S}, \boldsymbol{E}). \tag{2.73}$$

Differentiating this relation yields:

$$d\tilde{U} = \left(\frac{\partial \tilde{U}}{\partial \tilde{S}}\right)_{E} d\tilde{S} + \left(\frac{\partial \tilde{U}}{\partial E}\right)_{\tilde{S}} : dE.$$
(2.74)

Comparing (2.74) with (2.71) shows that:

$$T = \left(\frac{\partial \tilde{U}}{\partial \tilde{S}}\right)_{E},\tag{2.75}$$

$$\boldsymbol{P} = \rho_0 \left(\frac{\partial \tilde{U}}{\partial \boldsymbol{E}}\right)_{\tilde{S}}.$$
(2.76)

Extension of (2.59), the total differential for the specific Helmholtz free energy \tilde{F} , for general media, yields,

$$d\tilde{F} = -\tilde{S} dT + \frac{1}{\rho_0} \boldsymbol{P} : d\boldsymbol{E}, \qquad (2.77)$$

from which it can be shown that:

$$\boldsymbol{P} = \rho_0 \left(\frac{\partial \tilde{F}}{\partial \boldsymbol{E}}\right)_T,\tag{2.78}$$

$$\tilde{S} = -\left(\frac{\partial \tilde{F}}{\partial T}\right)_{E}.$$
(2.79)

The total differential of the specific Gibbs free energy \tilde{G} (2.64) we extend in a similar way:

$$d\tilde{G} = -\tilde{S} dT - \frac{1}{\rho_0} \boldsymbol{E} : d\boldsymbol{P}, \qquad (2.80)$$

from which we see that:

$$\tilde{S} = -\left(\frac{\partial \tilde{G}}{\partial T}\right)_{P},\tag{2.81}$$

$$\boldsymbol{E} = \rho_0 \left(\frac{\partial \tilde{G}}{\partial \boldsymbol{P}}\right)_T.$$
(2.82)

The extensive form of the enthalpy \tilde{H} can also derived this way. The result is shown in Table 3.

TABLE 3. Thermodynamic potentials.

name	definition	total differential
internal energy	Ũ	$d\tilde{U} = Td\tilde{S} + \frac{1}{ ho_0}P: dE$
enthalpy	$\tilde{H} = \tilde{U} - \frac{1}{\rho_0} \boldsymbol{P} : \boldsymbol{E}$	$d\tilde{H} = Td\tilde{S} - \frac{1}{\rho_0}\boldsymbol{E}: d\boldsymbol{P}$
Helmholtz free energy	$\tilde{F}=\tilde{U}-T\tilde{S}$	$d\tilde{F}=-\tilde{S}dT+\frac{1}{\rho_{0}}\boldsymbol{P}:d\boldsymbol{E}$
Gibbs free energy	$\tilde{G}=\tilde{H}-T\tilde{S}$	$d\tilde{G} = -\tilde{S}dT - \frac{1}{ ho_0}\boldsymbol{E}:d\boldsymbol{P}$

2.5. The second law and constitutive behaviour

To trace the mechanical state of a continuum, constitutive equations for the material behaviour are also needed as well as the corresponding initial and boundary conditions. For the choice of the constitutive equations several limitations apply. The next requirements have to be satisfied [Schreurs, 1993; Oomens, 1993d]:

- definiteness;
- objectivity;
- thermodynamic permissibility;
- equipresence.

The third demand implies that the constitutive equations have to be chosen such, that the entropy inequality (2.46) is satisfied for all possible states and variations of state of the continuum. This means that restrictions can be obtained using the second law for a general form of the constitutive equations, that describe the material behaviour. We will use this demand frequently during this course. Equipresence demands that all dependent variables depend on all independent variables unless the third demand makes this impossible. To illustrate this, we will apply this routine first for the simple case of a 1-component mixture.

First we eliminate the term $\rho \tilde{r}$ from expression (2.46), using (2.42) for the first law, which results in:

$$\rho(T\dot{\tilde{S}} - \dot{\tilde{U}}) + \boldsymbol{\sigma} : \boldsymbol{D} + T\boldsymbol{h} \cdot \boldsymbol{\nabla}\left(\frac{1}{T}\right) \ge 0.$$
(2.83)

Transition to the specific Helmholtz free energy \tilde{F} (2.59) yields:

$$-\rho(\dot{\tilde{F}} + \dot{T}\tilde{S}) + \boldsymbol{\sigma} : \boldsymbol{D} + T\boldsymbol{h} \cdot \boldsymbol{\nabla}\left(\frac{1}{T}\right) \ge 0.$$
(2.84)

We now assume the following:

- the material is incompressible;
- volume forces and forces of inertia are neglected;
- the temperature of the continuum is constant in time and space.

The last demand holds under the assumption that the source term \tilde{r} is chosen such that temperature remains constant. Therefore this equation will not be considered any further. Our final choice for the constitutive behaviour has to satisfy the following second law,

$$-\rho\dot{\tilde{F}} + \boldsymbol{\sigma} : \boldsymbol{D} \ge 0, \tag{2.85}$$

with additional conditions, the balance of mass and momentum:

$$\boldsymbol{\nabla} \cdot \boldsymbol{v} = 0, \tag{2.86}$$

$$\boldsymbol{\nabla} \cdot \boldsymbol{\sigma} = \boldsymbol{0}. \tag{2.87}$$

One way of processing of these subsidiary conditions is *substitution*, where a variable in a side condition is first isolated and then eliminated from the main equation. The number of equations as well as the number of unknowns decreases. If the isolation of a variable is impossible or inconvenient, a subsidiary condition can be accounted for using a *Lagrange-multiplier*. The subsidiary condition is written as an equation in which all terms are moved to the left. The right hand side of the equation is zero. The left hand side of this equation, multiplied by the Lagrange-multiplier, is added to the inequality. Because the number of unknowns increases in this situation, the method of substitution is preferable, if at all applicable.

Let us nevertheless try to account for the incompressibility condition using a Lagrange-multiplier λ :

$$-\rho \tilde{F} + \boldsymbol{\sigma} : \boldsymbol{D} + \lambda \boldsymbol{\nabla} \cdot \boldsymbol{v} \ge 0, \qquad (2.88)$$

which can also be written as:

$$-\rho\dot{\tilde{F}} + (\boldsymbol{\sigma} + \lambda \boldsymbol{I}) : \boldsymbol{D} \ge 0.$$
(2.89)

The balance laws (2.86) and (2.87) are equivalent to 4 scalar equations with 9 (6 stresses and 3 velocities) unknown variables. We need therefore 5 additional equations. Since balance laws are no more available we need at least 5 constitutive equations. We choose the quantities \tilde{F} and $\sigma + \lambda I$ as dependent variables that depend on independent variables through constitutive relationships. These relationships are equivalent to 7 scalar equations (1 for \tilde{F} and 6 for $\sigma + \lambda I$). They provide the 5 missing equations plus 2 equations to compensate for the law quantities \tilde{F} and λ . Then the set of equations is closed.

We chose the Green-Lagrange strain, E, as an independent variable. Such choice equates to an assumption of elasticity. Using the principle of *equipres*ence we have to make all dependent variables function of all independent variables. In this simple case, it means:

$$\tilde{F} = \tilde{F}(\boldsymbol{E}), \tag{2.90}$$

$$\boldsymbol{\sigma} + \lambda \boldsymbol{I} = \boldsymbol{F} \cdot \boldsymbol{\sigma}^*(\boldsymbol{E}) \cdot \boldsymbol{F}^c. \tag{2.91}$$

The pre and post multiplication with F ensures that the constitutive function σ^* is objective. The choice of dependent and independent variables doesn't result from theory, but is based on physical insight. The number of dependent variables should be such as to ensure that the final set of equations is closed,

i.e. the number of unknowns should equal the number of equations. Finally, the extent to which the resulting constitutive equations describe the observed experimental behaviour of the continuum, is a justification for the choice. Substitution of the expressions (2.90) and (2.91) in (2.89) yields:

$$\boldsymbol{F} \cdot \left(-\rho \frac{\partial \tilde{F}}{\partial \boldsymbol{E}} + \boldsymbol{\sigma}^*\right) \cdot \boldsymbol{F}^{\mathrm{c}} : \boldsymbol{D} \ge 0.$$
(2.92)

This expression has to apply for arbitrary values of D. Because the factor with which D is multiplied, is dependent of D we can satisfy (2.92) by setting this factor to zero. This means that the entropy-production is equal to zero, which is in agreement with our assumption of elastic material behaviour.

Filling of expression (2.91) for σ^* yields:

$$\boldsymbol{\sigma} = \rho \boldsymbol{F} \cdot \frac{\partial \tilde{F}}{\partial \boldsymbol{E}} \cdot \boldsymbol{F}^{c} - \lambda \boldsymbol{I}.$$
(2.93)

Let's compare this expression with (2.18). We find that the Lagrange - multiplier can physically be interpreted as the hydrodynamic pressure p. The deviatoric stress σ^{d} can be written as:

$$\boldsymbol{\sigma}^{\mathrm{d}} = \rho \boldsymbol{F} \cdot \frac{\partial \tilde{F}}{\partial \boldsymbol{E}} \cdot \boldsymbol{F}^{\mathrm{c}}.$$
(2.94)

If we now switch to the second Piola-Kirchhoff stress tensor P, based upon σ^{d} , we can also write:

$$\boldsymbol{P} = \det(\boldsymbol{F}) \ \boldsymbol{F}^{-1} \cdot \boldsymbol{\sigma}^{d} \cdot \boldsymbol{F}^{-c} = \rho_0 \frac{\partial F}{\partial \boldsymbol{E}}, \qquad (2.95)$$

where $\rho/\rho_0 = \det(\mathbf{F})$ is used. The elastic behaviour of biological materials is often described with a strain energy density function or the elastic potential, and indicated with the symbol W. This yields:

$$\boldsymbol{P} = \frac{\partial W}{\partial \boldsymbol{E}}.$$
 (2.96)

We can interpret this W as $\rho_0 \tilde{F}$, the amount of Helmholtz free energy per unit volume.

Exercises

1. Use the second law according to (2.84) to derive the general form of the constitutive equations for thermo-elastic media.

- First, choose the Green-Lagrange strain tensor E, the temperature T and the temperature gradient $\nabla_0 T = F^c \cdot \nabla T$ as independent variables and the Helmholtz free energy \tilde{F} , the entropy \tilde{S} , the second Piola-Kirchhoff stress P and the heat flux vector $h_0 = F^{-1} \cdot h$ as dependent variables.
- Then choose the Green-Lagrange strain tensor \boldsymbol{E} , the entropy \tilde{S} and the heat flux vector $\boldsymbol{h}_0 = \boldsymbol{F}^{-1} \cdot \boldsymbol{h}$ as independent variables and the internal energy \tilde{U} , the temperature T, the second Piola-Kirchhoff stress \boldsymbol{P} and the temperature gradient $\nabla_0 T = \boldsymbol{F}^c \cdot \nabla T$ as dependent variables.
- 2. In an incompressible biological material the relation between the deviatoric Cauchy stress tensor σ^{d} and the Green–Lagrange strain tensor is described using (2.95) and (2.96). For the elastic potential W applies:

$$W(E) = a \exp \left[b(E_{11}^2 + E_{22}^2 + 2E_{33}^2) + b(E_{12}^2 + E_{21}^2 + E_{23}^2 + E_{32}^2 + E_{31}^2 + E_{13}^2) \right],$$

where the components E_{ij} are chosen with respect to a Cartesian base $\{e_1, e_2, e_3\}$. A cubic-like specimen is created of the material of which the edges are oriented along the base vectors. The specimen is tested in a uniaxial extension and compression test by loading along the e_3 -direction. The elongation factor in this direction is called λ . Calculate the hydrostatic pressure and the components of σ as a function of λ .

3. General theory of mixtures

We generalize the theory obtained in the last chapter for a description of the mechanical behaviour of mixtures, substances consisting of several components. A component is defined in this context as a set of material constituents that moves jointly in the mixture.

In this chapter we will derive a general form of the theory of mixtures. The description has mainly be taken from Bowen (1976).

3.1. Quantities of mixtures

Let's consider a general mixture of ν components. Microscopically, only one component is present at a certain moment at a certain place in space. Furthermore, the composition of the mixture will differ in general from one point to another. In the theory of mixtures we try not to describe the behaviour of every separate particle. We use a continuum approach instead, in which we spread the properties of the components over a representative

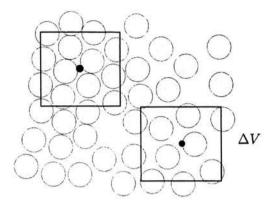


FIGURE 6. Illustration of the averaging procedure for a mixture of a solid and a fluid.

volume unit (RVU) ΔV . This volume has to be big enough to provide a good continuum representation of the quantities on microscopic level, but also small enough to avoid averaging of macroscopic variations. If the RVU is displaced through every possible position in the mixture and the average quantities are ascribed to the position of the centre of the RVU, we can determine the average quantities as a function of the position in the mixture (Fig. 6). A consequence of the averaging concept is that every component, that is present in the mixture, occupies every position x in that mixture. We express the amount of component α in terms of mass m^{α} or moles n^{α} . In the theory of mixtures we usually take the *apparent density* ρ of the components, concerned with the RVU, V, and the present amount of mass, m^{α} , in it:

$$\rho^{\alpha} = \frac{m^{\alpha}}{V}, \qquad \alpha = 1, \dots, \nu.$$
(3.1)

If component α is immiscible with other components, the volume of component α is indicated with V^{α} . The real *intrinsic density* ρ_i^{α} of the components of immiscible components is then:

$$\rho_i^{\alpha} = \frac{m^{\alpha}}{V^{\alpha}}, \qquad \alpha = 1, \dots, \nu.$$
(3.2)

We define the volume fraction ϕ^{α} of an immiscible component as:

$$\phi^{\alpha} = \frac{V^{\alpha}}{V}, \qquad \alpha = 1, \dots, \nu \tag{3.3}$$

in which V^{α} is the volume occupied by component α within the volume V.

It will be obvious that:

$$\sum_{\alpha=1}^{\nu} \phi^{\alpha} = 1 \tag{3.4}$$

and

$$\rho^{\alpha} = \phi^{\alpha} \rho_i^{\alpha}, \qquad \alpha = 1, \dots, \nu. \tag{3.5}$$

We define the density ρ of the whole mixture as:

$$\rho = \sum_{\alpha=1}^{\nu} \rho^{\alpha}.$$
(3.6)

3.2. Kinematics and stress

3.2.1. Kinematics. We consider the mixture of ν components again. The collection of material points ξ of a component α ($\alpha = 1, ..., \nu$) is indicated with \mathcal{B}^{α} . These points occupy an area \mathcal{G}^{α} in the three-dimensional space at time t:

$$\mathcal{G}^{\alpha}(t) = \{ \boldsymbol{x}^{\alpha} = \boldsymbol{\chi}^{\alpha}(\underline{\xi}^{\alpha}, t) \mid \forall \underline{\xi}^{\alpha} \in \mathcal{B}^{\alpha} \}.$$
(3.7)

The areas \mathcal{G}^{α} ($\alpha = 1, ..., \nu$) coincide according to the theory of mixtures and every position \boldsymbol{x} is occupied by particles of every single component at the same time. Therefore, the following holds:

$$\mathbf{x}(t) = \mathbf{x}^{1}(t) = \mathbf{x}^{2}(t) = \ldots = \mathbf{x}^{\alpha}(t) = \ldots = \mathbf{x}^{\nu}(t).$$
 (3.8)

We can now define a *deformation tensor* F^{α} per component:

$$\boldsymbol{F}^{\alpha} = (\boldsymbol{\nabla}_{0}^{\alpha} \boldsymbol{x}^{\alpha})^{c}. \tag{3.9}$$

In this equation the symbol ∇_0^{α} represents the gradient operator concerning the state of reference of component α . We define the *Green-Lagrange strain* tensor E^{α} with respect to component α as:

$$\boldsymbol{E}^{\alpha} = \frac{1}{2} \left\{ (\boldsymbol{F}^{\alpha})^{c} \cdot \boldsymbol{F}^{\alpha} - \boldsymbol{I} \right\}.$$
(3.10)

The velocity v^{α} of a material point from component α is defined as:

$$\boldsymbol{v}^{\alpha} = \left. \frac{\partial \boldsymbol{\chi}^{\alpha}(\underline{\xi}^{\alpha}, t)}{\partial t} \right|_{\underline{\xi}^{\alpha}}.$$
(3.11)

We define the velocity of the whole mixture v as the mass weighted average of the velocities of the components:

$$\boldsymbol{v}(\boldsymbol{x},t) = \frac{1}{\rho} \sum_{\alpha=1}^{\nu} \rho^{\alpha} \boldsymbol{v}^{\alpha}(\boldsymbol{x},t).$$
(3.12)

We can point several velocities in every point of the continuum. Therefore several material time derivatives are defined. Let's consider a quantity a^{α} , a quantity *a* connected to the component α . We now define two material time derivatives of a^{α} :

$$\dot{a}^{\alpha} = \frac{Da^{\alpha}}{Dt} = \frac{\partial a^{\alpha}}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} a^{\alpha}, \qquad (3.13)$$

$$\dot{a}^{\alpha} = \frac{D^{\alpha}a^{\alpha}}{Dt} = \frac{\partial a^{\alpha}}{\partial t} + \boldsymbol{v}^{\alpha} \cdot \boldsymbol{\nabla} a^{\alpha}.$$
(3.14)

Using time derivative \dot{a}^{α} we move with the average velocity of the mixture, while we move with the component α if we use \dot{a}^{α} .

We define the deformation velocity tensor D^{α} and the rotational velocity tensor Ω^{α} as:

$$\boldsymbol{D}^{\alpha} = \frac{1}{2} \left\{ \boldsymbol{\check{F}}^{\alpha} \cdot (\boldsymbol{F}^{\alpha})^{-1} + (\boldsymbol{\check{F}}^{\alpha} \cdot (\boldsymbol{F}^{\alpha})^{-1})^{c} \right\}, \qquad (3.15)$$

$$\boldsymbol{\Omega}^{\alpha} = \frac{1}{2} \left\{ \dot{\boldsymbol{F}}^{\alpha} \cdot (\boldsymbol{F}^{\alpha})^{-1} - (\dot{\boldsymbol{F}}^{\alpha} \cdot (\boldsymbol{F}^{\alpha})^{-1})^{c} \right\}.$$
(3.16)

In these definitions we take the material time derivative of the deformation tensor F^{α} while we move with component α .

Finally we define the velocity u^{α} of component α with respect to the velocity of the mixture as:

$$\boldsymbol{u}^{\alpha} = \boldsymbol{v}^{\alpha} - \boldsymbol{v}. \tag{3.17}$$

3.2.2. Stress. Let's consider a small surface with normal unit vector n_0 and surface area A_0 in this mixture. We can subdivide a force f, that works on this surface, in several contributions f^{α} , working on each of the components α in the mixture. As a result of the force f the surface deforms, during which it gets a normal unit vector n and a surface area A. We now define the *partial stress vector* t^{α} as the force working on component α , divided by the *total* surface area:

$$\boldsymbol{t}^{\alpha} = \frac{\boldsymbol{f}^{\alpha}}{A}.\tag{3.18}$$

For the choice of size of the averaging surface A the same considerations apply as for the averaging volume V. Analoguously to (2.17) we now define the partial Cauchy stress tensor σ^{α} :

$$\boldsymbol{t}^{\alpha} = \boldsymbol{\sigma}^{\alpha} \cdot \boldsymbol{n}. \tag{3.19}$$

The tensor σ^{α} projects the normal unit vector n of a surface to the *partial* stress vector t^{α} , that represents the force that is applied per unit of surface area of the mixture of component α .

3.3. Balance of mass, momentum and moment of momentum

3.3.1. Balance of mass. We consider an arbitrary volume V in space with surface area A. The balance of mass for component α reads in integral form:

$$\frac{\partial}{\partial t} \int_{V} \rho^{\alpha} \, dV = -\int_{A} \rho^{\alpha} \boldsymbol{v}^{\alpha} \cdot \boldsymbol{n} \, dA + \int_{V} \hat{c}^{\alpha} \, dV. \tag{3.20}$$

This equation is equal to (2.20), with an extra source term added that accounts for the variation in mass of component α with respect to interactions with other components. The quantity \hat{c}^{α} is defined as the rate of mass transfer from component α to other components changes per unit volume of mixture. We can think of phase-changes (mass-exchange between liquid and vapour), variation of ionisation (mass-exchange between the ion-component and the solid phase), or chemical reactions. Applying Gauss' theorem yields the *local form of the balance of mass per component* α :

$$\frac{\partial \rho^{\alpha}}{\partial t} + \boldsymbol{\nabla} \cdot (\rho^{\alpha} \boldsymbol{v}^{\alpha}) = \hat{c}^{\alpha}.$$
(3.21)

The exchange of mass between the mutual components does not influence on the total mass:

$$\sum_{\alpha=1}^{\nu} \int_{V} \hat{c}^{\alpha} \, dV = 0. \tag{3.22}$$

At the local level this results in the local balance of mass for the whole mixture:

$$\sum_{\alpha=1}^{\nu} \hat{c}^{\alpha} = 0. \tag{3.23}$$

3.3.2. Balance of momentum. We consider an arbitrary, but fixed part of space with volume V and surface area A again. In integral form the balance of momentum for component α is given by:

$$\frac{\partial}{\partial t} \int_{V} \rho^{\alpha} \boldsymbol{v}^{\alpha} \, dV = -\int_{A} (\rho^{\alpha} \boldsymbol{v}^{\alpha}) \boldsymbol{v}^{\alpha} \cdot \boldsymbol{n} \, dA$$
$$+ \int_{V} \rho^{\alpha} \boldsymbol{q}^{\alpha} \, dV + \int_{A} \boldsymbol{t}^{\alpha} \, dA + \int_{V} (\hat{\boldsymbol{p}}^{\alpha} + \hat{c}^{\alpha} \boldsymbol{v}^{\alpha}) \, dV.$$
(3.24)

We recognize the integral form for one-phase materials again (2.26), completed with an interaction-term. The volume force that works upon α is

indicated with q^{α} . The term in t^{α} represents the force per unit surface area mixture on component α . Based on (3.18) a contribution of the surface forces has to be calculated by integrating the partial stress vectors t^{α} over the surface of the mixture A. In the interaction term the volume force \hat{p}^{α} represents the momentum transfered from other components to component α , counted per unit volume mixture and per unit of time. Transition of momentum occurs for example in friction forces, that are a result of relative movement of the components. The term $\hat{c}^{\alpha}v^{\alpha}$ represents momentum transfer associated with the exchange of mass \hat{c}^{α} . It is assumed that the added mass of component α gets the same velocity as the already present mass of component α . Using Gauss' theorem we find the local form of the balance of momentum per component α again:

$$\rho^{\alpha} \left\{ \frac{\partial \boldsymbol{v}^{\alpha}}{\partial t} + \boldsymbol{v}^{\alpha} \cdot \boldsymbol{\nabla} \boldsymbol{v}^{\alpha} \right\} = \rho^{\alpha} \boldsymbol{\dot{v}}^{\alpha} = \boldsymbol{\nabla} \cdot (\boldsymbol{\sigma}^{\alpha})^{c} + \rho^{\alpha} \boldsymbol{q}^{\alpha} + \boldsymbol{\hat{p}}^{\alpha}$$
(3.25)

in which σ^{α} represents the partial Cauchy stress tensor. The term $\hat{c}^{\alpha} v^{\alpha}$ doesn't show up again in this equation, because we used the balance of mass (3.21). For the total mixture the net conversion of momentum with respect to the interaction terms has to be zero, so the *local balance of momentum for the total mixture* holds:

$$\sum_{\alpha=1}^{\nu} (\hat{c}^{\alpha} \boldsymbol{v}^{\alpha} + \hat{\boldsymbol{p}}^{\alpha}) = \boldsymbol{0}.$$
(3.26)

3.3.3. Balance of moment of momentum. The integral form of the balance of momentum for component α is:

$$\frac{\partial}{\partial t} \int_{V} \boldsymbol{x}^{\alpha} \cdot \rho^{\alpha} \boldsymbol{v}^{\alpha} \, dV = -\int_{A} (\boldsymbol{x}^{\alpha} \cdot \rho^{\alpha} \boldsymbol{v}^{\alpha}) \boldsymbol{v}^{\alpha} \cdot \boldsymbol{n} \, dA$$

$$+ \int_{V} \boldsymbol{x}^{\alpha} \cdot \rho^{\alpha} \boldsymbol{q}^{\alpha} \, dV + \int_{A} \boldsymbol{x}^{\alpha} \cdot \boldsymbol{t}^{\alpha} \, dA$$

$$+ \int_{V} \left(\boldsymbol{x}^{\alpha} \cdot (\hat{c}^{\alpha} \boldsymbol{v}^{\alpha} + \hat{\boldsymbol{p}}^{\alpha}) + \hat{\boldsymbol{m}}^{\alpha} \right) dV. \qquad (3.27)$$

The last term accounts for the transfer of the moment of momentum from other components to component α . The term $\boldsymbol{x}^{\alpha} \cdot (\hat{c}^{\alpha} \boldsymbol{v}^{\alpha} + \hat{\boldsymbol{p}}^{\alpha})$ is the moment of momentum transfer associated with the momentum interaction $(\hat{c}^{\alpha} \boldsymbol{v}^{\alpha} + \hat{\boldsymbol{p}}^{\alpha})$. The term $\hat{\boldsymbol{m}}^{\alpha}$ represents the direct moment of momentum transfer to component α by the other components, counted per unit of volume mixture

and per unit of time. An example of such direct moment of momentum interaction is the case of friction forces transfered from fluid to solid in flow through helical pore structure with preferential helicity. The local form of the balance of moment of momentum is:

$$\hat{\boldsymbol{M}}^{\alpha} = (\boldsymbol{\sigma}^{\alpha})^{c} - \boldsymbol{\sigma}^{\alpha} \tag{3.28}$$

in which \hat{M}^{α} is the anti-symmetric tensor corresponding to the axial vector \hat{m}^{α} , defined such that for all vectors a applies:

$$\hat{\boldsymbol{m}}^{\alpha} \cdot \boldsymbol{a} = \hat{\boldsymbol{M}}^{\alpha} \cdot \boldsymbol{a}. \tag{3.29}$$

The reader is referred to specialized literature for the proof of Eq. (3.28). At this moment we consider \hat{M}^{α} as a quantity, analoguous to the terms \hat{c}^{α} and \hat{p}^{α} .

3.4. Thermodynamics

3.4.1. The first law. We formulate the first law of thermodynamics for a component α in the mixture as the first law for a one component continuum (2.39), completed with an interaction term :

$$\frac{\partial}{\partial t} \int_{V} \rho^{\alpha} \left(\tilde{U}^{\alpha} + \frac{1}{2} \boldsymbol{v}^{\alpha} \cdot \boldsymbol{v}^{\alpha} \right) dV dV =
- \int_{A} \rho^{\alpha} \left(\tilde{U}^{\alpha} + \frac{1}{2} \boldsymbol{v}^{\alpha} \cdot \boldsymbol{v}^{\alpha} \right) \boldsymbol{v}^{\alpha} \cdot \boldsymbol{n} \, dA + \int_{V} \rho^{\alpha} \boldsymbol{q}^{\alpha} \cdot \boldsymbol{v}^{\alpha} \, dV
+ \int_{A} \boldsymbol{t}^{\alpha} \cdot \boldsymbol{v}^{\alpha} \, dA + \int_{V} \rho^{\alpha} \tilde{r}^{\alpha} \, dV - \int_{A} \boldsymbol{h}^{\alpha} \cdot \boldsymbol{n} \, dA + \int_{V} \hat{e}^{\alpha} \, dV
+ \int_{V} \left(\boldsymbol{v}^{\alpha} \cdot \hat{\boldsymbol{p}}^{\alpha} + \frac{1}{2} \boldsymbol{\Omega}^{\alpha} : \hat{\boldsymbol{M}}^{\alpha} + \hat{c}^{\alpha} (\tilde{U}^{\alpha} + \frac{1}{2} \boldsymbol{v}^{\alpha} \cdot \boldsymbol{v}^{\alpha}) \right) dV$$
(3.30)

in which \tilde{U}^{α} represents the specific internal energy of component α , h^{α} represents the heat flux density vector for component α and \tilde{r}^{α} represents the specific heat supply to component α by heat sources. In the second of these term the symbol \hat{e}^{α} represents the direct energy transfer from the other components to component α , calculated per unit volume mixture and per unit of time. The last term represents the energy supply caused by interaction effects with respect to the exchange of mass \hat{c}^{α} , the exchange of momentum \hat{p}^{α} and the exchange of moment of momentum \hat{M}^{α} . Using Gauss' theorem

and the balance of mass, momentum and moment of momentum the local form of the balance of energy per component α is derived:

$$\rho \,\tilde{U}^{\alpha} = \rho^{\alpha} \tilde{r}^{\alpha} - \boldsymbol{\nabla} \cdot \boldsymbol{h}^{\alpha} + \boldsymbol{\sigma}^{\alpha} : \boldsymbol{D}^{\alpha} + \hat{e}^{\alpha}. \tag{3.31}$$

Equation (2.41) shows that only the term \hat{e}^{α} is added in the case of mixture. In analogy to the other balance laws, we demand that the balance of energy for the components is consistent with the balance of energy for the total mixture:

$$\sum_{\alpha=1}^{\nu} \left(\hat{e}^{\alpha} + \boldsymbol{u}^{\alpha} \cdot \hat{\boldsymbol{p}}^{\alpha} + \hat{c}^{\alpha} (\tilde{U}^{\alpha} + \frac{1}{2} \boldsymbol{u}^{\alpha} \cdot \boldsymbol{u}^{\alpha}) \right) = 0.$$
(3.32)

Notice that the velocities u^{α} , defined in (3.17), are found in this equation, i.e. the component velocities with respect to the mixture velocity.

3.4.2. The second law. The second law of thermodynamics, as formulated in (2.44), describes thermodynamic properties of a system. For a mixture it isn't clear how the system has to be defined: is the system formed by the total mixture or forms every component a system on its own? In the last case the entropy production per component has to be greater or equal to zero. In the first case this demand applies for the total mixture, and there can be components for which the entropy production is less than zero. We formulate the second law for the whole mixture as this is the only restriction which is agreed upon by the whole scientific community. Starting from (2.46), we postulate the *local form of the second law for the whole mixture*:

$$\sum_{\alpha=1}^{\nu} \left\{ \rho^{\alpha} \check{\tilde{S}}^{\alpha} - \frac{\rho^{\alpha} \check{r}^{\alpha}}{T^{\alpha}} + \boldsymbol{\nabla} \cdot (\frac{\boldsymbol{h}^{\alpha}}{T^{\alpha}}) + \hat{c}^{\alpha} \check{S}^{\alpha} \right\} \ge 0$$
(3.33)

in which \tilde{S}^{α} is the specific entropy of component α , and T^{α} is the temperature of component α . The term $\sum \hat{c}^{\alpha} \tilde{S}^{\alpha}$ discounts the interaction between the components again. If we eliminate the term $\rho^{\alpha} \tilde{r}^{\alpha}$ using the balance of energy per component (3.31) and eliminate the term $\sum \hat{e}^{\alpha}$ using the balance of energy for the total mixture (3.32), it follows that:

$$\sum_{\alpha=1}^{\nu} \left\{ \rho^{\alpha} \check{\tilde{S}}^{\alpha} - \frac{\rho^{\alpha} \check{\tilde{U}}^{\alpha}}{T^{\alpha}} + \frac{\boldsymbol{\sigma}^{\alpha} : \boldsymbol{D}^{\alpha}}{T^{\alpha}} - \frac{\hat{\boldsymbol{p}}^{\alpha} \cdot \boldsymbol{u}^{\alpha}}{T^{\alpha}} + \boldsymbol{h}^{\alpha} \cdot \boldsymbol{\nabla} \left(\frac{1}{T^{\alpha}} \right) - \frac{\hat{c}^{\alpha}}{T^{\alpha}} (\tilde{U}^{\alpha} + \frac{1}{2} \boldsymbol{u}^{\alpha} \cdot \boldsymbol{u}^{\alpha} + T^{\alpha} \tilde{S}^{\alpha}) \right\} \ge 0.$$

$$(3.34)$$

If we finally define the Helmholtz free energy per unit mass for component

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quantities	balance law for component (c) and mixture (m)	
mass	с	$\dot{\rho}^{\alpha} + \rho^{\alpha} \nabla \cdot \boldsymbol{v}^{\alpha} = \hat{c}^{\alpha},$
	m	$\sum \hat{c}^{lpha} = 0,$
momentum	с	$ ho^lpha \dot{v}^lpha = abla \cdot (\sigma^lpha)^{ m c} + ho^lpha q^lpha + \hat{p}^lpha,$
	m	$\sum (\hat{c}^{lpha} v^{lpha} + \hat{p}^{lpha}) = 0,$
moment of momentum	с	$\sigma^{lpha}-(\sigma^{lpha})^{ m c}=\hat{M}^{lpha},$
energy	с	$ ho \dot{ ilde{U}}^lpha = ho^lpha ilde{r}^lpha - oldsymbol{ abla} \cdot oldsymbol{h}^lpha + oldsymbol{\sigma}^lpha : oldsymbol{D}^lpha + \hat{e}^lpha,$
	m	$\sum \left\{ \hat{e}^{lpha} + oldsymbol{u}^{lpha} \cdot \hat{oldsymbol{p}}^{lpha} + \hat{c}^{lpha} (ilde{U}^{lpha} + rac{1}{2} oldsymbol{u}^{lpha} \cdot oldsymbol{u}^{lpha}) ight\} = 0,$
entropy	m	$\sum \left\{ \rho^{\alpha} \dot{\tilde{S}}^{\alpha} - \frac{\rho^{\alpha} \tilde{r}^{\alpha}}{T^{\alpha}} + \boldsymbol{\nabla} \cdot \left(\frac{\boldsymbol{h}^{\alpha}}{T^{\alpha}} \right) + \hat{c}^{\alpha} \tilde{S}^{\alpha} \right\} \geq 0.$

TABLE 4. Balance laws for mixtures.

 α as,

$$\tilde{F}^{\alpha} = \tilde{U}^{\alpha} - T^{\alpha} \tilde{S}^{\alpha}, \qquad (3.35)$$

we can tramsform (3.34) into:

$$\sum_{\alpha=1}^{\nu} \frac{1}{T^{\alpha}} \left\{ -\rho^{\alpha} (\dot{\tilde{F}}^{\alpha} - \tilde{S}^{\alpha} \dot{T}^{\alpha}) + \boldsymbol{\sigma}^{\alpha} : \boldsymbol{D}^{\alpha} + \hat{\boldsymbol{p}}^{\alpha} \cdot \boldsymbol{u}^{\alpha} - T^{\alpha} \boldsymbol{h}^{\alpha} \cdot \boldsymbol{\nabla} \left(\frac{1}{T^{\alpha}} \right) - \hat{c}^{\alpha} (\tilde{F}^{\alpha} + \frac{1}{2} \boldsymbol{u}^{\alpha} \cdot \boldsymbol{u}^{\alpha}) \right\} \ge 0.$$
(3.36)

3.5. Thermodynamic potentials

3.5.1. Partial quantities. The total mass of a mixture is equal to the sum of the masses of the components of which the mixture consists. The total volume V of the mixture is generally not equal to the sum of the component volumes:

$$V \neq \sum_{\alpha=1}^{\nu} V^{\alpha}.$$
 (3.37)

This is caused, because the interaction between molecules of the same constituent is generally different from that between molecules of different constituent. To account for the independence of mixture composition partial quantities are used. We define the partial molar volume \bar{V}^{α} of component α

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as:

$$\bar{V}^{\alpha} = \left(\frac{\partial V}{\partial n^{\alpha}}\right)_{p,T,n^{\beta},\beta\neq\alpha} \qquad \alpha = 1,\dots,\nu.$$
(3.38)

So, \bar{V}^{α} represents the increase of the volume of the mixture as a result of adding a little amount of component α , figured per mol of the added component. Furthermore, the thermodynamic state of the mixture, here characterized by p and T, has to stay constant, as well as the composition of the mixture. If \bar{V}^{α} is independent of the composition of the mixture, then integration of (3.38) yields:

$$V = \sum_{\alpha=1}^{\nu} n^{\alpha} \bar{V}^{\alpha}.$$
(3.39)

Generally, the partial volume of a component in the mixture is not equal to the molar volume of the pure component. If this is the case, we say the mixture is ideal.

3.5.2. Ideal media. Also for mixtures we can define potentials (Katchalsky and Curran, 1965). We will restrict ourselves to an ideal mixture of ν components, in which an amount n^{α} moles of every component α is present. In the former chapter it turned out that for an ideal medium the Gibbs free energy G is a function of the pressure p and the temperature T. In the mixture, G is also a function of the mixture composition:

$$G = G(T, p, n^1, \dots, n^{\nu}).$$
(3.40)

For variations dG the following differential applies:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n^{\alpha}}^{dT} + \left(\frac{\partial G}{\partial p}\right)_{T,n^{\alpha}}^{dp} + \sum_{\alpha=1}^{\nu} \left(\frac{\partial G}{\partial n^{\alpha}}\right)_{p,T,n^{\beta},\beta\neq\alpha}^{dn^{\alpha}}$$
(3.41)

We now define the partial molar Gibbs free energy \bar{G}^{α} of a component α in a mixture as:

$$\bar{G}^{\alpha} = \left(\frac{\partial G}{\partial n^{\alpha}}\right)_{p,T,n^{\beta},\beta\neq\alpha}$$
(3.42)

We can consider \bar{G}^{α} as an increase in free energy of the mixture if we add one mole of component α to that mixture. The partial molar Gibbs free energy is usually called the *chemical potential* μ^{α} :

$$\mu^{\alpha} = \bar{G}^{\alpha} = \left(\frac{\partial G}{\partial n^{\alpha}}\right)_{p,T,n^{\beta},\beta\neq\alpha}$$
(3.43)

Now (3.41) can be transformed to:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,n^{\alpha}}^{dT} + \left(\frac{\partial G}{\partial p}\right)_{T,n^{\alpha}}^{dp} + \sum_{\alpha=1}^{\nu} \mu^{\alpha} dn^{\alpha}.$$
 (3.44)

The part of the chemical potential in thermodynamics is comparable with that of the potential energy in mechanics. To illustrate this statement, let's consider a process - for a constant temperature and pressure - in which an amount dn^{α} of component α is converted from state A to state B. The variation dG in Gibbs free energy then reads:

$$dG = (\mu_{\rm B}^{\alpha} - \mu_{\rm A}^{\alpha})dn^{\alpha}. \tag{3.45}$$

According to (2.68) the convertion from A to B will initiate spontaneously if dG is negative, i.e. if $\mu_{\rm A}^{\alpha} > \mu_{\rm B}^{\alpha}$. If $\mu_{\rm A}^{\alpha} < \mu_{\rm B}^{\alpha}$, the process will go in the opposite direction. In equilibrium dG = 0 applies, such that $\mu_{\rm A}^{\alpha} = \mu_{\rm B}^{\alpha}$. The chemical potential therefore indicates in what direction the process will go. We will see in Chapter 5 that we can describe processes like osmosis well using the chemical potential.

3.5.3. Non-ideal media. For mixtures of ideal media we could characterize the state of stress per component with the total pressure of the mixture p and the mixture composition n^1, \ldots, n^{ν} (3.40), because these quantities fix the partial pressures p^{α} totally. For mixtures of non-ideal media the state of stress has to be described with a whole stress tensor σ^{α} , that cannot be derived unambiguously from the total mixture stress σ and the mixture composition. Therefore we have to make G explicitly dependent on all component stresses. Starting from (2.80) we characterize the state of stress per component with the second Piola-Kirchhoff stress tensor P^{α} .

For mixtures of ideal media, like gasses, it is in addition usual to express the amount of a component in moles, indicated with n^{α} . For non-ideal media it is sometimes more convenient to convert to masses m^{α} . The Gibbs free energy G for mixtures of non-ideal media can therefore be written as:

$$G = G(T, \mathbf{P}^{1}, \dots, \mathbf{P}^{\nu}, m^{1}, \dots, m^{\nu}).$$
(3.46)

For the variation of the Gibbs free energy after adding a small amount of component α , counted per unit mass, now applies:

$$\tilde{\mu}^{\alpha} = \left(\frac{\partial G}{\partial m^{\alpha}}\right)_{T,P^{1},\dots,P^{\nu},m^{\beta},\beta\neq\alpha}$$
(3.47)

We call $\tilde{\mu}^{\alpha}$ the specific chemical potential of component α .

Exercise

1. A petrochemical company wants to get insight in the state of stress of a formation around a well at 2 km depth. The formation is a mixture of mineral solid, water and oil. A finite-element mixture computation shows that the partial stresses of the water and oil (hydrostatic) are -2 MPa and -5 MPa. The volume fraction of water is 0.05 and that of oil 0.08. The responsible engineer wants to compare these values with the measured pressures. What is the predicted water pressure and oil pressure?

4. 2-component porous media

In this chapter we analyse a mixture of an incompressible liquid and an incompressible porous solid. This type of saturated porous medium is a good model for numerous types of soil mechanics problems and is therefore studied since many years in civil engineering. It can also be used in the field of biomechanics to model the coupling between fluid flow and mechanical loading in e.g. cartilage or skin. We will highlight this subject in a somewhat gradual fashion. The equations are first derived in the engineering style of Terzaghi for a simple one-dimensional infinitesimal strain case. This, together with a number of illustrating exercises, ensures that the reader first keeps his/her attention on the physics of the phenomenon. In a subsequent derivation we use the rigorous approach from the mixture theory for the case of three-dimensional finite deformation.

4.1. The concepts

4.1.1. Permeability. The French engineer Darcy initiated a number of experiments in the context of the design of fountains in the city of Dijon. These experiments aimed at quantifying the permeation of water through sand beds [7] (Darcy, 1856). In the experiments water saturated cylindrical sand samples were subjected to a constant pressure gradient. The flow through the specimens was measured for varying pressure difference, cross-sections and lengths of the specimens. (Fig. 7). These experiments showed that the flow is proportional to the pressure difference $p_1 - p_2$ and the cross-section A of the sample and inversely proportional to the length L of the sample:

$$Q = \frac{K(p_1 - p_2)A}{L}.$$
 (4.1)

The proportionality constant K is the *permeability*. Experiments showed that biological tissues comply with Darcy's law reasonably well (Maroudas, 1968,

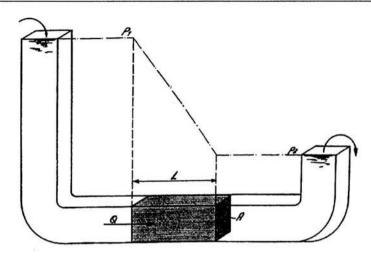


FIGURE 7. Darcy's experiment

1979) when the fluid is a physiological salt solution. In soil mechanics Darcy's law has been shown valid for sand and coarse lime. For clays a conclusive experiment has never been done. When different Newtonian fluids are used in the same sand samples, the permeability of the sample has been shown to be inversely proportional to the viscosity of the fluid. The permeability depends on the size and the structure of the pores of the sample also. If the sample is compressed, the permeability drops. Different relationships between permeability and fluid volume fraction are proposed in the literature. In very deformable porous media, like soft biological tissues, only the viscous forces of the flowing liquid are sufficient to cause compression of the porous medium and thus a reduction of the permeability.

4.1.2. Effective stress. Consider a mixture of an incompressible solid and an incompressible liquid (Fig. 8). We assume that the solid is composed of grains – to focus the attention and without loss of generality. The dimensions of the grains and the pores between the grains are small relative to the macroscopic dimensions of the material. Every grain is subject to two types of external load: (1) the liquid pressure (2) the contact forces with neighbouring grains. The liquid pressure is an isotropic load which cannot result into deformation of the grains as they are incompressible. Only the contact forces with neighbouring grains result in a stress field in the grains and thus deformation of the solid skeleton. The latter stress field, averaged over a large number of grains and measured per unit mixture surface is the effective stress. The effective stress in a mixture of an incompressible solid

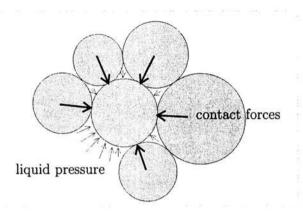


FIGURE 8. The mechanical stress in a fluid solid mixture.

and an incompressible liquid is that part of the stress that causes deformation. The total stress σ is given by the sum of the effective stress σ_e and the hydrostatic pressure -pI:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}_{\mathbf{e}} - p\boldsymbol{I}.\tag{4.2}$$

In this example we assumed that only the pressure of the liquid contributes to the total stress. In principle every component – and therefore also the liquid component – can contribute to the effective stress in a mixture. Therefore it is wrong to consider (4.2) a division of the stress in an effective stress caused by the solid and a pressure caused by the liquid. In general both components contribute to both terms. In soil and rock mechanics, the fields from which the effective stress concept originates, the effective stress is often called the grain stress, because for lots of soil mixtures contribution of the liquid to the the effective stress is negligible.

In the former chapter we saw that in the more recent theory of mixtures, it is common practise to subdivide the total stress in a mixture in partial stresses, in analogy to the much older concept of partial pressure from the kinetic theory of gasses. These partial stresses can be associated with every individual component. For the porous medium this means:

$$\boldsymbol{\sigma} = \boldsymbol{\sigma}^{\mathrm{s}} + \boldsymbol{\sigma}^{\mathrm{f}}.\tag{4.3}$$

The stress-strain relation becomes a relation between the effective stress and the pressure in a porous medium. Notice that in force equilibrium the total stress appears.

4.2. Theory of consolidation of Terzaghi

During this presentation of porous media mechanics the historical development will be followed, because that is the easiest way to comprehend it.

One of the major enemies of civil engineering is the phenomenon consolidation. After constructing a big building or a bridge the foundation of the construction appears to sink several inches into the ground. As long as this sinking is distributed homogeneously over the total area of the foundation consequences are not yet disastrous. If there is differential sinking, the consequences can be catastrophic. Cracks in the construction, leakage in case of a dam or pulling a building out of position (tower of Pisa). Consolidation can usually be attributed to the construction pushing the fluid beneath the foundation aside. Therefore, this problem can only be studied with porous media mechanics.

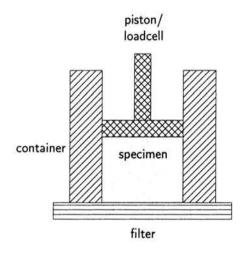


FIGURE 9. Setup for a one-dimensional consolidation test.

The problem of consolidation has been studied by Terzaghi in the nineteen twenties. Terzaghi restricted himself to a one-dimensional consolidation, in which the liquid flow and the displacement of the solid occur in only one direction. This situation is reasonable for a very wide foundation plate where the sideward outflow of fluid is only a local boundary effect. We can create this situation on purpose in a one-dimensional consolidation experiment (Fig. 9), which is often used to study cartilage.

In this experiment a cylindrical specimen is placed in a fitting rigid cylinder. The bottom of the specimen has contact with a porous filter in which the permeability is much higher than the permeability in the specimen itself. The top of the cylinder has contact with an impermeable piston with surface area A, that is loaded with an axial force F. For an incremental increase of the force F, this force will first be intercepted by the hydrostatic pressure (4.2), because no deformation of the solid has taken place yet:

$$p = \frac{F}{A},$$
 $0 < z < h, \quad t = 0^+.$ (4.4)

At z = 0 a steep pressure gradient appears that causes the liquid to flow out of the specimen. This outflow of liquid results in a smooth downward motion of the piston. The deformation of the sample causes an effective stress within the sample that gradually will take over the load from the hydrostatic pressure.

We now consider Terzaghi's way to derive the equations that describe this process. We restrict ourselves to small deformations.

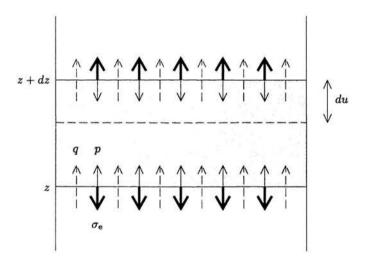


FIGURE 10. One-dimensional consolidation of a porous medium.

Consider a layer [z, z+dz] of a one-dimensional medium that is subjected to consolidation. The medium consists of a porous, incompressible, elastic solid saturated with an incompressible fluid. Similarly to (4.1) we subdivide the total stress σ in a hydrostatic pressure p, present in the liquid + solid (pressure positive, see Fig. 8) and an elastic stress caused by deformation $\sigma_{\rm e}$,

measured per unit surface area (extension positive). The liquid flux per unit mixture area is indicated with a q (z-direction positive). If we neglect the forces of inertia and the volume forces, we can write the balance of momentum as:

$$\sigma_{\rm e}(z+dz) - \sigma_{\rm e}(z) - p(z+dz) + p(z) = 0. \tag{4.5}$$

After dividing by dz, we find:

$$\frac{\partial \sigma_{\rm e}}{\partial z} - \frac{\partial p}{\partial z} = 0. \tag{4.6}$$

Because of incompressibility the balance of mass reduces to the balance of volume:

$$du(t+dt) - du(t) - q(z)dt + q(z+dz)dt = 0.$$
 (4.7)

After division by dzdt, we find:

$$\frac{D^s}{Dt}\left(\frac{\partial u}{\partial z}\right) + \frac{\partial q}{\partial z} = 0. \tag{4.8}$$

In addition to the balance laws we need two constitutive equations. The first is the Darcy equation :

$$q = -K\frac{\partial p}{\partial z} \tag{4.9}$$

in which we consider the permeability K a constant. Substitution of (4.9) into (4.8) yields:

$$\frac{D^s}{Dt}\left(\frac{\partial u}{\partial z}\right) - \frac{\partial}{\partial z}K\frac{\partial p}{\partial z} = 0.$$
(4.10)

The second constitutive relation is the law of Hooke:

$$\sigma_{\rm e} = H \frac{\partial u}{\partial z} \tag{4.11}$$

in which H is the compressive modulus. We consider H a constant, i.e. linear elasticity. The compressive modulus is related to the modulus of elasticity, E, and Poisson's ratio, ν , for an isotropic medium:

$$H = E \frac{1 - \nu}{(1 + \nu)(1 - 2\nu)}.$$
(4.12)

The equations (4.6), (4.8), (4.9) and (4.11) form a complete set of partial differential equations (check this!). Integration of Eq. (4.6) yields:

$$\sigma(z,t) - p(z,t) = -p_0(t), \qquad (4.13)$$

with $p_0(t)$ the top load. For a classical consolidation test the top load is a step function. After applying this step the function is constant in time, so:

$$\frac{D^s \sigma_{\rm e}}{Dt} - \frac{D^s p}{Dt} = 0 \quad \text{for} \quad t > t_0.$$
(4.14)

Substitution of (4.11) into (4.14), yields

$$H\frac{D^s}{Dt}\left(\frac{\partial u}{\partial z}\right) - \frac{D^s p}{Dt} = 0 \quad \text{for} \quad t > t_0.$$
(4.15)

Substitution of (4.15) and (4.9) into (4.8) yields the consolidation equation of Terzaghi:

$$\frac{D^s p}{Dt} - KH \frac{\partial^2 p}{\partial z^2} = 0.$$
(4.16)

Notice the analogy with the diffusion equation. The characteristic time that is needed to start the consolidation process of a porous layer with thickness Δz , permeability K and compressive modulus H, follows from (4.16):

$$\frac{\Delta p}{\Delta t} = KH \frac{\Delta p}{(\Delta z)^2} \tag{4.17}$$

or:

$$\Delta t = \frac{(\Delta z)^2}{KH}.\tag{4.18}$$

The consolidation time t is therefore inversely proportional to the permeability K and the stiffness H, and proportional to the square of the thickness of the layer Δz . The analytical solution for the consolidation Eq. (4.13) for a specimen with thickness h holds:

$$P = \sum_{n=0}^{\infty} \frac{2}{M} \sin M Z e^{-M^2 T},$$
(4.19)

with

$$P = \frac{p}{p_0},\tag{4.20}$$

$$M = \frac{\pi}{2}(2n+1), \tag{4.21}$$

$$Z = \frac{z}{h}, \tag{4.22}$$

$$T = \frac{KHt}{h^2}.$$
 (4.23)

Notice that for T > 1 the consolidation process of the specimen is largely completed (Fig. 11).

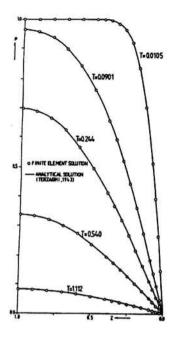


FIGURE 11. Dimensionless pressure P versus dimensionless position Z at different times during linear, one-dimensional consolidation.

4.3. Mixture description of saturated porous media

We shall derive equations applicable to the behaviour of elastic incompressible fluid saturated porous media from mixture theory.

4.3.1. Assumptions. We consider the porous medium as a two-component mixture, composed of a solid (superscript s) and a fluid component (superscript f). We can rewrite Eq. (3.4) as:

$$\phi^{\mathrm{s}} + \phi^{\mathrm{f}} = 1. \tag{4.24}$$

Equation (4.24) is the saturation condition. We assume that no mass-exchange occurs between the components. Each component is assumed incompressible:

$$\rho_i^{\alpha} = \frac{\rho^{\alpha}}{\phi^{\alpha}} = \text{constant} \qquad \alpha = \text{s, f.}$$
(4.25)

The apparent densities ρ^{α} however do change as a function of time. We consider processes which are sufficiently slow so as to ensure that inertia forces are negligible. Volume forces are neglected as well. We assume that all

components have the same temperature and no gradients in temperature are present either in time or space.

4.3.2. Conservation laws.

Conservation of mass. In the absence of mass exchange the local law of conservation of mass (3.20) of component α reduces to:

$$\frac{\partial \rho^{\alpha}}{\partial t} + \boldsymbol{\nabla} \cdot (\rho^{\alpha} \boldsymbol{v}^{\alpha}) = 0 \qquad \alpha = \mathrm{s}, \ \mathrm{f}.$$
(4.26)

Using (3.5) and (4.25) we can rewrite (4.26):

$$\frac{\partial \phi^{\alpha}}{\partial t} + \boldsymbol{\nabla} \cdot (\phi^{\alpha} \boldsymbol{v}^{\alpha}) = 0 \qquad \alpha = \mathrm{s}, \ \mathrm{f}.$$
(4.27)

Summation of Eq. (4.27) yields the local mass balance of the mixture:

$$\boldsymbol{\nabla} \cdot (\phi^{\mathrm{s}} \boldsymbol{v}^{\mathrm{s}}) + \boldsymbol{\nabla} \cdot (\phi^{\mathrm{f}} \boldsymbol{v}^{\mathrm{f}}) = 0$$
(4.28)

or:

$$\boldsymbol{\nabla} \cdot \boldsymbol{v}^{\mathrm{s}} + \boldsymbol{\nabla} \cdot \left(\phi^{\mathrm{f}}(\boldsymbol{v}^{\mathrm{f}} - \boldsymbol{v}^{\mathrm{s}}) \right) = 0.$$
(4.29)

The first term of (4.29) represents the rate of volume increase of a unit volume of mixture. The second term represents the fluid flux from this unit volume. Equation (4.29) states that every volume-increase or decrease of the mixture is associated with an equal inflow or outflow of liquid. At this point it is useful to refer current descriptors of the mixture with respect to an initial state of the porous solid. As is usual in continuum mechanics, we define the deformation gradient tensor F mapping an infinitesimal material line segment in the initial state onto the corresponding infinitesimal line segment in the current state. The relative volume change from the initial to the current state is the determinant of the deformation gradient tensor $J = \det F$. If we introduce volume fractions

$$\Phi^{\alpha} = J\phi^{\alpha},\tag{4.30}$$

per unit initial volume, we can rewrite the mass balance Eq. (4.27) as follows:

$$\frac{D^{\mathbf{s}}\Phi^{\alpha}}{Dt} + J\boldsymbol{\nabla} \cdot [\phi^{\alpha}(\boldsymbol{v}^{\alpha} - \boldsymbol{v}^{\mathbf{s}})] = 0, \qquad (4.31)$$

when using the identity (2.15):

$$\frac{D^{\mathbf{s}}}{Dt}J = J\boldsymbol{\nabla}\cdot\boldsymbol{v}^{\mathbf{s}}.\tag{4.32}$$

Conservation of momentum. Considering the assumptions stated earlier, momentum balance (3.25) reduces to:

$$\boldsymbol{\nabla} \cdot (\boldsymbol{\sigma}^{\alpha})^{c} + \hat{\boldsymbol{p}}^{\alpha} = \boldsymbol{0} \qquad \alpha = s, \text{ f.}$$
(4.33)

The momentum interaction \hat{p}^{α} arises e.g., as a consequence of friction between the fluid and the solid. We assume no moment of momentum interaction between fluid and solid. Therefore we tacitly assume the symmetry of the partial Cauchy stress tensor in (4.33). Summation of the Eq. (4.33) yields the local momentum balance for the mixture as a whole:

$$\boldsymbol{\nabla} \cdot \boldsymbol{\sigma}^{\mathrm{s}} + \boldsymbol{\nabla} \cdot \boldsymbol{\sigma}^{\mathrm{f}} = \boldsymbol{\nabla} \cdot \boldsymbol{\sigma} = \boldsymbol{0}, \qquad (4.34)$$

provided that:

$$\hat{\boldsymbol{p}}^{\mathrm{s}} + \hat{\boldsymbol{p}}^{\mathrm{f}} = \boldsymbol{0}. \tag{4.35}$$

The entropy inequality. The local form of the entropy inequality (3.36) applied to the mixture as a whole, reduces to:

$$\sum_{\alpha=s, f} \left(-\rho^{\alpha} \check{\tilde{F}}^{\alpha} + \sigma^{\alpha} : D^{\alpha} - \hat{p}^{\alpha} \cdot u^{\alpha} \right) \ge 0.$$
(4.36)

We introduce the strain energy function

$$W = J \sum_{\alpha=s,f} \rho^{\alpha} \tilde{F}^{\alpha} = J \sum_{\alpha=s,f} \psi^{\alpha}, \qquad (4.37)$$

as the Helmholtz free energy of a mixture volume which in the *initial* state of the solid equals unity. ψ^{α} is the Helmholz free energy of constituent α per unit mixture volume. Rewriting the inequality (4.36) for the entropy production per initial mixture volume – i.e. we multiply inequality (4.36) by the relative volume change J - we find:

$$-\frac{D^{s}}{Dt}W + J\boldsymbol{\sigma}: \boldsymbol{\nabla}\boldsymbol{v}^{s} + J\boldsymbol{\nabla}\cdot [(\boldsymbol{v}^{f} - \boldsymbol{v}^{s})\cdot\boldsymbol{\sigma}^{f} - (\boldsymbol{v}^{f} - \boldsymbol{v}^{s})\psi^{f}] \ge 0.$$
(4.38)

4.3.3. Constitutive restrictions. Similarly to Section 2.5, we use the entropy inequality to derive constitutive restrictions for the mixture. The entropy inequality should hold for an arbitrary state of the mixture, complying with the balance laws and with incompressibility. There are two ways to comply with these restrictions. One is substitution of the restriction into the inequality, resulting in elimination of a field variable. The other is by introduction of a Lagrange multiplier. The mass balance of the mixture (4.29) is

accounted for by means of a Lagrange multiplier. Other balance laws and the incompressibility conditions (4.25) are accounted for by means of substitution. From the inequality 4.38 we see that the apparent density and the momentum interaction \hat{p}^{α} is already eliminated from the inequality. In other words the conditions of incompressibility and the momentum balance of the constituents have already been substituted into the second law. The divergence of the partial stress tensor of the solid $\nabla \cdot \sigma^s$ and the heat supplies r^{α} also are absent in (4.38). Thus the momentum balance of the mixture and the energy balance have already been substituted in the second law. Therefore, restrictions still to be fulfilled are the mass balances of the constituents (4.26) and mass balance of the mixture (4.29). The latter is substituted by means of the Lagrange multiplier p:

$$-\frac{D^{s}}{Dt}W + J\boldsymbol{\sigma}_{e}: \boldsymbol{\nabla}\boldsymbol{v}^{s}$$

+ $J[\boldsymbol{\sigma}^{f} + (p\boldsymbol{\phi}^{f} - \boldsymbol{\psi}^{f})\boldsymbol{I}]: \boldsymbol{\nabla}(\boldsymbol{v}^{f} - \boldsymbol{v}^{s})$ (4.39)
+ $J(\boldsymbol{v}^{f} - \boldsymbol{v}^{s}) \cdot (-\boldsymbol{\nabla}\boldsymbol{\psi}^{f} + p\boldsymbol{\nabla}\boldsymbol{\phi}^{f} + \boldsymbol{\nabla}\cdot\boldsymbol{\sigma}^{f}) \geq 0,$

in which the effective stress $\sigma_{\rm e}$ is defined as

$$\boldsymbol{\sigma}_{\mathbf{e}} = \boldsymbol{\sigma} + p\boldsymbol{I}.\tag{4.40}$$

Choice of independent and dependent variables. We choose as dependent variables the dynamic variables appearing in inequality (4.39): W, $\psi^{\rm f}, \sigma_{\rm e}, \sigma^{\rm f} + p\phi^{\rm f}I, \nabla \cdot \sigma^{\rm f} + p\nabla\phi^{\rm f}$. Their number should be equal to the number of unknown variables appearing in the balance equations minus the number of balance equations. The number of dependent variables should be as small as possible to describe the state of the tissue well. Their choice is a key assumption of the continuum theory and is based on insight in the physical phenomena involved in the behaviour of the material. If the dependent variables include only variables describing the local state of the tissue (e.g. E), the theory is a local theory. If the dependent variables include variables describing the state of the tissue some distance away from the point of consideration (e.g. ∇E), the theory is a non-local theory. Throughout this book we consider only local dependent variables. We choose as independent variables the kinematic variables: the Green strain of the solid E^{s} , the fluid volume fraction Φ^{f} and the fluid velocity relative to the solid $v^{f} - v^{s}$. For reasons of objectivity we need to transform all the vectors and tensors among the dependent and independent variables back to the initial state. This yields

for the constitutive relationships:

$$W = W(\boldsymbol{E}^{s}, \Phi^{f}, \boldsymbol{v}^{ts}),$$

$$\psi^{f} = \psi^{f}(\boldsymbol{E}^{s}, \Phi^{f}, \boldsymbol{v}^{fs}),$$

$$\boldsymbol{\sigma}_{e} = \boldsymbol{F} \cdot \boldsymbol{S}_{e}(\boldsymbol{E}^{s}, \Phi^{f}, \boldsymbol{v}^{fs}) \cdot \boldsymbol{F}^{c},$$

$$\boldsymbol{\sigma}^{f} - \phi^{f} \boldsymbol{p} \boldsymbol{I} = \boldsymbol{F} \cdot \boldsymbol{S}^{f}(\boldsymbol{E}^{s}, \Phi^{f}, \boldsymbol{v}^{fs}) \cdot \boldsymbol{F}^{c},$$

$$\hat{\boldsymbol{p}}^{f} - \boldsymbol{p} \nabla \phi^{f} = \boldsymbol{F} \cdot \hat{\boldsymbol{P}}^{f}(\boldsymbol{E}^{s}, \Phi^{f}, \boldsymbol{v}^{fs}),$$

(4.41)

with

$$\boldsymbol{v}^{\rm fs} = \boldsymbol{F}^{-1} \cdot (\boldsymbol{v}^{\rm f} - \boldsymbol{v}^{\rm s}). \tag{4.42}$$

The principle of equipresence requires that all dependent variables appear in each of the constitutive relationships. The choice of independent variables is of primal importance for the form of the constitutive relationships that are derived. For instance, including for the solid the Green strain only and no measure of strain rate, implies elasticity of the solid. In mixture mechanics it is also important to realise that each of the variables is an averaged value of a physical quantity over an averaging volume. It may seem surprising that the shear rate of the fluid is not included in the list of independent variables, although the viscosity of the fluid is absolutely essential for the behaviour of the mixture. The reason for this is that in a porous medium the shear rate at one side of the pore has a sign opposite to the shear rate at the other side of the pore. The expectation value of the shear rate in a representative elementary volume is therefore the shear rate of the solid, i.e. a generally very low value, not representative for the dissipation in the fluid. It is therefore more obvious to use the fluid velocity relative to the solid as a macroscopic measure of the microvalues of the shear rate. The fluid volume fraction Φ^{f} is not independent of the Green strain because of incompressibility:

$$\Phi^{\rm f} = \det \mathbf{F} - 1 + \phi_0^{\rm f} = \sqrt{\det(2\mathbf{E}^{\rm s} + \mathbf{I})} - 1 + \phi_0^{\rm f}.$$
(4.43)

Because of the strong non-linearity of Eq. (4.43), elimination of one of the variables is tedious. In fact, the way we deal with the interdependence of these two variables is by means of the Lagrange multiplier p. The condition (4.29) is in fact a differentiated form of Eq. (4.43). This justifies the use of E^{s} and Φ^{f} as independent variables.

Constitutive relationships. Applying the chain rule for time differentiation of W:

$$\frac{D^{\mathbf{s}}W}{Dt} = \frac{\partial W}{\partial \boldsymbol{E}^{\mathbf{s}}} : \frac{D^{\mathbf{s}}\boldsymbol{E}^{\mathbf{s}}}{Dt} + \frac{\partial W}{\partial \Phi^{\mathbf{f}}}\frac{D^{\mathbf{s}}\Phi^{\mathbf{f}}}{Dt} + \frac{\partial W}{\partial \boldsymbol{v}^{\mathbf{fs}}}$$
(4.44)

and substituting the mass balance of the constituents (4.31) for the elimination of $\frac{D^{s}\Phi^{f}}{Dt}$ from inequality (4.39)we get

$$(J\boldsymbol{\sigma}_{e} - \boldsymbol{F} \cdot \frac{\partial W}{\partial \boldsymbol{E}} \cdot \boldsymbol{F}^{c}) : \boldsymbol{\nabla}\boldsymbol{v}^{s} + \frac{\partial W}{\partial \boldsymbol{v}^{fs}} \cdot \frac{D^{s}}{Dt} \boldsymbol{v}^{fs}$$
$$+ J[\boldsymbol{\sigma}^{f} + (\mu^{f}\boldsymbol{\phi}^{f} - \psi^{f})\boldsymbol{I}] : \boldsymbol{\nabla}(\boldsymbol{v}^{f} - \boldsymbol{v}^{s})$$
$$+ J(\boldsymbol{v}^{f} - \boldsymbol{v}^{s}) \cdot (-\boldsymbol{\nabla}\psi^{f} + \mu^{f}\boldsymbol{\nabla}\boldsymbol{\phi}^{f} + \boldsymbol{\nabla} \cdot \boldsymbol{\sigma}^{f}) \ge 0$$
(4.45)

in which μ^{f} is the chemical potential of the fluid:

$$\mu^{\rm f} = \frac{\partial W}{\partial \Phi^{\rm f}} + p. \tag{4.46}$$

Inequality (4.45) should be true for any value of the state variables. Close inspection of the choice of independent variables and inequality (4.45), reveals that the first term of (4.45) is linear in the solid velocity gradient ∇v^s , the second term linear in $\frac{D^s}{Dt}v^{fs}$ and the third term linear in the relative velocity gradients $\nabla (v^f - v^s)$. Therefore, by a standard argument, we find:

$$\boldsymbol{\sigma}_{\mathrm{e}} = \frac{1}{J} \boldsymbol{F} \cdot \frac{\partial W}{\partial \boldsymbol{E}} \cdot \boldsymbol{F}^{\mathrm{c}}, \qquad (4.47)$$

$$\frac{\partial W}{\partial \boldsymbol{v}^{\rm fs}} = \boldsymbol{0},\tag{4.48}$$

$$\boldsymbol{\sigma}^{\mathrm{f}} = (\psi^{\mathrm{f}} - \mu^{\mathrm{f}} \phi^{\mathrm{f}}) \boldsymbol{I}, \qquad (4.49)$$

leaving as inequality:

$$J(\boldsymbol{v}^{\mathrm{f}} - \boldsymbol{v}^{\mathrm{s}}) \cdot (-\boldsymbol{\nabla}\psi^{\mathrm{f}} + \boldsymbol{\mu}^{\mathrm{f}}\boldsymbol{\nabla}\phi^{\mathrm{f}} + \boldsymbol{\nabla}\cdot\boldsymbol{\sigma}^{\mathrm{f}}) \ge 0.$$
(4.50)

Equation (4.47) indicates that the effective stress of the mixture can be derived from a strain energy function W which represents the free energy of the mixture. Equation (4.48) shows that the strain energy function cannot depend on the relative velocity of fluid versus solid. Thus, the effective stress of a biphasic medium can be derived from a regular strain energy function, which physically has the same meaning as in single phase media. According to Eq. (4.49) the partial stress of the fluid and the ions are scalars. Transforming the relative velocities to their Lagrangian equivalents, we find instead of (4.50):

$$\boldsymbol{v}^{\mathrm{fs}} \cdot \left[-\boldsymbol{\nabla}_{0} \boldsymbol{\psi}^{\mathrm{f}} + \boldsymbol{\mu}^{f} \boldsymbol{\nabla}_{0} \boldsymbol{\phi}^{\mathrm{f}} + \boldsymbol{\nabla}_{0} \cdot \boldsymbol{\sigma}^{\mathrm{f}} \right] \ge 0$$

$$(4.51)$$

in which $\nabla_0 = F^c \cdot \nabla$ is the gradient operator with respect to the initial configuration. Note that since $\mu^f \nabla_0 \phi^f + \nabla_0 \cdot \sigma^f$ depends on v^{fs} according

to the constituive relationships (4.41), the l.h.s. of inequality (4.51) is not a linear function of $\boldsymbol{v}^{\rm fs}$ and therefore it is incorrect to equate the factor $-\boldsymbol{\nabla}_0 \boldsymbol{\psi}^{\rm f} + \boldsymbol{\mu}^f \boldsymbol{\nabla}_0 \boldsymbol{\phi}^{\rm f} + \boldsymbol{\nabla}_0 \cdot \boldsymbol{\sigma}^{\rm f}$ to zero. From a physical point of view it is obvious that unlike the elastic deformation of the solid the flow of fluid relative the solid results in an entropy production. If we assume that the system is not too far from equilibrium, we can express the dissipation (4.51) associated with relative flow of fluid and ions as a quadratic function of the relative velocity:

$$-\boldsymbol{\nabla}_{0}\boldsymbol{\psi}^{\mathrm{f}} + \boldsymbol{\mu}^{\mathrm{f}}\boldsymbol{\nabla}_{0}\boldsymbol{\phi}^{\mathrm{f}} + \boldsymbol{\nabla}_{0}\cdot\boldsymbol{\sigma}^{\mathrm{f}} = \boldsymbol{B}\cdot\boldsymbol{v}^{\mathrm{fs}}.$$
(4.52)

Here B is a semi-positive definite matrix of frictional coefficients. Substituting Eq. (4.49) into Eq. (4.52) yields the Lagrangian form of Darcy's law:

$$-\phi^{\mathbf{f}} \boldsymbol{\nabla}_{0} \boldsymbol{\mu}^{\mathbf{f}} = \boldsymbol{B} \cdot \boldsymbol{v}^{\mathbf{fs}}.$$
(4.53)

The constitutive behaviour of the fluid-solid mixture is thus described by a strain energy function W and frictional tensor B. From the strain energy function we derive both the effective stress and the chemical potential of the fluid.

4.3.4. Physical interpretation of the constitutive variables. Comparing Eq. (4.40) with Eq. (4.2) reveals that the Lagrange multiplier p should be interpreted as the hydrostatic pressure in fluid.

$$\boldsymbol{\nabla} \cdot \boldsymbol{\sigma}_{\mathbf{e}} - \boldsymbol{\nabla} p = \mathbf{0}. \tag{4.54}$$

If we define the permeability tensor K as:

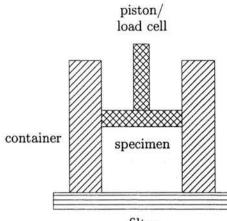
$$K = (\phi^{\rm f})^2 B^{-1}. \tag{4.55}$$

Equation (4.53) becomes:

$$\phi^{\rm f}(\boldsymbol{v}^{\rm f} - \boldsymbol{v}^{\rm s}) = -\boldsymbol{K} \cdot \boldsymbol{\nabla}(p + \frac{\partial W}{\partial \Phi^{\rm f}}). \tag{4.56}$$

Equation (4.56) is the three-dimensional form of Darcy's law (4.9). The difference between the chemical potential $\mu^{\rm f}$ and the pressure p is the matric potential. The matric potential accounts for adsorption and capillary forces. It can be quantified experimentally using capillary rising heights (Fig. 12). In Terzaghi's consolidation theory the matric potential is neglected, not because it is negligible in absolute terms but because its gradient is negligible in an homogenous medium with limited variation of fluid volume fraction and coarse pore structure.

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FIGURE 12. Matric potential as a function of fluid volume fraction ϕ^{f} for different materials: clay minerals – montmorillonite, illite and kaolinite – and stratum corneum

4.3.5. Resulting equations. The resulting equations are: Momentum balance of the mixture:

$$\boldsymbol{\nabla} \cdot \boldsymbol{\sigma}_{\mathrm{e}} - \boldsymbol{\nabla} p = \boldsymbol{0}. \tag{4.57}$$

Mass balance of the mixture:

$$\boldsymbol{\nabla} \cdot \boldsymbol{v}^{\mathrm{s}} - \boldsymbol{\nabla} \cdot (\phi^{\mathrm{f}}(\boldsymbol{v}^{\mathrm{f}} - \boldsymbol{v}^{\mathrm{s}})) = 0.$$
(4.58)

Darcy's law:

$$\boldsymbol{v}^{\mathrm{f}} - \boldsymbol{v}^{\mathrm{s}} = \boldsymbol{\phi}^{\mathrm{f}} \boldsymbol{B}^{-1} \cdot \boldsymbol{\nabla} \boldsymbol{\mu}^{\mathrm{f}}.$$
(4.59)

Stress-strain relationship:

$$\boldsymbol{\sigma}_{\mathbf{e}} = (\det \boldsymbol{F})^{-1} \boldsymbol{F} \cdot \frac{\partial W}{\partial \boldsymbol{E}^{\mathbf{s}}} \cdot \boldsymbol{F}^{\mathbf{c}}.$$
(4.60)

Constitutive law for the chemical potential of the fluid:

$$\mu^{\mathbf{f}} = p + \frac{\partial W}{\partial \Phi^{\mathbf{f}}}.\tag{4.61}$$

The total stress in the mixture is composed of the effective stress and the hydrodynamic pressure: $\sigma = \sigma_e - pI$. The effective stress σ_e is derived from the strain energy function of the mixture W. In Eq. (4.60) F is the deformation gradient tensor of the solid and E^s the Green strain tensor of

the solid. The strain energy W is a function of the solid strain E. In onedimensional space Eq. (4.57) reduces to Eq. (4.6) from Terzaghi's confined compression theory.

Dynamic boundary conditions are:

$$[(\boldsymbol{\sigma}_{\rm e} - p\boldsymbol{I}) \cdot \boldsymbol{n}] = \boldsymbol{0}, \qquad (4.62)$$

with n the outer normal along the boundary and the square brackets represent the difference between the value at either side of the boundary;

$$[\overline{V}^{\mathrm{f}}\mu^{\mathrm{f}}] = 0, \qquad (4.63)$$

with as a special case represented by the evaporation boundary condition:

$$\overline{V}^{\rm f}\mu^{\rm f} = RT \ln \frac{p^{\rm d}}{p^{\rm d}_{\rm s}}.$$
(4.64)

Equations (4.63) and (4.64) enforce continuity of molar chemical potential. Discontinuity of chemical potential would lead to an infinite fluid flux which is physically impossible. For this reason we claim that even if the material properties are sharply discontinuous the chemical potential should be continuous. This is not true for the pressure p. For instance, at the interface between a sand layer and a clay layer the pressure is not continuous, at least if capillary effects are not neglected. Similarly interstititial pressure along the surface of the skin is not equal to atmospheric pressure. We use the molar chemical potential instead of the volumetric chemical potential because the volumetric chemical potential can be used only for incompressible media. Although the medium we consider is incompressible, the medium outside the boundary need not be incompressible as is the case for evaporation. Kinematic boundary conditions are:

$$[\boldsymbol{u}] = \boldsymbol{0},\tag{4.65}$$

$$[(\boldsymbol{v}^{\mathrm{f}} - \boldsymbol{v}^{\mathrm{s}}) \cdot \boldsymbol{n}] = 0. \tag{4.66}$$

4.4. Conclusion

We derived the equations, that describe the behaviour of a porous medium, in two different ways. The traditional approach of Terzaghi has the advantage that we know the physical meaning of the parameters from the start. Its a disadvantage is that we have insufficient insight in to the assumptions that we – often unconsciously – accept. For example, it appears from comparison of the resulting equations with mixture theory equations that we neglected the capillary forces.

In the second approach, using the theory of mixtures, all effects are taken into account, and simplifications have to be done explicitly. It is done by neglecting specific terms in the balance laws or by the choice of the independent variables. This approach is also suitable for generalisation to mixtures with more components. A disadvantage of this approach is the complexity of the derivation.

Exercises

- 1. Cartilage is a porous solid with a volume fraction of 80%. Suppose that the Darcy-flow or specific liquid velocity, Q, perpendicular to the lubrication surface measures $500 \,\mu$ m/s. What is the average velocity of the liquid particles perpendicular to the lubrication surface?
- 2. Suppose that in cartilage the highest effective normal tensile stress is 0.3 MPa, while the liquid pressure is of the order of 0.2 MPa. From literature it turns out that ca 90% of the effective stress is born by the collagen. The remaining 10% is intercepted by the macromolecular network of proteoglycans. 15% of the volume of cartilage is collagen. Estimate the actual stress in the collagen fibers in that normal stress direction.
- 3. During walking the fluid is squeezed in and out of the cartilage in the vicinity of the contact face of the femur condyle and the tibia plateau by the periodic loading (frequency ca 0.5 Hz). From consolidation tests it turns out that the permeability of the cartilage is of the order of 10^{-16} m⁴/N s and the stiffness of order 0.5 MPa. Estimate the depth over which this process of in and outflow of fluid takes place.
- 4. The permeability of clay is of the order of $10^{-16} \text{ m}^4/\text{N}$ s. The porosity of clay is 20 to 50%. The stiffness is hard to estimate, because it is not an elastic material. Suppose that the Young's modulus is of the order of 100 MPa. Show that the stiffness of a layer of clay (thickness = 6 m), estimated from the force-displacement relation measured during driving a foundation pile, is not a measure for the supporting ability of the pile over a longer period of time.
- 5. A rectangular piece of tissue is tested on material properties in a cosmetic research lab. Because the material shows time dependent behaviour and there is a strong suspicion that it is correlated to the squeezing and suction of water, a biphasic model (incompressible liquid and solid; stress-free situation before the test) is assumed for the interpretation of the data. The strips (thickness 1 mm) are submersed in a physiological solution (p = 0) and subjected to an incremental increase of the axial strain from 0 up to 4%. The stress decreases gradually to 0.4 kPa. The average thickness of the specimen has first lowered to 0.98 mm after

which it has lifted to 0.986 mm. In the third dimension one finds a comparable progress of the transverse contraction. Matric potential can be neglected. Assume linear isotropic elasticity and estimate the Young's modulus and the Poisson's ratio of the biphasic model. What should the liquid pressure in the specimen be after applying the load, if the assumption of linear, isotropic elasticity is right? What is the momentary increase in stress in the loading direction, immediately after application of the load?

 Show that the derivation above reduces to Terzaghi's theory in the onedimensional case if small deformations, linear isotropic elasticity and the absence of capillary forces are assumed.

5. Solution of exercises

5.1. Exercises for Section 2

5.1.1. Exercise 1. From (2.16) and (2.19), we infer that

$$\boldsymbol{\sigma}: \boldsymbol{D} = \frac{1}{J}\boldsymbol{P}: \dot{\boldsymbol{E}}.$$
 (5.1)

Substituting (5.1) into in Eq. (2.84) yields:

$$-\rho(\dot{\tilde{F}}+\dot{T}\tilde{S})+\frac{1}{J}\boldsymbol{P}:\dot{\boldsymbol{E}}-\frac{\boldsymbol{h}}{T}\cdot\boldsymbol{\nabla}T\geq0.$$
(5.2)

The principle of equipresence requires that all dependent variables depend on all independent variables:

$$\tilde{F} = \tilde{F}(\boldsymbol{E}, T, \boldsymbol{\nabla}_0 T),$$

$$\tilde{S} = \tilde{S}(\boldsymbol{E}, T, \boldsymbol{\nabla}_0 T),$$

$$\boldsymbol{P} = \boldsymbol{P}(\boldsymbol{E}, T, \boldsymbol{\nabla}_0 T),$$

$$\boldsymbol{h}_0 = \boldsymbol{h}_0(\boldsymbol{E}, T, \boldsymbol{\nabla}_0 T).$$

(5.3)

Applying the chain rule for time differentiation of \tilde{F} , we find instead of inequality (5.2):

$$\left(-\rho \frac{\partial \tilde{F}}{\partial E} + \frac{1}{J} P \right) : \dot{E} + \left(-\rho \frac{\partial \tilde{F}}{\partial T} - \rho \tilde{S} \right) \dot{T} - \rho \frac{\partial \tilde{F}}{\partial \nabla_0 T} \cdot \overline{\nabla_0 T} - \frac{h_0}{T} \cdot \nabla_0 T \ge 0.$$

$$(5.4)$$

The first, second and third term in (5.4) are linear in \dot{E} , \dot{T} and $\overline{\nabla_0 T}$ respectively. Therefore, the inequality can only be satisfied for all values of \dot{E} , \dot{T} and $\overline{\nabla_0 T}$ if:

$$\boldsymbol{P} = \rho_0 \frac{\partial \tilde{F}}{\partial \boldsymbol{E}},\tag{5.5}$$

$$\tilde{S} = -\frac{\partial \tilde{F}}{\partial T},\tag{5.6}$$

$$\frac{\partial \bar{F}}{\partial \nabla_0 T} = 0. \tag{5.7}$$

Equation (5.5) is equivalent to (2.95) and Eq. (5.6) to Eq. (2.79). Equation (5.7) requires that \tilde{F} does not depend on the temperature gradient. Therefore, by virtue of (5.5) and (5.6) the stress and the entropy does not depend on temperature gradients either. The remaining inequality

$$-\frac{1}{T}\boldsymbol{h}_0\cdot\boldsymbol{\nabla}_0 T \ge 0, \tag{5.8}$$

states that the heat flux vector should be opposite to the temperature gradient, i.e. heat flows from hot to cold. At thermodynamic equilibrium entropy is maximum and the material exhibits uniform temperature distribution. In non-equilibrium we assume that the state of the material is close to equilibrium. In the vicinity of the state of equilibrium, the left hand side of inequality (5.8) can be approximated by a quadratic function of the temperature gradient. Therefore we find that:

$$\boldsymbol{h}_0 = -\boldsymbol{G} \cdot \boldsymbol{\nabla}_0 \boldsymbol{T} \tag{5.9}$$

in which G is a positive definite tensor. G is the heat conductivity tensor. Equation (5.9) is Fourier's law and shows that – unlike the free energy, the entropy and the stress – the heat flux vector depends on temperature gradients. An alternative choice of variables requires to rewrite the second law in a somewhat different format. Substituting (5.1) into inequality (2.85) yields:

$$\rho(T\dot{\tilde{S}} - \dot{\tilde{U}}) + \frac{1}{J}\boldsymbol{P} : \dot{\boldsymbol{E}} - \frac{\boldsymbol{h}}{T} \cdot \boldsymbol{\nabla}T \ge 0.$$
(5.10)

The principle of equipresence requires that all dependent variables depend

on all independent variables:

$$\begin{aligned}
\tilde{U} &= \tilde{U}(\boldsymbol{E}, \boldsymbol{S}, \boldsymbol{h}_{0}), \\
T &= \tilde{S}(\boldsymbol{E}, \tilde{\boldsymbol{S}}, \boldsymbol{h}_{0}), \\
\boldsymbol{P} &= \boldsymbol{P}(\boldsymbol{E}, \tilde{\boldsymbol{S}}, \boldsymbol{h}_{0}), \\
\boldsymbol{\nabla}_{0}T &= \boldsymbol{R}(\boldsymbol{E}, \tilde{\boldsymbol{S}}, \boldsymbol{h}_{0}).
\end{aligned}$$
(5.11)

Applying the chain rule for time differentiation of \tilde{U} , we find instead of in Eq. (5.10):

$$\left(-\rho\frac{\partial\tilde{U}}{\partial\boldsymbol{E}}+\frac{1}{J}\boldsymbol{P}\right):\dot{\boldsymbol{E}}+\left(-\rho\frac{\partial\tilde{U}}{\partial\tilde{S}}+\rho T\right)\dot{\tilde{S}}$$

$$-\rho\frac{\partial\tilde{U}}{\partial\boldsymbol{h}_{0}}\cdot\dot{\boldsymbol{h}_{0}}-\frac{1}{T}\boldsymbol{h}_{0}\cdot\boldsymbol{\nabla}_{0}T\geq0.$$
(5.12)

The first, second and third term of inequality (5.12) are linear in \dot{E} , $\dot{\tilde{S}}$ and \dot{h}_0 respectively. Therefore, the inequality can only be satisfied for all values of \dot{E} , $\dot{\tilde{S}}$ and \dot{h}_0 provided that

$$\boldsymbol{P} = \rho_0 \frac{\partial \tilde{U}}{\partial \boldsymbol{E}},\tag{5.13}$$

$$T = \frac{\partial \tilde{U}}{\partial \tilde{S}},\tag{5.14}$$

$$\frac{\partial U}{\partial h_0} = 0. \tag{5.15}$$

Equation (5.13) is equivalent to (2.76) and Eq. (5.14) to Eq. (2.76). Equation (5.15) requires that \tilde{U} does not depend on the heat flux. Therefore, by virtue of (5.13) and (5.14) the stress and the temperature does not depend on the heat flux either. The remaining inequality is identical to inequality (5.8) and leads to Fourier's law as shown above and states that – unlike the stress, the internal energy and the temperature – the temperature gradient depends on the heat flux.

5.1.2. Exercise 2.

$$\boldsymbol{F} = \begin{bmatrix} \boldsymbol{e}_1 & \boldsymbol{e}_2 & \boldsymbol{e}_3 \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{\lambda}} & 0 & 0\\ 0 & \frac{1}{\sqrt{\lambda}} & 0\\ 0 & 0 & \lambda \end{bmatrix} \begin{bmatrix} \boldsymbol{e}_1\\ \boldsymbol{e}_2\\ \boldsymbol{e}_3 \end{bmatrix}, \quad (5.16)$$

$$J = \det(\boldsymbol{F}) = 1, \tag{5.17}$$

$$\rho = \rho_0, \tag{5.18}$$

$$\boldsymbol{E} = \begin{bmatrix} \boldsymbol{e}_1 & \boldsymbol{e}_2 & \boldsymbol{e}_3 \end{bmatrix} \begin{bmatrix} \frac{1}{2} (\frac{1}{\lambda} - 1) & 0 & 0\\ 0 & \frac{1}{2} (\frac{1}{\lambda} - 1) & 0\\ 0 & 0 & \frac{\lambda^2 - 1}{2} \end{bmatrix} \begin{bmatrix} \boldsymbol{e}_1 \\ \boldsymbol{e}_2 \\ \boldsymbol{e}_3 \end{bmatrix}, \quad (5.19)$$

with E the Green-Lagrange strain tensor as defined in (2.10). Lateral boundary conditions require that

$$\sigma_{11} = \sigma_{22} = 0 \tag{5.20}$$

or

$$\sigma_{11}^{\rm d} - p = \frac{1}{\sqrt{\lambda}} P_{11} \frac{1}{\sqrt{\lambda}} - p = 0.$$
 (5.21)

From the strain energy function, we evaluate the second Piola-Kirchhoff stress P_{11} , P_{22} and P_{33} :

$$P_{11} = \frac{\partial W}{\partial E_{11}} = 2abE_{11}e^{b(E_{11}^2 + E_{22}^2 + 2E_{33}^2)},$$
(5.22)

$$P_{22} = P_{11}, \tag{5.23}$$

$$P_{33} = \frac{\partial W}{\partial E_{33}} = 4abE_{33}e^{b(E_{11}^2 + E_{22}^2 + 2E_{33}^2)}.$$
 (5.24)

Substitution of Eq. (5.19) into (5.22) and Eq. (5.22) into (5.21) yields the expression for the hydrostatic pressure as a function of the extension ratio λ :

$$p = \frac{ab(\frac{1}{\lambda} - 1)}{\lambda} e^{\frac{b}{2}((\frac{1}{\lambda} - 1)^2 + (\lambda^2 - 1)^2)}.$$
 (5.25)

The stress component σ_{33} is:

$$\sigma_{33} = P_{33}(\lambda)^2 - p \tag{5.26}$$

and others vanish.

5.2. Exercises for Section 3

5.2.1. Exercise 1. One can write the partial pressure of component α as:

$$\sigma^{\alpha} = \frac{F^{\alpha}}{A}, \quad \alpha = \text{water, oil}$$
 (5.27)

in which A is the total surface. The surface area per component can be calculated using the volume fraction.

$$\phi^{\alpha} = \frac{V^{\alpha}}{V} = \frac{A^{\alpha}}{A}.$$
(5.28)

Substitution of this relation into Eq. (5.27) gives:

$$p^{\alpha} = \frac{-F^{\alpha}}{A\phi^{\alpha}} = \frac{-\sigma^{\alpha}}{\phi^{\alpha}}.$$
 (5.29)

Since $(\phi^{\text{water}} = 0.05)$ and $(\sigma^{\text{water}} = -2 \text{ MPa})$, the actual water pressure is 40 MPa. For the oil $(\phi^{\text{oil}} = 0.08)$ and $(\sigma^{\text{oil}} = -5 \text{ MPa})$, which gives an actual oil pressure of 62.5 MPa.

5.3. Exercises for Section 4

5.3.1. Exercise 1. For the specific velocity (Darcy flow) of the fluid through the porous solid applies:

$$v_{\text{specific}} = \frac{Q}{A} = 500 \,\mu\text{m/s.} \tag{5.30}$$

However, the fluid can only flow through 80% of the surface (0.8A), which results in an average velocity of:

$$v_{\text{average}} = \frac{Q}{0.8A} = 625 \,\mu\text{m/s.}$$
 (5.31)

5.3.2. Exercise 2. The effective stress (σ_e) is intercepted for 90% by the collagen fibers, which takes up 15% V of the cartilage. The stress in the collagen fibers resulting from the effective stress is:

$$\sigma_{\text{collagen}} = \frac{0.9\sigma_{\text{e}}}{\phi^{\text{collagen}}} = 1.8 \,\text{MPa}$$
(5.32)

which results in a total stress of:

$$\sigma_{\text{collagen}}^{\text{total}} = \sigma_{\text{collagen}} - p = (1.8 - 0.2) \text{ MPa} = 1.6 \text{ MPa}.$$
(5.33)

5.3.3. Exercise 3. The maximum loading time is $\frac{1}{0.5 \text{ Hz}} = 2 s$. Since the permeability and the stiffness are also known, the depth, over which in and outflow takes place, can be determined using the consolidation equation of Terzaghi (4.17).

$$\Delta z = \sqrt{KH\Delta t} = \sqrt{10^{-16} \cdot 0.5 \cdot 10^6 \cdot 2} = 10^{-5} \,\mathrm{m}.\tag{5.34}$$

5.3.4. Exercise 4. Using the permeability, thickness of the clay layer and the compressive modulus, an estimate for the consolidation time can be made.

$$\Delta t = \frac{(\Delta z)^2}{KH} = \frac{6^2}{10^{-16} \cdot 100 \cdot 10^6} = 3.6 \cdot 10^9 \,\mathrm{s} \tag{5.35}$$

$$\approx$$
 114 years. (5.36)

So the consolidation takes a very long time. The damming of the piles is a sort of an instantaneous loading that will be carried by the fluid. During years this fluid will flow away and therefore no forecast can be made for load bearing over a longer period of time.

5.3.5. Exercise 5. We have two conditions to consider: one is immediately after application of the load, one is a long time later $(t = \infty)$, when a steady-state is established. In the latter situation the pressure p in the skin sample has adopted the pressure value of the external bath, in the former situation the fluid has had no time to flow in or out of the sample and incompressibility can be assumed (in small displacement theory: $\varepsilon_{11} + \varepsilon_{22} + \varepsilon_{33} = 0$, check it!).

We have 2 momentum equations in both situations; one in the loading direction and one in the transverse directions:

$$\sigma^{11} = \sigma_{\rm e}^{11} - p = \text{external load}, \tag{5.37}$$

$$\sigma^{22} = \sigma_{\rm e}^{22} - p = 0. \tag{5.38}$$

Equation (5.38), $t = \infty$. As the pressure vanishes inside the sample Eq. (5.38) requires:

$$\sigma_{\rm e}^{22} = 0$$
 (5.39)

or

$$\frac{E}{1+\nu}\left(\varepsilon_{22} + \frac{\nu}{1-2\nu}(\varepsilon_{11}+2\varepsilon_{22})\right) = 0.$$
(5.40)

Hence

$$(1 - 2\nu)\varepsilon_{22} + \nu(\varepsilon_{11} + 2\varepsilon_{22}) = 0 \tag{5.41}$$

or

$$\nu = -\frac{\varepsilon_{22}}{\varepsilon_{11}} \tag{5.42}$$

which is nothing else but the definition of the Poisson's ratio, resulting in

$$\nu = -\frac{-0.014}{0.04} = 0.35 \quad . \tag{5.43}$$

which is consistent with the classical requirement:

$$0 < \nu < 0.5.$$
 (5.44)

Equation (5.38) requires that:

$$\sigma_{\rm e}^{11} = 0.4\,\rm kPa \tag{5.45}$$

or

$$\frac{E}{1+\nu}\left(\varepsilon_{11} + \frac{\nu}{1-2\nu}(\varepsilon_{11} + 2\varepsilon_{22})\right) = 0.4 \,\mathrm{kPa.}$$
(5.46)

Hence

$$\frac{E}{1+\nu}\left(\varepsilon_{11} + \frac{\nu}{1-2\nu}(\varepsilon_{11} - 2\nu\varepsilon_{11})\right) = 0.4\,\mathrm{kPa} \tag{5.47}$$

or

$$E = \frac{0.4 \,\mathrm{kPa}}{\varepsilon_{11}} = 10 \,\mathrm{kPa}. \tag{5.48}$$

Equation (5.38), $t = t_0$. It is obvious that the values of E and ν computed for $t = \infty$ are also valid at $t = t_0$; however, the fluid does not allow the material to change its volume, and the pressure p is an unknown. Equation (5.38) requires:

$$\sigma_{\rm e}^{22} - p = 0, \tag{5.49}$$

$$\frac{E}{1+\nu}\left(\varepsilon_{22} + \frac{\nu}{1-2\nu}\underbrace{(\varepsilon_{11}+2\varepsilon_{22})}_{0}\right) - p = 0, \qquad (5.50)$$

$$p = \frac{E\varepsilon_{22}}{1+\nu} = -\frac{10\cdot 0.02}{1.35} = -0.148 \,\mathrm{kPa.} \tag{5.51}$$

In other words, the fluid is under negative pressure or traction. This traction will attract water, and cause the thickness to increase from 0.980 mm to 0.986 mm. Equation (5.38) requires

$$\sigma_{\rm e}^{11} - p = \sigma^{11} \tag{5.52}$$

or

$$\sigma^{11} = \frac{E}{1+\nu} \left(\varepsilon_{11} + \frac{\nu}{1-2\nu} \underbrace{(\varepsilon_{11}+2\varepsilon_{22})}_{0} \right) - p = 0 \qquad (5.53)$$

$$= \frac{10 \cdot 0.04}{1.35} + 0.148 = 0.444 \,\mathrm{kPa.} \tag{5.54}$$

Therefore, we get

$$\sigma_{\rm e}^{11} = 0.296 \,\rm kPa. \tag{5.55}$$

5.3.6. Exercise 6. When the capillary forces are negligible the chemical potential reduces from

$$\mu^{\rm f} = p + \frac{\partial W}{\partial \Phi^{\rm f}} \tag{5.56}$$

to

$$\mu^{\rm f} = p. \tag{5.57}$$

In the case of 1D small deformations the stress-strain relation changes from

$$\boldsymbol{\sigma}_{\mathrm{e}} = (\det \boldsymbol{F})^{-1} \boldsymbol{F} \cdot \frac{\partial W}{\partial \boldsymbol{E}^{\mathrm{s}}} \cdot \boldsymbol{F}^{\mathrm{c}}$$
(5.58)

to Hooke's law,

$$\sigma_{\rm e} = H \nabla u = H \frac{\partial u}{\partial z},\tag{5.59}$$

as $F \approx I$ and $W = \frac{H}{2} (\nabla u)^2$. Darcy's law (4.59) takes the form:

$$\phi^{\rm f}(v^{\rm f} - v^{\rm s}) = -K \frac{\partial p}{\partial z} \tag{5.60}$$

and the mass balance Eq. (4.58) reduces to

$$\frac{D^s}{Dt}\left(\frac{\partial u}{\partial z}\right) - \frac{\partial}{\partial z}(\phi^{\rm f}(v^{\rm f} - v^{\rm s})) = 0.$$
(5.61)

Equation (5.60) is now substituted into the mass balance (5.61), and we find,

$$\frac{D^s}{Dt}\left(\frac{\partial u}{\partial z}\right) - \frac{\partial}{\partial z}K\frac{\partial p}{\partial z} = 0$$
(5.62)

which is also Eq. (4.10). Now, Terzaghi's consolidation theory is further derived as done in Sec. 4.2.

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