THERMODYNAMIC THEORY FOR FIBER SUSPENSIONS

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ABSTRACT. In this paper three different approaches towards a continuum theory of fiber suspensions are discussed. The first one is the classical Thermodynamics of Irreversible Processes with internal variables. It derives constitutive equations for fiber suspensions on the basis of ONSAGERs phenomenological coefficients, which are related to the mechanical properties of the fibers. Secondly another method of exploiting the dissipation inequality, the method introduced by LIU is applied in order to derive results on constitutive equations. Finally a mesoscopic background theory is discussed. In this approach a distribution of different fiber orientations and fiber deformations is assumed. The fiber orientation and deformation are additional variables in the domain of field quantities. The new field quantities on the enlarged set of variables obey balance equations. The mesoscopic balance of mass results in an equation of motion for the distribution of fiber orientations and deformations. The usual macroscopic fields of continuum mechanics are averages of mesoscopic fields over the different orientations and deformations. Macroscopic quantities characterizing the orientational order, the alignment tensors are defined by the help of the orientation distribution function. They are internal variables in the macroscopic theory characterizing the distribution of fiber orientations.

The result of the Irreversible Thermodynamics approach mainly concerns the stress tensor. Cauchy’s stress is usually assumed to be symmetric, but in fiber suspensions it has an anti-symmetric part, too. The skew-symmetric part of the stress shows up in the balance equation of angular momentum; it is related to the torque density, the rate of internal moment of momentum, and the couple stress. The latter is a result of the internal structure of the material. The fibers are assumed to be microscopic and the stress field smooth on macroscopic length scale. If the local structure of the flowing medium may be characterized by second order pseudo (axial) tensors as internal variables then in the linear Onsager equations there appears couple stress coupled to the gradient of the angular velocity.

The results of the Liu-procedure are consistent with this observation. The couple stress can be calculated as a combination of derivatives of the free energy density (see equation (3.31)), which may have an anti-symmetric part, too. This result may be used to calculate the couple stress from an ansatz for the free energy density, taking into account the deformation of fibers.

Another result of the Liu-exploitation of the dissipation inequality is that the assumption of the entropy flux being heat flux over temperature does not contradict the second law of thermodynamics, but it does not necessarily follow from the dissipation inequality.
1. Introduction

A phenomenological theory of suspensions and emulsions of weakly deformable spheres has been presented in [1]. The equations of motion for the particle deformation, and the constitutive equation for the stress tensor have been derived in the whole range of concentrations of the emulsion. They are generalizations of earlier work on dilute suspensions [2, 3] and emulsions [4, 5]. Thermodynamic arguments have been applied in order to reduce the number of unknown constitutive coefficients. In semi-dilute suspensions hydrodynamic interactions between particles are important and their contribution to the stress tensor has been investigated. As it is expected for all materials with an internal structure the resulting stress tensor has an anti-symmetric part. An overview over calculations of the stress tensor of suspensions of elastic fibers of fixed orientation as well as on the stress tensor of rigid orientable fibers can be found in [6].

A constitutive model taking into account the possible damage of fibers of a glass-fiber woven polyester composite is presented in [7]. The material is viscoelastic with a dependency of elastic properties on the micro-structural damage. The constitutive model is derived within the framework of continuum mechanics and thermodynamics with an internal variable. The phenomenological constitutive coefficients have been obtained from experimental tests. Other experimental applications can be found in [8, 9, 10].

The derivation of constitutive equations on the ground of kinetic theory is similar for polymers (see f. i. [11]) and suspensions of fibers. An application of the stress tensor derived by Batchelor [12, 13] from a kinetic background theory to corner flow of suspensions of orientable rigid rods can be found in [14].

Finally the methods applied in the present paper, namely continuum mechanics with internal variables and Thermodynamics of Irreversible Processes has been applied successfully in other fields: liquid crystals [15], plasticity of metals and other solids [16], polymer solutions. Composites with inextensible fibers have been treated in [17] with continuum thermodynamics, exploiting the dissipation inequality according to Liu [18]. In contrast to the present paper, where the same method is applied in the second part, in [17] the material is a solid fiber composite.

In the last section the methods of the so called mesoscopic theory are applied. This theory has been developed for liquid crystals [19, 20, 21, 22]. For an overview over other possible applications see [23, 24].
2. **Irreversible Thermodynamics of Flexible Fibers**

The thermodynamic description of systems with dynamic (internal) variables has been applied with success to several kinds of physical phenomena such as electric conduction \[25\], electric and magnetic polarization \[26, 27, 28\], heat conduction and radiation \[29, 30, 31, 32, 33, 34\], viscoelastic and plastic deformations \[35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49\], liquid crystals \[50\]. The thermodynamic theory of visco-elasticity is based on dynamic variables which are second order symmetric tensors. They are related to the deformation of elastic micro-particles or to the distribution function of the orientation of rod like or disk like rigid particles. For example some proteins, certain saccharoides, and liquid crystals are well approximated by the above model, but it fails, if particles are like elastic slender bars, e.g., in the case of fiber suspensions, in which the particles may be twisted and bent; their affine deformation is not relevant.

In the first part the flow induced anisotropy is neglected, and the orientation distribution of the fibers is presumed isotropic. The purpose here is to investigate the consequences of the flexibility of the particles.

The deformation of a particle (bend and twist) stores energy, so influencing the macroscopic mechanical properties of the fluid.

In the following we will denote by the symbol : the contraction of second order tensors over all indices, in components: \( A : B = A_{ik} B_{ki} \). The scalar product between vectors \( \mathbf{a} \) and \( \mathbf{b} \) is denoted by \( \mathbf{a} \cdot \mathbf{b} \).

### 2.1. Deformation of a Fiber

In our model the fibers are assumed to be straight if not loaded. Then one can chose a coordinate \( s \) along this fiber orientation and an orthogonal tensor \( U(s) \) describing the distortion of the fiber. The macroscopic angular distortion tensor defined by

\[
\varphi := U^T \cdot \frac{dU}{ds}
\]

(2.1)

takes into account the local deformation of the flexible fibers, and is the average over all fiber orientations in the continuum element. \( s \) is the local coordinate along the fiber, and \( x \) is the position of the continuum element. \( s \) is only introduced in order to describe the local fiber deformation.

The tensor \( \varphi \) is obviously skew-symmetric as \( U \) is orthogonal,

\[
U^T \cdot U = \delta,
\]

(2.2)

where \( \delta \) is the unit tensor and

\[
\frac{dU^T}{ds} \cdot U + U^T \cdot \frac{dU}{ds} = 0,
\]

(2.3)

i.e.

\[
\left( U^T \cdot \frac{dU}{ds} \right)^T + U^T \cdot \frac{dU}{ds} = 0.
\]

(2.4)
This way, we introduce the angular distortion vector (the vector invariant of the angular distortion tensor) as

\[ \vec{\varphi} \times \delta = \varphi. \]  

Only in this case we will denote the vector by the symbol \( \vec{\varphi} \) in order to distinguish it from the tensor \( \varphi \).

Let \( \mathbf{n} \) denote the unit vector tangential to the undeformed fiber. The scalar product of \( \vec{\varphi} \) and \( \mathbf{n} \) gives the twist:

\[ t = \vec{\varphi} \cdot \mathbf{n}, \]

and the component of \( \vec{\varphi} \) perpendicular to \( \mathbf{n} \) is the bend:

\[ b = \vec{\varphi} - \mathbf{n}(\mathbf{n} \cdot \vec{\varphi}) \]

As the fibers are elastic, two material coefficients \( \mu_t \) and \( \mu_b \) have to be introduced to describe their stiffness. The torque acting in a cross section of the fiber is given by

\[ \tau = \mu_t \mathbf{n} \cdot (\mathbf{n} \cdot \vec{\varphi}) + \mu_b [\vec{\varphi} - \mathbf{n}(\mathbf{n} \cdot \vec{\varphi})] \]

The coefficient \( \mu_t \) is the torsion stiffness, and \( \mu_b \) is the bend stiffness of the fiber. The elastic energy stored per unit length of a fiber is given by

\[ u_e = \frac{\mu_t}{2}(\vec{\varphi} \cdot \mathbf{n})^2 + \frac{\mu_b}{2}(\varphi^2 - (\vec{\varphi} \cdot \mathbf{n})^2). \]

This way, we have obtained the expression for the energy stored by a deformed fiber.

The fibers are deformed by flow and they continuously relax. The angular distortion of an individual fiber \( \vec{\varphi} \) depends on the local orientation of the fiber,

\[ \vec{\varphi} = \vec{\varphi}(\mathbf{n}). \]

The function is odd, \( \vec{\varphi}(-\mathbf{n}) = -\vec{\varphi}(\mathbf{n}) \), according to the definition of \( \vec{\varphi} \) eq. (2.1), as turning the fiber (changing \( \vec{\varphi}(\mathbf{n}) \) to \( \vec{\varphi}(-\mathbf{n}) \)) gives a sign in the line element \( ds \).

An obvious approximation for the function \( \vec{\varphi}(\mathbf{n}) \) is the first term of its expansion by spherical harmonics;

\[ \vec{\varphi}(\mathbf{n}) = \alpha \cdot \mathbf{n}, \]

where \( \alpha \) is a second order pseudo tensor as \( \vec{\varphi} \) is an axial vector. VERHAS [51] elaborated the theory based on this linear approximation and the theory gives only one relaxation time, while the relaxation times for twist and bend are expected to differ. As it will be shown in this section, the above shortcoming is ceased if the approximation (2.11) is improved with a third order term (with a traceless tensor \( \beta \)):

\[ \vec{\varphi}(\mathbf{n}) = \alpha \cdot \mathbf{n} + \mathbf{n}(\mathbf{n} \cdot \beta \cdot \mathbf{n}), \]

which can be decomposed as

\[ \vec{\varphi}(\mathbf{n}) = \alpha^0 \mathbf{n} + \alpha^a \cdot \mathbf{n} + \alpha^d \cdot \mathbf{n} - \mathbf{n}(\mathbf{n} \cdot \alpha^d \cdot \mathbf{n}) + \mathbf{n}(\mathbf{n} \cdot T \cdot \mathbf{n}), \]

where \( \alpha^0 = \frac{1}{3} \text{tr} \alpha \), \( \alpha^a \) is the skew symmetric part of \( \alpha \), \( \alpha^d \) is the deviatoric part of \( \alpha \) and \( T \) is the deviatoric part of the sum of the tensors \( \alpha \) and \( \beta \). The latter form shows the twist and bend separately.
the first and the last term are due to twist, while the others are due to bend.

Inserting the approximation equation (2.12), the elastic energy of a fiber per unit fiber length reads

\[
(2.14) \quad u_e(n) = \frac{\mu_t}{2} (\alpha^0 + n \cdot T \cdot n)^2 + \frac{\mu_b}{2} (\alpha^a \cdot n + \alpha^d \cdot n - n(n \cdot \alpha^d \cdot n))^2,
\]

the average of which over all possible fiber orientations is

\[
(2.15) \quad u_{em} = \frac{1}{4\pi} \oint_{S^2} u_e(n) d^2 n = \frac{\mu_t}{2} \left( \alpha^0 + \frac{2}{15} T : T \right) + \frac{\mu_b}{2} \left( \frac{1}{3} \alpha^a : \alpha^a + \frac{1}{5} \alpha^d : \alpha^d \right)
\]

if uniform distribution of the fiber orientations is supposed, i.e. the fiber orientations are distributed isotropically. A more refined description introducing a non-uniform distribution of orientations is discussed in the third chapter.

If the total length of the fibers in a unit volume is denoted by \( l \), we obtain

\[
(2.16) \quad u_{nd} = l u_{em}
\]

for the part of the specific internal energy stored in the deformation of the fibers, and not being dissipated. From the formula, one can see that this not dissipated part of the energy is a homogeneous quadratic function of the scalar \( \alpha^0 \), and the tensors \( \alpha^a, \alpha^d \), and \( T \).

2.2. Balance equations. The balance equation for mass is

\[
(2.17) \quad \frac{d\rho}{dt} + \rho \nabla \cdot \mathbf{v} = 0,
\]

which, for volume preserving motions (incompressible liquids), reduces to

\[
(2.18) \quad \nabla \cdot \mathbf{v} = 0.
\]

The derivative \( \frac{d}{dt} \) is the material (or total) time derivative

\[
(2.19) \quad \frac{d}{dt} = \frac{\partial}{\partial t} + (\mathbf{v} \cdot \nabla).
\]

The balance equation of linear momentum is the usual one

\[
(2.20) \quad \rho \frac{d\mathbf{v}}{dt} = \rho \mathbf{f} + \nabla \cdot \mathbf{t}
\]

where \( \mathbf{t} \) is CAUCHY's stress tensor, \( \mathbf{f} \) is the body force per unit mass, \( \rho \) is the density, and \( \mathbf{v} \) is the velocity of the material. The definition for the divergence used here reads in components:

\[
(2.21) \quad \left( \nabla \cdot \mathbf{t} \right)_i = \nabla_j t_{ij}.
\]

Although the internal angular momentum and the torque will be neglected later, we write down the balance for the angular momentum in general

\[
(2.22) \quad \rho \frac{d\mathbf{s}}{dt} = 2 \mathbf{w}(t) + \rho \mathbf{m} + \nabla \cdot \mathbf{P},
\]
Here $s$ is the internal angular momentum per unit mass, $m$ stands for the torque exerted on the material by external fields and $\Pi$ is the couple stress tensor. The vector $w(t)$ stands for the vector invariant of Cauchy’s stress tensor. In the following we suppose that the average rotation of the fibers (in addition to thermal fluctuations) is generated by the macroscopic mechanical motion. Consequently, the internal angular momentum (due to thermal motion) can be neglected compared to the moment of momentum (due to macroscopic motion). Moreover, the rotational energy of internal angular momentum need not be regarded. If we also neglect the torque, which is reasonable as long as no electro-magnetic fields are present, equation (2.22) reduces to

\begin{equation}
2w(t) + \nabla \cdot \Pi = 0
\end{equation}

The balance equation of internal energy is of basic importance for constitutive modelling. For the total energy, we can write

\begin{equation}
\frac{d}{dt} \int \rho (u + \frac{v^2}{2}) dV = - \oint \mathbf{q} \cdot d\mathbf{A} + \oint \mathbf{v} \cdot \mathbf{t} \cdot d\mathbf{A} + \oint \omega_\Pi \cdot \Pi \cdot d\mathbf{A} + \oint \rho \mathbf{m} \cdot \mathbf{m} dV
\end{equation}

The left hand side is the change of the total (internal plus kinetic) energy of the part of the material regarded. Kinetic energy due to particle rotations has already been neglected. The terms on the right hand side are heat flow, and power of stress, of couple stress, of forces, and of couple forces. The vectors $\omega_\Pi$ and $\omega_m$ are the angular velocities of what the couple stress and the torque act on, respectively.

Now, we assume that both $\omega_m$ and $\omega_\Pi$ are equal to the macroscopic angular velocity of the body,

\begin{equation}
\omega_m = \omega_\Pi = \omega = \frac{1}{2} \nabla \times \mathbf{v}.
\end{equation}

Making use of the other balance equations and of Gauss’ theorem, we get

\begin{equation}
\rho \frac{du}{dt} + \nabla \cdot q = \dot{d} : t^d + \Pi : \nabla \omega
\end{equation}

where $\dot{d}$ and $t^d$ stand for the symmetric part of the velocity gradient and of Cauchy’s stress tensor, respectively.

2.3. Entropy. The independent state variables in the domain of the entropy are the internal energy, the pseudo scalar $\mathbf{a}^0$ and the tensors $\mathbf{a}^a$, $\mathbf{a}^d$ and $\mathbf{T}$; the latter taking into account the state of the deformation of the fibers.

Assume that the entropy depends on the dissipated energy only,

\begin{equation}
\eta = \eta^e \left( u - \frac{1}{2} u_{nd} \right).
\end{equation}
where \( u_{nd} \) is the non-dissipated energy (stored in the deformation of the fibers). From here and from equations (2.15) and (2.16) we get (2.28)
\[
\eta = \eta_e \left( u - \frac{l\mu_t}{2\rho} \left[ \alpha^0 a^2 - \frac{2}{15} T : T \right] - \frac{l\mu_b}{2\rho} \left[ \frac{1}{3} \alpha^a : \alpha^a + \frac{1}{5} \alpha^d : \alpha^d \right] \right).
\]

The balance equation for the entropy, for vanishing entropy supply, is
\[
\rho \frac{d\eta}{dt} + \nabla \cdot \phi = \sigma \geq 0
\]
(2.29)

The entropy flux is supposed to obey the constitutive equation for local equilibrium systems
\[
\phi = \frac{1}{T} q \quad \text{where} \quad \frac{1}{T} = \frac{\partial s}{\partial u}.
\]
(2.30)

Making use of the entropy function in equation (2.28) and the balance equation of the internal energy, we obtain the expression of the entropy production density
\[
\sigma = \frac{1}{T} \left\{ \dot{\alpha} : t^d + \Pi : \nabla \omega - l\mu_t \alpha^0 \dot{\alpha^0} - \frac{2l\mu_t}{15} T : \dot{T} - \frac{l\mu_b}{3} \alpha^a : \dot{\alpha^a} - \frac{l\mu_b}{5} \alpha^d : \dot{\alpha^d} - \frac{1}{T} q \cdot \nabla T \right\}.
\]
(2.31)

Here \( \dot{T}, \dot{\alpha^a}, \) and \( \dot{\alpha^d} \) are the co-rotational time derivatives of the tensors \( T, \alpha^a, \) and \( \alpha^d, \) respectively. The introduction of co-rotational derivatives is here arbitrary, because it holds
\[
T : \dot{T} = T : \dot{T}
\]
(2.32)
\[
\alpha^a : \dot{\alpha^a} = \dot{\alpha^a} \quad \text{and} \quad \alpha^d : \dot{\alpha^d} = \dot{\alpha^d}.
\]
(2.33)

It is motivated by the fact that later fluxes and forces should be expressed in terms of co-rotational time derivatives, i.e. the time derivatives in a co-moving frame:
\[
\dot{T} = \frac{dT}{dt} + T \cdot \omega - \omega \cdot T, \quad \dot{\alpha^a} = \frac{d\alpha^a}{dt} + \alpha^a \cdot \omega - \omega \cdot \alpha^a, \quad \dot{\alpha^d} = \frac{d\alpha^d}{dt} + \alpha^d \cdot \omega - \omega \cdot \alpha^d.
\]

The tensors \( \Pi \) and \( \nabla \omega \) are decomposed into their symmetric and anti-symmetric parts:
\[
\Pi : \nabla \omega = \Pi^d : (\nabla \omega)^d + \Pi^a : (\nabla \omega)^a.
\]
(2.35)

It results the entropy production density
\[
T \sigma_s = \dot{d} : t^d + \Pi^d : (\nabla \omega)^d + \Pi^a : (\nabla \omega)^a - l\mu_t \alpha^0 \dot{\alpha^0}
\]
\[
- \frac{2l\mu_t}{15} T : \dot{T} - \frac{l\mu_b}{3} \alpha^a : \dot{\alpha^a} - \frac{l\mu_b}{5} \alpha^d : \dot{\alpha^d} - q \cdot \frac{1}{T} \nabla T.
\]
(2.36)

The first term on the right hand side refers to affine deformations, the second and the third to distortions, the next terms to the relaxations.
of the distortions of the fibers while the last term is due to heat propagation. The set of process rates is

\[ \{ q, t^d, \Pi^d, \alpha^d, \hat{T}, \Pi^a, \hat{\alpha}^a, \hat{\alpha}^0 \} \]

and the set of corresponding forces is

\[ \{ -\frac{1}{T} \nabla T; \hat{d}; (\nabla \omega)^d; -l\mu_b; \frac{2l\mu_t}{15} T; (\nabla \omega)^a; -\frac{l\mu_b}{3} \alpha^a; -l\mu_t \alpha^0 \} \]

2.4. Constitutive Equations. In an isotropic material, with the above thermodynamic fluxes and forces ONSAGER’s linear laws read (54, 55, 56, 57, 58, 59, 60, 61, 62)

\[ q = -\frac{1}{T} L^d \nabla T = -\lambda \nabla T, \]

\[ \Pi^d = L^d_{00} (\nabla \omega)^d - L^d_{01} \frac{l\mu_a}{3} \alpha^d - L^d_{02} \frac{2l\mu_t}{15} T, \]

\[ \alpha^d = L^d_{10} (\nabla \omega)^d - L^d_{11} \frac{l\mu_a}{3} \alpha^d - L^d_{12} \frac{2l\mu_t}{15} T, \]

\[ \alpha^a = L^a_{00} (\nabla \omega)^a - L^a_{01} \frac{l\mu_a}{3} \alpha^a, \]

\[ \frac{d}{dt} \alpha^0 = -L^0 l\mu_t \alpha^0. \]

The pseudo scalar \( \alpha^0 \) and the tensors \( \alpha^d \), and \( T \) are related to the distortion of the fibers, so we suppose they are of \( \alpha \)-type, i.e., not changing under time inversion. On the other hand \( \omega \) is of \( \beta \)-type, i.e., changing sign under time inversion. The ONSAGER-CASIMIR reciprocal relations are

\[ L^d_{10} = -L^d_{01}, \quad L^d_{20} = -L^d_{02}, \quad L^d_{12} = L^d_{21}, \quad L^a_{00} = -L^a_{00}. \]

The inequalities

\[ \lambda > 0, \quad \eta > 0, \quad L^d_{00} \geq 0, \quad L^d_{11} \geq 0, \]

\[ L^d_{22} \geq 0, \quad L^a_{00} \geq 0, \quad L^a_{11} \geq 0, \quad L^0 \geq 0, \quad L^d_{11} L^d_{22} \geq (L^d_{12})^2 \]

are the consequences of the Second Law of Thermodynamics.

According to CASIMIR’s reciprocal relations, the Second Law gives no restrictions on the values of \( L^d_{01} \) and \( L^d_{20} \). The general theory does not imply any further restriction on the value of the coefficients but the analysis of some particular situations makes other simplifications obvious.

Equation (2.41) shows that the pseudo scalar \( \alpha^0 \) tends to zero even if it were nonzero some time ago and it cannot be excited at later times, because there is no coupling to other variables. Therefore, after some relaxation time, \( \alpha^0 \) is always zero.
Because the trace of $\Pi$ does not appear in the balance of energy and in the entropy production it is not relevant, and we conclude that the distinction between the symmetric and the deviatoric parts of the tensor $\Pi$ is not necessary, i.e.,

$$\Pi^s = \Pi^d.$$ 

There is no coupling between the symmetric part of the velocity gradient (the affine deformation of the fluid) and the distortion of the fibers because $\dot{\alpha}$ is the only second order polar tensor among the thermodynamic forces. If we had regarded the affine deformation of particles in the liquid, equation (2.38) should have turned to the relation known in visco-elasticity [49], [53].

2.5. **Further considerations.** Up to here, the balance equations in general and the dissipation inequality have been used only. Now we consider a special case, a flow field which is such that the distortion of a previously un-distorted fiber is the same as that of a fluid element, i.e., the equation

$$(2.44) \quad \dot{\varphi} = \nabla \omega \cdot n$$

holds if $\alpha^a = \alpha^d = T = 0$. Comparing it with equation (2.13) and using equations (2.39) and (2.40) and (2.41) we get that

$$\nabla \omega \cdot n = L_{10}^a (\nabla \omega)^a \cdot n + L_{10}^d (\nabla \omega)^d \cdot n - L_{10}^d n [n \cdot (\nabla \omega)^d \cdot n] + L_{20}^d [n \cdot (\nabla \omega)^d \cdot n]$$

must hold for any $n$. This equation is compared with the general decomposition of the tensor $\nabla \omega$ into its symmetric part and antisymmetric part. As the phenomenological coefficients do not depend on the flow geometry, we conclude that

$$\nabla \omega \cdot n = L_{10}^a (\nabla \omega)^a \cdot n + L_{10}^d (\nabla \omega)^d \cdot n - L_{10}^d n [n \cdot (\nabla \omega)^d \cdot n] + L_{20}^d [n \cdot (\nabla \omega)^d \cdot n]$$

must hold for any $n$. This equation is compared with the general decomposition of the tensor $\nabla \omega$ into its symmetric part and antisymmetric part. As the phenomenological coefficients do not depend on the flow geometry, we conclude that

$$(2.46) \quad L_{10}^a = L_{10}^d = 1 \quad \text{and} \quad L_{10}^d = L_{20}^d.$$ 

If we make the reasonable assumption that the bend relaxes with a single relaxation time and that the twist and the bend relax separately, we get that

$$\nabla \omega \cdot n = L_{10}^a (\nabla \omega)^a \cdot n + L_{10}^d (\nabla \omega)^d \cdot n - L_{10}^d n [n \cdot (\nabla \omega)^d \cdot n] + L_{20}^d [n \cdot (\nabla \omega)^d \cdot n]$$

must hold for any $n$. This equation is compared with the general decomposition of the tensor $\nabla \omega$ into its symmetric part and antisymmetric part. As the phenomenological coefficients do not depend on the flow geometry, we conclude that

$$(2.46) \quad L_{10}^a = L_{10}^d = 1 \quad \text{and} \quad L_{10}^d = L_{20}^d.$$ 

If we make the reasonable assumption that the bend relaxes with a single relaxation time and that the twist and the bend relax separately, we get that

$$(2.47) \quad 3L_{11}^d = 5L_{11}^a \quad \text{and} \quad L_{12}^d = 0.$$ 

These are relations between the constant (within the linear theory) constitutive coefficients, and therefore they are valid not only in the special case.

With these results the constitutive equations (2.39) get the form

$$\Pi = L_{00} (\nabla \omega)^d + L_{00}^a (\nabla \omega)^a - \frac{L_{10}^a}{3} \alpha^d - \frac{L_{10}^d}{3} \alpha^a - \frac{2L_{10}^d}{15} T,$$

$$(2.48) \quad \dot{\alpha} = (\nabla \omega) - L_{11}^d \frac{L_{10}^d}{3} \alpha,$$

$$\dot{T} = (\nabla \omega)^a - L_{22}^d \frac{2L_{10}^d}{15} T.$$ 

The number of material coefficients to be determined experimentally has been reduced to six.

We have shown that the stress tensor may have a skew symmetric part in a fiber suspension. The equations of motion are those of a micropolar continuum. Moreover, the theory based on the approximation in equation (2.13) takes into account the fact that the twist
and the bend of the fibers relax with different relaxation times. The authors expect, that the improvement of the approximation (2.13) to higher orders does not change the equations because of the nature of the isotropic tensors. To decide if it is really so needs further investigations.

3. Exploitation of the dissipation inequality according to LIU

In this section we want to derive the restrictions on constitutive functions for fiber suspensions by the method of LIU [18]. From a very basic amendment to the second law of thermodynamics on physical arguments [63] one can show that the requirement of a positive entropy production density restricts possible constitutive functions and does not rule out certain process directions in non-equilibrium. The most general way to derive these restrictions on constitutive functions is the method by LIU [18]. The restrictions follow after the set of variables for material properties, the state space, has been chosen. They do not completely determine the material behavior, as it is natural, because there are different materials with the same set of variables, but different constitutive properties. The results of this method give the most general framework compatible with the second law of thermodynamics. In the example of fiber suspensions we chose the state space

\begin{equation}
Z = \{\rho, T, \mathbf{v}, \nabla \mathbf{v}, \mathbf{Q}, \mathbf{O}, \Omega\}
\end{equation}

where all constitutive quantities are assumed not to depend on \( \mathbf{v} \). This state space is related to the set of variables in the domain of the constitutive functions entropy and internal energy in the previous section. Apart from the equilibrium variables mass density and temperature it includes the velocity gradient, an orthogonal second order tensor \( \mathbf{Q} \) describing the local fiber orientation (which is assumed variable here). \( \mathbf{Q} \) is the mapping between the orientation vector of the (undistorted) fiber and a reference coordinate system. With the tensor \( \mathbf{Q} \) it would also be possible to account for the orientation of biaxial elements, such as plates, but this is out of the scope of the present paper. It is possible here, that there is an arbitrary distribution of fiber orientations. Then the orientation distribution function can be approximated by a second order tensor, denoted as \( \mathbf{A} \). The definition of this second order tensor from the distribution function will be discussed in section 4. Then the tensor \( \mathbf{Q} \) is the mapping between the coordinate axes and the principal axes of the tensor \( \mathbf{A} \).

We also include the second order tensor \( \mathbf{O} \) for the local deformation of the fibers. \( \mathbf{O} \) is defined as

\begin{equation}
\mathbf{O} = \frac{1}{2} (\langle \nabla \mathbf{Q}^T \rangle \cdot \mathbf{Q} : \epsilon)
\end{equation}

with the totally antisymmetric third order tensor \( \epsilon \).
In contrast to the previous section we also include the time derivative \( \Omega \) of the fiber orientation:

\[
\frac{\partial Q}{\partial t} = \Omega \times Q
\]

in the set of relevant variables for constitutive functions.

As the materials discussed here are micropolar media we will take into account the balance of internal angular momentum in addition to the balances of mass, momentum, and energy. The following inequality has to be exploited:

\[
\rho \frac{d\eta}{dt} + \nabla \cdot \phi - \frac{r}{T} + \lambda^\rho \left( \frac{d\rho}{dt} + \rho \nabla \cdot v \right) + \lambda^p \left( \frac{dv}{dt} - \nabla \cdot t - \rho f \right) + \lambda^\alpha \left( \rho \frac{du}{dt} + \nabla \cdot q - \nabla v - r + \Pi : \nabla \Omega \right) + \lambda^s \cdot \left( \rho \frac{ds}{dt} - \epsilon : t + \nabla \cdot \Pi T + \rho m \right) \geq 0
\]

After exploiting the differentiations of the constitutive functions, defined on the state space \((3.1)\), according to the chain rule it results an inequality linear in the following higher derivatives:

\[
\hat{T}, \hat{\rho}, \hat{v}, \frac{d(\nabla v)}{dt}, \hat{O}, \hat{\Omega}, \nabla \rho, \nabla T, \nabla \nabla v, \nabla O, \nabla \Omega
\]

These higher derivatives are not all independent, but one constraint between them has to be taken into account. To show this we will use components with respect to a cartesian coordinate system:

**Proposition:**

\[
\frac{dO}{dt} = (\nabla \Omega)^T + \frac{1}{2} \left( \epsilon \cdot Q : \frac{\partial Q^T}{\partial x} \right) \cdot \frac{\partial v}{\partial x}
\]

or in components

\[
\frac{dO_{ik}}{dt} = \frac{\partial O_i}{\partial x_k} + \frac{1}{2} \epsilon_{ilm} Q_{ls} \frac{\partial Q_{rs}}{\partial x_m} \frac{\partial v_m}{\partial x_k}.
\]

The proof of this proposition is shown in the appendix. \( Q, \nabla v \) and \( \nabla Q \) are state space variables, whereas \( \nabla \Omega \) is not included in the state space. This gradient shows up in the list of higher derivatives.
After inserting this constraint we can write down the LIU-equations, corresponding to the different higher derivatives:

\[
\begin{align*}
\dot{\rho} : & \quad \rho \frac{\partial \eta}{\partial \rho} + \lambda^u \rho \frac{\partial u}{\partial \rho} + \lambda^p + \rho \lambda^s \cdot \frac{\partial s}{\partial \rho} = 0 \\
\dot{T} : & \quad \rho \frac{\partial \eta}{\partial T} + \lambda^u \rho \frac{\partial u}{\partial T} + \rho \lambda^s \cdot \frac{\partial s}{\partial T} = 0 \\
\nabla v : & \quad \rho \frac{\partial \eta}{\nabla v} + \lambda^u \rho \frac{\partial u}{\nabla v} + \rho \lambda^s \cdot \frac{\partial s}{\nabla v} = 0 \\
\nabla \Omega : & \quad \rho \frac{\partial \eta}{\nabla \Omega} + \frac{\partial \Phi}{\nabla \Omega} - \lambda^p \cdot \frac{\partial t}{\nabla \Omega} + \\
& \quad \rho \lambda^s \cdot \left( \frac{\partial s}{\nabla \Omega} - \frac{\partial \Pi}{\nabla \Omega} \right) + \lambda^u \frac{\partial q}{\nabla \Omega} = 0 \\
\dot{\omega} : & \quad \rho \frac{\partial \eta}{\dot{\omega}} + \lambda^u \frac{\partial u}{\dot{\omega}} + \rho \lambda^s \cdot \frac{\partial s}{\dot{\omega}} = 0 \\
\nabla \rho : & \quad \frac{\partial \Phi}{\nabla \rho} - \lambda^p \cdot \frac{\partial t}{\nabla \rho} - \lambda^s \cdot \frac{\partial \Pi}{\nabla \rho} + \lambda^u \frac{\partial q}{\nabla \rho} = 0 \\
\nabla T : & \quad \frac{\partial \Phi}{\nabla T} - \lambda^p \cdot \frac{\partial t}{\nabla T} - \lambda^s \cdot \frac{\partial \Pi}{\nabla T} + \lambda^u \frac{\partial q}{\nabla T} = 0 \\
\nabla \rho : & \quad \frac{\partial \Phi}{\nabla \rho} - \lambda^p \cdot \frac{\partial t}{\nabla \rho} - \lambda^s \cdot \frac{\partial \Pi}{\nabla \rho} + \lambda^u \frac{\partial q}{\nabla \rho} = 0 \\
\frac{dv}{dt} : & \quad \rho \lambda^p = 0 \; .
\end{align*}
\]

From this set of equations the multipliers \( \lambda^p, \lambda^v, \lambda^s, \) and \( \lambda^u \) can be calculated. Between the specific spin density and the orientation change velocity \( \Omega \) the relation

\[
(3.18) \quad s = \Theta \cdot \Omega
\]

holds. \( \Theta \) is the moment of inertia tensor, which is assumed to be constant. In case of suspensions of flexible fibers this is only an approximation, because in principle this tensor changes if the fibers are deformed. We assume here that these deformations are small and the variation of \( \Theta \) can be neglected. Then the specific spin density \( s \) depends only on the orientation change velocity \( \Omega \), and all other partial derivatives vanish. In this case we have

\[
(3.19) \quad \frac{\partial s}{\partial \Omega} = \Theta
\]
and the equations for the multipliers simplify to

\[
\lambda^u = -\frac{\partial \eta}{\partial T} = -\frac{1}{T}
\]

(3.20)

\[
\lambda^\rho = -\rho \frac{\partial \eta}{\partial \rho} + \frac{1}{T} \frac{\partial u}{\partial \rho}
\]

(3.21)

\[
\lambda^s = -\frac{\partial \left( \eta - \frac{1}{T} u \right)}{\partial \Omega} \cdot \Theta^{-1}
\]

(3.22)

\[
\lambda^p = 0
\]

(3.23)

for the derivative \(\frac{\partial \eta}{\partial T}\) we insert \(\frac{1}{T}\). This relation is known in equilibrium. In non-equilibrium it needs some additional argumentation, which can be found in [64].

The remaining equations (3.10), (3.11), (3.13), (3.14), (3.15), and (3.16) give after inserting the multipliers the restrictions on constitutive functions. This will be shown here only under the assumption of a constant moment of inertia tensor. We have:

\[
\frac{\partial \left( \eta - \frac{1}{T} u \right)}{\partial \nabla v} = 0
\]

(3.24)

\[
\Pi = -\frac{1}{T} \left( \rho \frac{\partial \left( \eta - \frac{1}{T} u \right)}{\partial \mathcal{O}} + \frac{\partial \Phi}{\partial \Omega} \right) + \frac{\partial \left( \eta - \frac{1}{T} u \right)}{\partial \mathcal{O}} \cdot (\Theta^{-1} \cdot \frac{\partial \Pi}{\partial \Omega})
\]

(3.25)

\[
\frac{\partial \Phi}{\partial \rho} - \frac{1}{T} \frac{\partial q}{\partial \rho} = -\frac{\partial \left( \eta - \frac{1}{T} u \right)}{\partial \Omega} \cdot (\Theta^{-1} \cdot \frac{\partial \Pi}{\partial \Omega})
\]

(3.26)

\[
\frac{\partial \Phi}{\partial T} - \frac{1}{T} \frac{\partial q}{\partial T} = -\frac{\partial \left( \eta - \frac{1}{T} u \right)}{\partial \mathcal{O}} \cdot (\Theta^{-1} \cdot \frac{\partial \Pi}{\partial \mathcal{O}})
\]

(3.27)

\[
\frac{\partial \Phi}{\partial \nabla v} - \frac{1}{T} \frac{\partial q}{\partial \nabla v} = -\frac{\partial \left( \eta - \frac{1}{T} u \right)}{\partial \mathcal{O}} \cdot (\Theta^{-1} \cdot \frac{\partial \Pi}{\partial \nabla v})
\]

(3.28)

\[
\frac{\partial \Phi}{\partial \mathcal{O}} - \frac{1}{T} \frac{\partial q}{\partial \mathcal{O}} = -\frac{\partial \left( \eta - \frac{1}{T} u \right)}{\partial \mathcal{O}} \cdot (\Theta^{-1} \cdot \frac{\partial \Pi}{\partial \mathcal{O}})
\]

(3.29)

Introducing the free energy density \(f := u - T \eta\) and the difference \(k = \Phi - \frac{1}{T} q\) the resulting restrictions on the constitutive functions can be written as:

\[
\frac{\partial f}{\partial \nabla v} = 0
\]

(3.30)

\[
\Pi = \frac{1}{T^2} \frac{\partial f}{\partial \Omega} + \frac{1}{T} \frac{\partial \Phi}{\partial \Omega} - \frac{1}{T^2} \frac{\partial f}{\partial \Omega} \cdot (\Theta^{-1} \cdot \frac{\partial \Pi}{\partial \Omega})
\]

(3.31)

\[
\frac{\partial k}{\partial u_i} = \frac{1}{T} \frac{\partial f}{\partial \mathcal{O}} \cdot (\Theta^{-1} \cdot \frac{\partial \Pi}{\partial u_i}) \quad \text{for} \quad u_i \in \{\rho, T, \nabla v, \mathcal{O}\}
\]

(3.32)

Equation (3.32) shows that the difference \(k = \Phi - \frac{1}{T} q\) is surely non-zero, if the free energy density depends on the orientation change velocity (\(\frac{\partial f}{\partial \mathcal{O}} \neq 0\)), and if the couple stresses \(\Pi\) depend on any of the constitutive functions.
variables $\rho, T, \nabla v, O$. In this case the very frequently made constitutive assumption (see for instance Irreversible Thermodynamics) of the entropy flux $\Phi$ being heat flux divided by temperature is not fulfilled.

Equation (3.31) is a differential equation for the couple stress. It reduces to an algebraic equation, if the free energy density does not depend on $\Omega$. In this case the couple stresses can be calculated as a derivative of the free energy density

$$
(3.33) \quad \Pi = \frac{1}{T^2 \rho} \frac{\partial f}{\partial O}.
$$

3.1. The entropy production. The residual inequality is built up by all terms in equation (3.3), which contain no higher derivatives, but only state space functions. The constraint equation (3.7) has been inserted, and $z = \frac{\tau}{T}$. We will deal here only with the case of a constant moment of inertia tensor. For the multipliers equations (3.20) to (3.23) have to be inserted:

$$
\sigma = \rho \frac{\partial \eta}{\partial Q} : \dot{Q} - \frac{\rho}{2} \frac{\partial \eta}{\partial O} \cdot \nabla v \cdot (\nabla Q) \cdot Q^T : \epsilon + \frac{\partial \Phi}{\partial Q} \cdot \frac{\partial Q}{\partial x} + \lambda^p \nabla \cdot v - \lambda^s \left( \frac{\partial \Pi^T}{\partial Q} : \frac{\partial Q}{\partial x} + \rho m - \epsilon : t \right)
$$

$$
+ \lambda^u \left( \rho \frac{\partial u}{\partial Q} : \dot{Q} - \frac{\rho}{2} \frac{\partial u}{\partial O} \cdot \nabla v \cdot (\nabla Q) \cdot Q^T : \epsilon + (\epsilon : t) \cdot s \right)
$$

$$
+ \frac{\partial q}{\partial Q} \cdot \frac{\partial Q}{\partial x} - t : (\nabla v) + \rho f \cdot v
$$

$$
= \frac{\rho}{2} \frac{\partial \eta}{\partial Q} \cdot \dot{Q} - \frac{1}{T} \rho \frac{\partial f}{\partial \rho} \cdot \nabla v \cdot \frac{1}{T} \frac{\partial f}{\partial \rho} \cdot \Theta^{-1} \cdot \left( \frac{\partial \Pi^T}{\partial Q} : \frac{\partial Q}{\partial x} + \rho g - \epsilon : t \right)
$$

$$
- \frac{1}{T} \left( \rho \frac{\partial u}{\partial Q} : \dot{Q} - \frac{\rho}{2} \frac{\partial u}{\partial O} \cdot \nabla v \cdot (\nabla Q) \cdot Q^T : \epsilon + (\epsilon : t) \cdot s \right)
$$

$$
+ \frac{\partial q}{\partial Q} \cdot \frac{\partial Q}{\partial x} - t : (\nabla v) + \rho f \cdot v
$$
\[
\begin{align*}
\dot{Q} &= \frac{\rho}{T} \frac{\partial f}{\partial Q} \\
\text{change of orientational order} \\
+ \frac{\rho}{2T} \frac{\partial f}{\partial Q} \cdot \nabla v \cdot (\nabla Q) \cdot Q^T : \varepsilon \\
\text{coupling between viscous flow and orientational order} \\
+ \frac{\partial k}{\partial Q} : \frac{\partial Q}{\partial x} + \frac{1}{T} \rho \frac{\partial f}{\partial \rho} \nabla \cdot v \\
\text{transport of orientation} & \quad \text{viscous flow} \\
- \frac{1}{T} \frac{\partial f}{\partial \Omega} \cdot \Theta^{-1} \cdot \left( \frac{\partial \Pi^T}{\partial Q} : \frac{\partial Q}{\partial x} \right) \\
\text{coupling between change of orientation and gradient of orientation} \\
- \frac{1}{T} \left( (\varepsilon : t) \cdot s - t : (\nabla v) + \rho f \cdot v \right) \geq 0.
\end{align*}
\]

The interpretation of the different terms is given in the equation.

The first term in the entropy production, due to change of the orientational order is analogous to the terms involving \( \alpha^0, \alpha^d, \) and \( T \) in the first section. Both are due to changes of the internal variable. The next term is new, because in this part here we have allowed for a dependence of the free energy density on the spatial gradient of the internal variable. A term due to transport of orientation does not show up in the entropy production according to Irreversible Thermodynamics because there the vector \( k \) is assumed to be always zero. The next term due to viscous flow and the term \( t : \nabla v \) appear in both method of exploiting the dissipation inequality. Terms involving the derivative of the free energy density with respect to the orientation change velocity are new, because the rotation of fibers was not taken into account in the Irreversible Thermodynamics treatment. On the other hand, in this section we were not interested in heat conduction, and the temperature gradient was not included in the state space.

4. **Mesoscopic theory of fiber suspensions**

Fiber suspensions are an example of so called complex materials, meaning materials with an internal structure, which can change under the action of external fields resulting in complex material behavior. The element of internal structure in our example is the orientation and deformation of the fiber. There are two principally different possibilities to deal with complex materials within continuum thermodynamics: The first way is to introduce additional fields depending on position and time. These fields can be internal variables [63, 66], order or damage parameters [67], Cosserat-triads [68], directors [69, 70], alignment and conformation tensors [71, 72]. The other way is a so called mesoscopic theory. The idea is to enlarge the domain of the field quantities. The
new mesoscopic fields are defined on the space \( \mathbb{R}_x^3 \times \mathbb{R}_t \times M \). The manifold \( M \) is given by the set of values the internal degree of freedom can take. Therefore the choice of \( M \) depends on the complex material under consideration. We will see later that the manifold \( M \) should be such that differentiation and integration is possible on it. We call this way of dealing with the internal structure of complex materials a mesoscopic concept, because it includes more information than a macroscopic theory on \( \mathbb{R}_x^3 \times \mathbb{R}_t \), but the molecular level is not considered like in a microscopic approach. The mesoscopic level is between the microscopic and the macroscopic level. The domain of the mesoscopic field quantities \( \mathbb{R}_x^3 \times \mathbb{R}_t \times M \) is called mesoscopic space. The orientation of an undeformed fiber is described by a unit vector \( \hat{n} \), where turning around the fiber by \( \pi \) does not change the orientation and therefore \( \hat{n} \to -\hat{n} \) is a symmetry transformation. The vector \( \hat{n} \) is an element of the unit sphere \( S^2 \). The deformation of the fiber is given by the vector \( \hat{\phi} \) introduced in the first part. The difference between that first part of the paper and the mesoscopic theory is, that now fiber orientation and deformation are not introduced as macroscopic quantities, but as variables in the domain of fields. To distinguish these two kinds of quantities all mesoscopic quantities are denoted with a \(^\wedge\). We will see later that this way we can deal with different fiber orientations and deformations within one volume element of continuum theory. In our example of fibers the manifold \( M \) is the product of the set of values the orientation and deformation of a fiber can take: \( M = S^2 \times \mathbb{R}_x^3 \) with \( \hat{n} \in S^2 \) and \( \hat{\phi} \in \mathbb{R}_x^3 \). In order to be treated within a mesoscopic theory the length of the fibers must be smaller than the linear dimension of the continuum element, meaning that the fibers must be smaller than any macroscopically interesting length scale. Therefore this mesoscopic concept cannot be applied to fiber composite materials with long fibers.

Beyond the use of additional variables \( m \) the mesoscopic concept introduces a statistical element, the so-called mesoscopic distribution function (MDF) generated by the different values of the mesoscopic variable in a volume element. Here this is a distribution of fiber orientations and deformations \( f(\hat{n}, \hat{\phi}, x, t) \) in the volume element at position \( x \) and time \( t \). This distribution function gives the probability density of finding a fiber of a specified orientation and deformation in this volume element. It is normalized

\[
\int_{\mathbb{R}_x^3} \int_{S^2} f(\hat{n}, \hat{\phi}, x, t) \, d^2\hat{n} d^3\hat{\phi} = 1.
\]

4.1. Mesoscopic balance equations. Now fields as mass density, momentum density, etc. are defined on the mesoscopic space. For distinguishing these fields from the macroscopic ones we add the word “mesoscopic”. For instance the mesoscopic mass density \( \hat{\rho}(\hat{n}, \hat{\phi}, x, t) \) is the mass density taking into account only fibers of a specified orientation \( \hat{n} \) and deformation \( \hat{\phi} \). The macroscopic mass density is the integral over all possible orientations and deformations:

\[
\int_{\mathbb{R}_x^3} \int_{S^2} \hat{\rho}(\hat{n}, \hat{\phi}, x, t) \, d^2\hat{n} d^3\hat{\phi} = \rho(x, t) .
\]
From this equation and the interpretation of the distribution function as probability density it is clear that the MDF is given by the mass fraction:

\[
(4.2) \quad f(\hat{n}, \hat{\varphi}, x, t) = \frac{\rho(\hat{n}, \hat{\varphi}, x, t)}{\rho(x, t)}.
\]

For any kind of set of mesoscopic variables balance equations can be derived for the mesoscopic field quantities (see for instance [23]) starting out from the macroscopic global ones [22, 73, 23, 74]. A generalized Reynolds transport theorem in the mesoscopic space [75] is used to transform the time derivative, and Gauss theorem is applied. For the fiber suspensions in regular points of the continuum there result the local mesoscopic balance equations. We will show here only the balance of mass and the balance of momentum with the abbreviation \((\cdot) = (\hat{n}, \hat{\varphi}, x, t)\). Similarly mesoscopic balance equations of energy and of angular momentum can be derived. There is a balance of angular momentum independently from the balance of momentum, because rotations of the fibers result in an internal angular momentum.

**Mesoscopic balance of mass**

\[
(4.3) \quad \frac{\partial}{\partial t} \hat{\rho}(\cdot) + \nabla_x \cdot (\hat{\rho}(\cdot) \hat{\mathbf{v}}(\cdot)) + \nabla_n \cdot \left( \hat{\rho}(\cdot) \hat{\mathbf{n}}(\cdot) \right) + \nabla_{\varphi} \left( \rho(\cdot) \dot{\varphi}(\cdot) \right) = 0.
\]

\(\hat{\mathbf{v}}(\cdot)\) is the material velocity of fibers of a specified orientation and length, \(\hat{\mathbf{n}}\) is the orientation change velocity, and \(\dot{\varphi}(\cdot)\) is the deformation change velocity.

**Mesoscopic balance of momentum**

\[
(4.4) \quad \frac{\partial}{\partial t} (\hat{\rho}(\cdot) \hat{\mathbf{v}}(\cdot)) + \nabla_x \cdot (\hat{\rho}(\cdot) \hat{\mathbf{v}}(\cdot) \hat{\mathbf{v}}(\cdot) - \hat{\mathbf{t}}(\cdot)) + \\
+ \nabla_n \cdot \left( \hat{\mathbf{n}}(x, t) \hat{\rho}(\cdot) \hat{\mathbf{v}}(\cdot) - \hat{T}(\cdot) \right) + \nabla_{\varphi} \left( \dot{\rho}(\cdot) \hat{\varphi}(\cdot) \hat{\mathbf{v}}(\cdot) - \hat{\tau}(\cdot) \right) = \\
\hat{\rho}(\cdot) \hat{\mathbf{f}}(\cdot).
\]

Here \(\hat{\mathbf{f}}(\cdot)\) is the external acceleration density, \(\hat{\mathbf{t}}(\cdot)\) the stress tensor, and \(\hat{T}(\cdot)\) the stress tensor on orientation space (non-convective momentum flux in orientation space), \(\hat{\tau}(\cdot)\) is the momentum flux vector with respect to the fiber deformation variable, all quantities defined on the mesoscopic set of variables.

As always in continuum theory the balance equations do not form a closed set of differential equations, but constitutive equations are needed, now on the mesoscopic level. We are interested here mainly in the constitutive equation for the stress tensor.

**4.2. Orientational order parameter and deformation variable.**

The aim is to introduce macroscopic quantities from this mesoscopic background, which describe the distribution of fiber orientations and the average distortion of fibers. These are internal variables in the sense of thermodynamics.
Orientational order parameters

\begin{equation}
A^k = \int_{S^2} \int_{\mathbb{R}^3} f(\hat{\varphi}, \hat{n}, x, t) \hat{n}_k \cdot \hat{n} d^3 \hat{\varphi} d^2 \hat{n},
\end{equation}

deformation order parameters:

\begin{equation}
\Phi^k = \int_{S^2} \int_{\mathbb{R}^3} f(\hat{\varphi}, \hat{n}, x, t) \hat{\varphi}_k \cdot \hat{n} d^3 \hat{\varphi} d^2 \hat{n}.
\end{equation}

These order parameters are tensors of successive order. They are macroscopic fields depending on position and time. With respect to fiber orientations we have the symmetry transformation \( \hat{n} \to -\hat{n} \). Therefore all odd order orientational order parameters vanish, and the first non-zero order parameter, apart from the isotropic part \( A^0 = 1 \) is the second order one: \( A^2 \). This can be included as an internal variable in a macroscopic exploitation of the dissipation inequality, like the tensor internal variable \( Q \) in section 3.

With the mesoscopic background it is possible to derive also equations of motion for these variables, which will be left for a future work.

4.3. Mesoscopic and macroscopic stress tensor. The extensive quantity momentum has to be the integral over all mesoscopic momenta:

\begin{equation}
\rho(x, t) v(x, t) = \int_{S^2} \int_{\mathbb{R}^3} \rho(x, t, \hat{\varphi}, \hat{n}) \hat{v}(x, t, \hat{\varphi}, \hat{n}) d^3 \hat{\varphi} d^2 \hat{n},
\end{equation}

Integrating equation (4.4) over all fiber orientations and fiber deformations we must obtain the macroscopic balance of momentum (2.20). This gives a relation between the mesoscopic and the macroscopic stress tensor. With the abbreviation \((\cdot) = (x, t, \hat{\varphi}, \hat{n})\) we have

\begin{equation}
\int_{S^2} \int_{\mathbb{R}^3} \left( \frac{\partial}{\partial t} (\hat{\varphi}(\cdot) \hat{\varphi}(\cdot)) + \nabla_x \cdot (\hat{\varphi}(\cdot) \hat{\varphi}(\cdot) \hat{v}(\cdot) - \hat{\varphi}(\cdot) \hat{\varphi}(\cdot)) +
\nabla_x \cdot \left( \hat{n}(x, t) \hat{\varphi}(\cdot) \hat{\varphi}(\cdot) - \hat{T}(\cdot) \right) + \nabla_\varphi \left( \hat{\varphi}(\cdot) \hat{\varphi}(\cdot) \hat{\varphi}(\cdot) - \hat{\varphi}(\cdot) \hat{T}(\cdot) \right) d^3 \hat{\varphi} d^2 \hat{n} \right) = 0
\end{equation}

Integrating the divergence terms over the whole mesoscopic space gives, according to GAUSS-theorem boundary terms. The orientational part of the mesoscopic space, the unit sphere, is a closed surface, i.e. without boundary. Concerning the deformation variable we suppose that deformation cannot have arbitrarily large values, and therefore there is no flux over the boundary at infinity. We conclude that the last two integrals on the left hand side vanish, and we end up with the equation

\begin{equation}
\frac{\partial}{\partial t} \int_{S^2} \int_{\mathbb{R}^3} (\hat{\varphi}(\cdot) \hat{\varphi}(\cdot)) d^3 \hat{\varphi} d^2 \hat{n} + \nabla_x \cdot \int_{S^2} \int_{\mathbb{R}^3} (\hat{\varphi}(\cdot) \hat{\varphi}(\cdot) \hat{v}(\cdot) - \hat{\varphi}(\cdot) \hat{\varphi}(\cdot)) d^3 \hat{\varphi} d^2 \hat{n} =
\end{equation}

\begin{equation}
\int_{S^2} \int_{\mathbb{R}^3} \hat{\varphi}(\cdot) \hat{\varphi}(\cdot) \hat{f}(\cdot) d^3 \hat{\varphi} d^2 \hat{n}.
\end{equation}
Comparing the divergence terms under the space derivative with those in the macroscopic balance of momentum we have:

\[
\int_{S^2} \int_{\mathbb{R}^3} \left( \hat{\mathbf{v}}(\cdot) \hat{\varrho}(\cdot) \hat{\mathbf{v}}(\cdot) - \hat{\mathbf{t}}(\cdot) \right) d^3 \hat{\varphi} d^2 \hat{n} = \rho \mathbf{v} - \mathbf{t} .
\]

We conclude that for the constitutive quantity stress tensor the following relation holds

\[
\mathbf{t}(\mathbf{x}, t) = \int_{S^2} \int_{\mathbb{R}^3} \left( \hat{\mathbf{t}}(\cdot) - \hat{\varrho}(\cdot) \hat{\delta \mathbf{v}}(\cdot) \hat{\delta \mathbf{v}}(\cdot) \right) d^3 \hat{\varphi} d^2 \hat{n}
\]

with the abbreviation

\[
\hat{\delta \mathbf{v}}(\cdot) = \hat{\mathbf{v}}(\cdot) - \mathbf{v}(\mathbf{x}, t)
\]

This result shows that the fluxes, (here the stress tensor) are in general not simply the integrals of the corresponding mesoscopic quantities over the mesoscopic variables. This is true only for the extensive quantities.

If all fibers have the same translational velocity, then \( \hat{\delta \mathbf{v}}(\cdot) = 0 \) and the macroscopic stress tensor is the integral over all mesoscopic ones:

\[
\mathbf{t} = \int_{S^2} \int_{\mathbb{R}^3} \hat{\mathbf{t}}(\cdot) d^3 \hat{\varphi} d^2 \hat{n} .
\]

The mesoscopic stress tensor is a constitutive quantity, defined on a suitable set of variables. This set of variables can include mesoscopic quantities as well as macroscopic quantities. A reasonable assumption for the set of variables is:

\[
\hat{\mathcal{Z}} = \{ \rho, T, \hat{\mathbf{n}}, \hat{\varphi}, \hat{\mathbf{d}}, \nabla \times \mathbf{v} \} .
\]

With this set of variables a representation theorem to linear order in the velocity gradient and the deformation variable \( \hat{\varphi} \) gives the following expression for the mesoscopic stress tensor:

\[
\hat{\mathbf{t}} = \frac{\hat{\varrho}}{\rho} \left( \alpha_1 \hat{\mathbf{n}} \hat{\mathbf{n}} + \alpha_2 \hat{\mathbf{n}} \hat{\varphi} + \alpha_3 \hat{\varphi} \hat{\mathbf{n}} + \alpha_4 \hat{\mathbf{n}} (\nabla \times \mathbf{v}) + \alpha_5 (\nabla \times \mathbf{v}) \hat{\mathbf{n}} + \alpha_6 \hat{\mathbf{d}} \right.
\]

\[
\left. + \alpha_7 \hat{\mathbf{n}} \cdot \hat{\mathbf{d}} + \alpha_8 \hat{\mathbf{n}} \cdot \hat{\mathbf{d}} \hat{\mathbf{n}} + \alpha_9 \hat{\mathbf{n}} \cdot \hat{\mathbf{d}} \cdot \hat{\mathbf{n}} \hat{\mathbf{n}} \right) ,
\]

where the material coefficients \( \alpha_1 \) to \( \alpha_9 \) may all depend on the (macroscopic) mass density \( \rho \) and temperature \( T \).

Averaging this over the mesoscopic variables we obtain according to equation (4.13):

\[
\mathbf{t} = \int_{S^2} \int_{\mathbb{R}^3} \frac{\hat{\varrho}}{\rho} \left( \alpha_1 \hat{\mathbf{n}} \hat{\mathbf{n}} + \alpha_2 \hat{\mathbf{n}} \hat{\varphi} + \alpha_3 \hat{\varphi} \hat{\mathbf{n}} + \alpha_4 \hat{\mathbf{n}} (\nabla \times \mathbf{v}) + \alpha_5 (\nabla \times \mathbf{v}) \hat{\mathbf{n}} + \alpha_6 \hat{\mathbf{d}} \right.
\]

\[
\left. + \alpha_7 \hat{\mathbf{n}} \cdot \hat{\mathbf{d}} + \alpha_8 \hat{\mathbf{n}} \cdot \hat{\mathbf{d}} \hat{\mathbf{n}} + \alpha_9 \hat{\mathbf{n}} \cdot \hat{\mathbf{d}} \cdot \hat{\mathbf{n}} \hat{\mathbf{n}} \right) d^3 \hat{\varphi} d^2 \hat{n} .
\]

\[
= \alpha_1 \mathbf{A}^2 + \alpha_2 \langle \hat{\mathbf{n}} \hat{\varphi} \rangle + \alpha_3 \langle \hat{\varphi} \hat{\mathbf{n}} \rangle + \alpha_6 \hat{\mathbf{d}} d^2 \hat{\varphi} d^2 \hat{n}
\]

\[
+ \alpha_4 \hat{\mathbf{n}} \cdot \hat{\mathbf{d}} + \alpha_5 \hat{\mathbf{n}} \cdot \hat{\mathbf{d}} \hat{\mathbf{n}} + \alpha_9 \hat{\mathbf{n}} \cdot \hat{\mathbf{d}} \cdot \hat{\mathbf{n}} \hat{\mathbf{n}} ,
\]
The average of $\alpha_4 \hat{n}(\nabla \times \mathbf{v})$ vanishes, because $\int_{S^2} f \hat{n} d^2 n = 0$ due to the symmetry $\hat{n} \leftrightarrow -\hat{n}$, analogously for the term with $\alpha_5$. The averages $\langle \hat{n} \hat{\phi} \rangle$ and $\langle \hat{\phi} \hat{n} \rangle$ are non-zero, because they are even functions of $\hat{n}$:

\begin{equation}
\hat{\phi}(\hat{n}) = -\hat{\phi}(\hat{n})
\end{equation}

(see the first section) and therefore

\begin{equation}
-\hat{n} \hat{\phi}(\hat{n}) = \hat{n} \hat{\phi}(\hat{n})
\end{equation}

The stress tensor (4.16) clearly can have an antisymmetric part $t^a$:

\begin{equation}
t^a = \frac{1}{2} (\alpha_2 - \alpha_3) (\langle \hat{n} \hat{\phi} \rangle - \langle \hat{\phi} \hat{n} \rangle) + \frac{1}{2} (\alpha_7 - \alpha_8) \left( \mathbf{A} \cdot \mathbf{d} - \mathbf{d} \cdot \mathbf{A} \right)
\end{equation}

5. Conclusions

We have investigated the constitutive properties of suspensions of long fibers, which can be deformed. In the second and in the third part we have taken into consideration in addition the possibility of different fiber orientations. This complex material has been treated with three different methods. Two of these methods are different ways of exploiting the second law of thermodynamics in macroscopic continuum thermodynamics. The first method was classical Thermodynamics of Irreversible Processes (TIP). The second method of exploitation, the method according to LIU, is more related to Rational Thermodynamics. In both methods the aim is a derivation of information on constitutive functions, and the first method shows that in fiber suspensions there can exist an antisymmetric part of the stress tensor due to internal degrees of freedom. The method of TIP gives additional relaxation equations for the internal variables introduced in the beginning in order to account for the internal structure. Such relaxation equations cannot be derived by the method of LIU. The assumptions made in the beginning by this method are less restrictive, and the constitutive equations consistent with the results of the method by LIU are more general than the equations derived from TIP. It could be shown that the assumption made in TIP concerning the entropy flux being heat flux divided by temperature does not contradict the results of the LIU-procedure, if the free energy density does not depend on the orientation change velocity of the fibers. This assumption was made by the choice of variables in the first section. Therefore this exploitation is in agreement with the results of the LIU-procedure. However, if the orientation change velocity is included in the set of variables, the entropy flux might be not simply heat flux divided by temperature, as a result of the exploitation of the dissipation inequality. This can be interpreted as non-convective entropy transport due to change of fiber orientations. In addition couple stress could be calculated as a derivative of the free energy.

Finally the idea of a so called mesoscopic theory was sketched. There we introduced a finer description considering single fibers with different orientations and different states of deformation. The macroscopic quantities of the usual continuum theory are obtained by averaging.
over the different fiber orientations and different states of deformation. This method gives, apart from the usual balance equations, a definition of internal variables in terms of averages. Equations of motion for these internal variables will be discussed in a future paper. Another result shown here is the fact that the stress tensor calculated as an average of mesoscopic quantities has an antisymmetric part.

In the mesoscopic theory we did not deal further with the possibility that the orientation distribution of fibers and also the distribution of fiber deformations can change, for instance under the action of a flow field. It is expected that both effects have influence on material properties, a problem, that will be dealt with in a future work.

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Appendix: Proof of the proposition on the time derivative of the state space variable $O$

Proposition:

(5.1) \[ \frac{dO}{dt} = (\nabla \Omega)^T + \frac{1}{2} \left( \epsilon \cdot Q : \frac{\partial Q^T}{\partial x} \right) \cdot \frac{\partial v}{\partial x} \]

or in components

(5.2) \[ \frac{dO_{ik}}{dt} = \frac{\partial O_i}{\partial x_k} + \frac{1}{2} \epsilon_{irl} Q_{ls} \frac{\partial Q_{rs}}{\partial x_m} \frac{\partial v_m}{\partial x_k} . \]

Proof:
In components we have

\[
\frac{dO_{ik}}{dt} = -\frac{1}{2} \epsilon_{irl} \frac{d}{dt} \left( \frac{\partial Q_{rs}}{\partial x_k} Q_{ls} \right) = -\frac{1}{2} \epsilon_{irl} \left( \frac{d}{dt} \left( \frac{\partial Q_{rs}}{\partial x_k} \right) Q_{ls} + \frac{\partial Q_{rs}}{\partial x_k} \frac{dQ_{ls}}{dt} \right) = -\frac{1}{2} \epsilon_{irl} \left( \left( \frac{\partial}{\partial t} + v_m \frac{\partial}{\partial x_m} \right) \left( \frac{\partial Q_{rs}}{\partial x_k} \right) Q_{ls} + \frac{\partial Q_{rs}}{\partial x_k} \epsilon_{lkm} \Omega_k Q_{ms} \right) = -\frac{1}{2} \epsilon_{irl} \left( \left( \frac{\partial}{\partial t} + v_m \frac{\partial}{\partial x_m} \right) \frac{dQ_{rs}}{dt} \right) Q_{ls} + \frac{\partial Q_{rs}}{\partial x_k} \epsilon_{lkm} \Omega_k Q_{ms} = -\frac{1}{2} \epsilon_{irl} \left( \left( \frac{\partial}{\partial x_k} \frac{\partial Q_{rs}}{\partial t} - v_m \frac{\partial Q_{rs}}{\partial x_m} \right) Q_{ls} + \frac{\partial Q_{rs}}{\partial x_k} \epsilon_{lkm} \Omega_k Q_{ms} \right) = -\frac{1}{2} \epsilon_{irl} \left( \left( \frac{\partial}{\partial x_k} \left( \epsilon_{rop} \Omega_{lo} Q_{ps} \right) - v_m \frac{\partial Q_{rs}}{\partial x_m} \right) Q_{ls} + \frac{\partial Q_{rs}}{\partial x_k} \epsilon_{lkm} \Omega_k Q_{ms} \right) = \frac{1}{2} \left( (\delta_{io} \delta_{lp} - \delta_{ip} \delta_{lo}) \frac{\partial Q_{ps}}{\partial x_k} + \Omega_o \frac{\partial Q_{ps}}{\partial x_k} \right) Q_{ls} = \frac{1}{2} \left( \frac{\partial Q_{ls}}{\partial x_k} Q_{is} Q_{ls} - \frac{\partial Q_{ls}}{\partial x_k} Q_{is} Q_{ls} + \epsilon_{lir} v_m \frac{\partial Q_{rs}}{\partial x_m} Q_{ls} \right) = \frac{\partial O_i}{\partial x_k} Q_{ls} Q_{ls} - \frac{\partial O_i}{\partial x_k} Q_{ls} Q_{ls} + \epsilon_{lir} v_m \frac{\partial Q_{rs}}{\partial x_m} Q_{ls} = \frac{\partial O_i}{\partial x_k} + \frac{1}{2} \epsilon_{lir} v_m \frac{\partial Q_{rs}}{\partial x_m} Q_{ls} .
\]
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