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by

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# Creep and recrystallization of large polycrystalline masses

## Part II: constitutive theory for crystalline media with transversely isotropic grains†

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By combining the theory of mixtures with continuous diversity with Liu's method of Lagrange multipliers, a thermodynamically consistent constitutive theory is derived for large polycrystalline masses made up of transversely isotropic crystallites. The media under study are supposed to be incompressible and subjected to strain-induced anisotropy and recrystallization effects. Owing to the fabric (texture) changes caused by lattice rotation and polygonization, the polycrystal and its composing grains are modelled as polar media. Among other results of the theory, the existence of a *dislocation potential* is inferred, which represents for polycrystals the counterpart to the chemical potential of physical chemistry. Furthermore, exploitation of the dissipation inequality gives rise to the notion of a *driving pressure for grain boundary migration*. Besides, the vanishing of the Voigt couple stress is analysed together with the existence of *internal stresses and couples* responsible for the bending/twisting of crystallites by polygonization and heterogeneous strain.

**Keywords:** polycrystal; mechanics; thermodynamics; micropolar media; continuous diversity; anisotropy; recrystallization; polygonization

### 1. Introduction

When students are introduced to continuum mechanics, they learn that most constitutive theories are based on two fundamental assumptions: *isotropy* and *homogeneity* (Truesdell & Noll 1965; Liu 2002). Although these assumptions may be justified in many situations, they represent in several other instances just a crude approximation to reality. A typical example is provided by polycrystals. Their heterogeneity stems from a 'cellular' structure of crystalline domains called *crystallites*, or *grains*. On the other hand, the polycrystalline anisotropy (also named *texture*, or *fabric*†) has its roots in peculiar symmetries of the crystalline lattice, which tends

† Dedicated to I-Shih Liu on the occasion of his 60th birthday.

† Following Part I (Faria 2005a), the terms *texture* and *fabric* are considered here synonyms to the preferred orientations of the lattice. No special word is used in regard to grain sizes and shapes.

to orient itself towards some preferred directions established in each grain by the deformation process. This means that the anisotropy of polycrystals can be *induced by strain*. Further, if the material is exposed to high temperatures, both properties (anisotropy and heterogeneity) may be affected also by energetic processes of *recovery* and *recrystallization* (Poirier 1985; Humphreys & Hatherly 2004).

Induced anisotropy and recrystallization have since long been recognized as scientifically and technologically relevant. While engineers and materials scientists aim at improving their knowledge of the mechanical properties of processed metals and ceramics, geophysicists wish to understand the slow geomorphological dynamics of rocks and minerals, with characteristic times ranging from hundreds to thousands of years. Now, whereas various (thermo-)mechanical models have been proposed for the plasticity of single- and polycrystalline specimens (see Svendsen 2002; Wenk & Van Houtte 2004; and references therein), there was until recently no adequate, thermodynamically consistent approach to creep, evolving anisotropy, *and* recrystallization of large<sup>†</sup> polycrystalline masses. In order to revert this situation, a general continuum theory has been advanced in Part I of this series (Faria 2005a).

The objective of this work is to employ the mentioned continuum approach of Part I to derive a constitutive theory suited to a whole class of polycrystals. The materials in focus are *large masses of incompressible, polycrystalline media made of transversely isotropic grains*. Seeing that most of the polycrystals included in this category belong to the hexagonal crystal system, the symmetry axis of transverse isotropy of the crystallites is for convenience called the *c axis*.

The *notation* follows the guidelines prescribed in Appendix A of Part I (Faria 2005a). Moreover, when some reference to an equation from Part I is needed, then the superscript ‘I’ will be added to the respective equation tag, in order to make evident that this particular equation does not pertain to the present work. For instance, (3.2)<sup>I</sup> refers to the second equation of the third section of Part I.

## 2. Fundamentals

Most of the concepts underlying the present theory rest on the notion of a mixture with continuous diversity, in the manner already discussed in Part I. Consequently, this section acts chiefly as a link between the general fundamentals put forward in Part I and the constitutive theory to be developed in the ensuing sections.

### (a) Thermodynamic processes in polycrystals

When a scientist attempts to model the dynamics of a large polycrystalline mass, his primary goal usually consists in determining the fields of mass density  $\rho$ , velocity  $v_i$  and temperature  $T$ , at every point  $x_j$  and instant  $t$ . Frequently, the mass density can be excluded beforehand by imposing  $\rho = \text{const.}$ , which implies via (3.11)<sup>I</sup> that the *incompressibility condition*  $\partial v_i / \partial x_i = 0$  holds. Hence, the number of basic fields is reduced to four: the temperature and the three components of the velocity.

On the other hand, it is widely acknowledged that the high-temperature creep of polycrystals is very sensitive to their fabrics. In the particular case of transversely isotropic grains, this means: sensitive to the orientational distribution of *c axes*. The fabric induces a complex anisotropic material behaviour, which evolves in time mainly through *lattice rotations*, but is simultaneously affected by diverse other

<sup>†</sup> By ‘large’ we mean ‘on a geological size scale’. See also the comments in Faria (2005a).

mechanisms subsumed into the generic term *recrystallization*, notably *polygonization*, *nucleation* and *grain boundary migration* (Humphreys & Hatherly 2004).

From the reasoning above it follows that a *thermodynamic process* in a polycrystal undergoing recrystallization can be characterized by nine basic fields of

$$\begin{aligned}
 \varrho^*(x_i, t, n_j) & \quad \text{mass density,} \\
 \rho_D^*(x_i, t, n_j) & \quad \text{dislocation density,} \\
 s_i^*(x_j, t, n_k) & \quad \text{c-axis spin velocity,} \\
 v_i(x_j, t) & \quad \text{translational velocity,} \\
 T(x_i, t) & \quad \text{absolute temperature.}
 \end{aligned} \tag{2.1}$$

Notice that the first five scalar fields depend not only on position and time, but also on *c*-axis orientation, the latter denoted by the unit *orientation vector*  $n_i$  (see §2b,c of Part I). Such orientation-dependent fields, identified by the superscript ‘\*’, describe the *microstructure* of the medium. In particular, the orientation-dependent mass density  $\varrho^*$  portrays the fabric, i.e. the amount of crystalline mass, in a unit volume of the polycrystal, with *c* axes oriented parallel to  $n_i$ . The rotation rate of the lattice is measured by the *c*-axis spin velocity  $s_i^*$ , which is necessarily dependent on  $n_i$ , otherwise all *c* axes in a particle would rotate with the same spin velocity and the fabric would not evolve. Further, recrystallization is modelled by the internal variable  $\rho_D^*$ , which is related to the stored energy of deformation. The interpretation of  $\rho_D^*$  as the total length of dislocations found in those grains with *c* axes oriented towards  $n_i$  and enclosed in a unit volume of the polycrystal is motivated by statistical arguments (Faria *et al.* 2003, and references therein) as well as by results of §3d. Finally, the fields  $v_i$  and  $T$  describe the ordinary thermomechanics of the polycrystal, in the manner outlined at the beginning of this section. As explained in remark 3.2 of Part I, the assumption of negligible grain shifting, viz.  $v_i^*(x_j, t, n_k) \equiv v_i(x_j, t)$ , is valid as long as the material does not flow in a *superplastic regime*; it has *no relation at all* to any kind of ‘Taylor-type’ hypothesis: the deformation of every grain remains *unconstrained* (cf. remark 2.1 of Part III).

Following the terminology introduced in Part I, crystallites possessing the same *c*-axis orientation constitute what is called a *species*. Slightly misoriented crystallites and subgrains are said to belong to *familiar species*. Low-angle interactions are interpreted as interactions between familiar species, i.e. *interspecies interactions*. Accordingly, orientation-dependent fields are also named *species fields*.

### (b) Fabric description

Before relating (2.1) to experimental data, it should be noticed that, in the same manner as a material particle at  $x_i \in \mathbb{R}^3$  actually refers to an infinitesimal volume centred at  $x_i$ , so does also a lattice orientation at  $n_i \in \mathcal{S}^2$  to an *infinitesimal normalized solid angle*†  $d^2n$  containing  $n_i$ . Therefore, density fields bearing the superscript ‘\*’ are, rigorously, distribution densities with respect to a unit hypervolume in  $\mathbb{R}^3 \times \mathcal{S}^2$  (cf. Aris & Gavalas 1966). In practice, this means that observable species densities in  $\mathbb{R}^3$  —called *spatial species densities*— are expressed by the products of the infinitesimal solid angle  $d^2n$  with their respective densities. For

† As explained in Part I, if  $\theta$  and  $\phi$  denote the polar and azimuthal angles of a spherical coordinate system, then the infinitesimal normalized solid angle reads  $d^2n = \sin \theta \, d\phi \, d\theta / 4\pi$ .

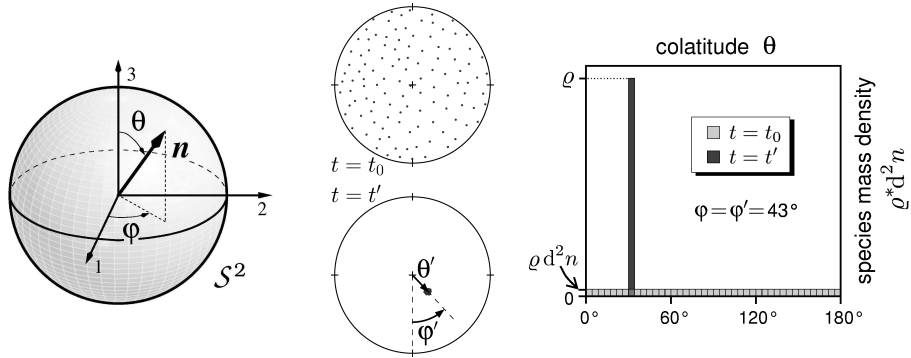


Figure 1. Fabric description. *Left*: any  $c$ -axis orientation is specified by two Euler angles  $(\varphi, \theta)$  representing the spherical coordinates of the unit *orientation vector*  $n_i$  (Faria 2005a). *Centre*: the *fore-aft symmetry* of  $c$  axes ( $n_i \leftrightarrow -n_i$ , see §3a) allows us to construct *fabric diagrams* by projecting each  $c$  axis onto the equatorial plane of  $\mathcal{S}^2$ . The figure shows two diagrams, corresponding to the isotropic distribution ( $t = t_0$ ) and the single-maximum fabric ( $t = t' > t_0$ ) discussed in the text. *Right*: schematic histogram of the spatial species mass density  $\varrho^* d^2 n$  versus the colatitude  $\theta$ , for  $\varphi = \varphi' = 43^\circ$ . Angular distributions of mass for the isotropic (light gray) and the single maximum (dark gray) fabrics are shown.

instance, the product  $\varrho^* d^2 n$  stands for the spatial species density of mass, which plays an important role in the description of fabrics, as outlined below.

By regarding lattice orientations as species, we can interpret fabric formation as the predominance of better-suited species for the current conditions. Clearly, such a thermomechanical selection is manifested by changes in  $\varrho^*$ . Figure 1 illustrates this notion through the classic example of a single-maximum fabric. Initially ( $t = t_0$ ), a material particle located at  $x_i = x_{i0}$  is *isotropic*, i.e. its species mass density corresponds to an homogeneous distribution of  $c$  axes:  $\varrho^*(x_{i0}, t_0, n_j) \equiv \varrho(x_{i0}, t_0)$ . Accordingly, the spatial species mass density  $\varrho^*(x_{i0}, t_0, n_j) d^2 n$  has the same small value for every  $n_i$ . During deformation, most  $c$  axes tend to rotate towards a preferred direction, under the action of localized, strain-induced torques. At a later time  $t' \gg t_0$ , the same material particle is found at  $x_i = x'_i$  and it may have developed a sharp *single-maximum fabric* at  $\theta' = 31^\circ$ ,  $\varphi' = 43^\circ$  (say). Hence, its species mass density reads now  $\varrho^*(x'_i, t', n_j) = \varrho(x'_i, t') \delta(n_j - n'_j) = \varrho(x'_i, t') \delta(\theta - \theta') \delta(\varphi - \varphi')$ , where  $\delta(\cdot)$  is the so-called Dirac delta function. In such a situation, the spatial species mass density  $\varrho^*(x'_i, t', n_j) d^2 n$  vanishes everywhere in  $\mathcal{S}^2$ , except for  $n_i = n'_i$ .

Besides lattice rotations, also recrystallization does affect the species mass density  $\varrho^*$ . Indeed,  $\varrho^*$  expresses not only the *number* of grains with a certain  $c$ -axis orientation, but also their *volume fraction*, seeing that  $\varrho^*$  is a mass density and the mass of an incompressible grain is proportional to its size. It should be noticed, though, that  $\varrho^*$  cannot distinguish between an aggregate of few large crystallites and a corresponding one with a greater number of smaller grains.† However, it does detect *changes* in the relative size and number of grains, like those produced by recrystallization (see figure 2). The effect is akin to changes in the concentrations of chemical substances in a reactive mixture: instead of ‘chemical substances’ there

† This distinction would require a more intricate theory, in which the polycrystal is regarded as a mixture not only of lattice orientations, but also of grain sizes. Attempts to construct such a theory have been made (Placidi & Hutter 2005) but are beyond the scope of this work.

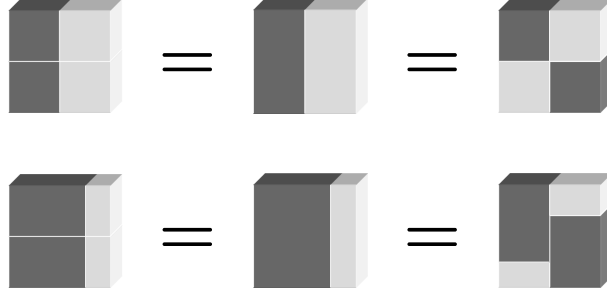


Figure 2. Sketches of two groups of equivalent particles. Dark and light blocks represent grains of two species. *Upper row*: no matter how the species are distributed, all three polycrystalline particles possess the same  $\varrho^*$ , and consequently the same fabric. *Lower row*: likewise, these three polycrystalline particles share the same fabric, being in this sense indistinguishable. However, they are different from the particles in the upper row ( $\varrho_{\text{up}}^* \neq \varrho_{\text{low}}^*$ ). Thus, changes in the grain size distribution do indeed affect  $\varrho^*$  and the fabric.

are crystallites with distinct lattice orientations, while the ‘reaction fronts’ are replaced by moving grain boundaries. The increase in the mass density of one species (with growing grains) is then supported by the decrease in the mass densities of other species (with shrinking grains). In this manner, the species mass density  $\varrho^*$  reveals fabric changes by recrystallization, without any rotation of the lattice.

(c) *Balance equations and the need of a constitutive theory*

In order to determine the basic fields (2.1) we need an appropriate system of differential equations, so-called *field equations*, the solution of which defines an *admissible thermodynamic process*. In continuum thermodynamics, the derivation of such field equations usually evolves through two steps. First, the evolution of the basic fields is related to general transport phenomena, like heat flux, stress, etc., through *balance equations*. Then, in a second step, these general transport phenomena are represented as functions of the basic fields (2.1) by means of *constitutive relations*, which epitomize the peculiar properties of a given material. The derivation of such relations establishes what is called a *constitutive theory*. It is through the combination of the balance equations —which are fairly general in character— with the particular constitutive relations, that we finally obtain a closed set of field equations, that can (hopefully) be solved as part of a given initial/boundary-value problem.

In the specific case considered here, nine differential equations are necessary in order to determine the nine scalar fields listed in (2.1). To derive such a set of field equations, we start with the following balance equations of (cf. §3b of Part I)

- mass

$$\dot{\varrho}^* + \partial_i (\varrho^* u_i^*) = \varrho^* \Gamma^* , \quad (2.2)$$

- dislocations

$$\dot{\rho}_D^* + \partial_i (\rho_D^* u_i^* + j_{D_i}^*) = \Pi_D^* , \quad (2.3)$$

- spin momentum (angular momentum)

$$(\varrho^* I s_i^*) \cdot - \frac{\partial m_{ij}^*}{\partial x_j} + \partial_j (\varrho^* I s_i^* u_j^* - \varpi_{ij}^*) - \varrho^* c_i^* = \epsilon_{ijk} t_{kj}^* + \varrho^* \nu_i^* , \quad (2.4)$$

- linear momentum

$$(\varrho^* v_i)' - \frac{\partial t_{ij}^*}{\partial x_j} + \partial_j (\varrho^* v_i u_j^* - \tau_{ij}^*) - \varrho^* g_i^* = \varrho^* \kappa_i^*, \quad (2.5)$$

- internal energy

$$\begin{aligned} (\varrho^* e^*)' + \frac{\partial q_i^*}{\partial x_i} + \partial_i (\varrho^* e^* u_i^* + \xi_i^*) - \varrho^* r^* \\ = \epsilon_{ijk} s_i^* t_{jk}^* + t_{ij}^* \frac{\partial v_i}{\partial x_j} + m_{ij}^* \frac{\partial s_i^*}{\partial x_j} + \varpi_{ij}^* \partial_j s_i^* + \varrho^* \varepsilon^*, \end{aligned} \quad (2.6)$$

where the incompressibility condition  $\partial v_i / \partial x_i = 0$  has already been taken into account. For brevity, all fields occurring in the equations above have been defined in Appendix A of Part I (Faria 2005a). Moreover, the differential operators

$$(\cdot)' := \frac{\partial}{\partial t} + v_i \frac{\partial}{\partial x_i} \quad \text{and} \quad \partial_i := \frac{\partial}{\partial n_i} - n_i n_j \frac{\partial}{\partial n_j} \quad (2.7)$$

denote, respectively, the *material time derivative* and the *orientational differential operator*. The peculiar form of the latter results from the normalization condition  $n_k n_k = 1$  (cf. (3.4)<sup>I</sup>). A further consequence of this condition is the identity  $n_i u_i^* = 0$ , which allows us to rewrite the transition rate  $u_i^*$  as (cf. (3.2)<sup>I</sup> and (3.3)<sup>I</sup>)

$$u_i^* := \epsilon_{ijk} s_j^* n_k = S_{ik}^* n_k. \quad (2.8)$$

Finally, the second law of thermodynamics is expressed by the *entropy inequality*

$$(\varrho^* \eta^*)' + \frac{\partial \phi_i^*}{\partial x_i} + \partial_i (\varrho^* \eta^* u_i^* + \varphi_i^*) - \varrho^* s^* = \varrho^* \varsigma^* \geq \varrho^* \delta^*, \quad (2.9)$$

(see §3c of Part I). For further reference, we recall also the tangentiality conditions

$$n_i \varpi_{ij}^* = n_i \tau_{ij}^* = n_i \xi_i^* = n_i \varphi_i^* = n_i j_{D_i}^* = 0, \quad (2.10)$$

which state that interspecies fluxes and stresses should be tangential to the spherical surface of  $\mathcal{S}^2$  (Faria 2001; Faria & Hutter 2002; cf. proposition 3.2 of Part I).

As already explained, the establishment of appropriate balance equations is just the first step towards the determination of the basic fields (2.1). Indeed, inspection of the balance equations proposed so far reveals that, in order to close the system (2.2)–(2.9), constitutive relations are required for the fields

$$\mathbf{F}_\sigma^* = \{j_{D_i}^*, t_{ij}^*, \tau_{ij}^*, \kappa_i^*, m_{ij}^*, \varpi_{ij}^*, \nu_i^*, e^*, q_i^*, \xi_i^*, \varepsilon^*, \eta^*, \phi_i^*, \varphi_i^*, \delta^*, \Gamma^*, \Pi_{D_i}^*\}, \quad (2.11)$$

with  $\sigma = 1, 2, \dots, 63$ . In other words, these quantities must be expressed as functionals of the basic fields (2.1) and their derivatives. Clearly, the explicit forms of these functionals should depend on the *material constitution*, and are therefore determined by means of a *constitutive theory*.

### 3. Constitutive theory for a class of polycrystalline media

We are now prepared to embark on the central objective of this work: the derivation of a thermodynamically-consistent constitutive theory for large polycrystalline masses made of incompressible, transversely isotropic crystallites.



## (a) Constitutive functionals

In order to derive appropriate constitutive relations for the quantities listed in (2.11), we start by considering a *first order gradient theory* in the thermomechanical fields  $v_i$  and  $T$ . This assumption, combined with Truesdell's *rule of equipresence* (Truesdell & Noll 1965; Müller 1985; Liu 2002) allows us to propose the following isotropic, generic form of constitutive functionals

$$F_\sigma^*(x_i, t, n_j) = \mathfrak{F}_\sigma \left( x_i, t, n_j; p_k, \varrho^\circ, \rho_\circ^\circ, S_{lm}^\circ; v_n, T, \frac{\partial v_p}{\partial x_q}, \frac{\partial T}{\partial x_r} \right), \quad (3.1)$$

where  $p_i \in \mathcal{S}^2$  and  $\mathcal{Q}^\circ$  stands for the set of values of the quantity  $\mathcal{Q}^*$  in all points of the orientation space, i.e.  $\mathcal{Q}^\circ = \{\mathcal{Q}^*(x_i, t, p_j) : p_j \in \mathcal{S}^2\}$ . Notice that the kind of dependence on multiple orientations proposed in (3.1) suggests that the functionals  $\mathfrak{F}_\sigma$  may eventually contain intricate integrals over  $\mathcal{S}^2$ . Further, we invoke the *principle of frame indifference* (also called *material objectivity*, Truesdell & Noll 1965; Müller 1985; Liu 2002) to deduce via standard arguments (see e.g. Faria 2001) that the fields  $F_\sigma^*$  should not depend explicitly on  $x_i, t$ , and  $v_i$ . Instead, a dependence of  $F_\sigma^*$  on  $S_{ij}^\circ$  and  $\partial v_k / \partial x_l$  is permitted only in the form

$$F_\sigma^*(x_i, t, n_j) = \mathfrak{H}_\sigma(n_j; p_k, \varrho^\circ, \rho_\circ^\circ, H_{lm}^\circ; T, D_{\langle pq \rangle}, T_{,r}), \quad (3.2)$$

$$H_{ij}^* := S_{ij}^* - W_{ij}, \quad W_{ij} := \frac{\partial v_{[i}}{\partial x_{j]}}, \quad D_{ij} := \frac{\partial v_{(i}}{\partial x_{j)}}, \quad D_{\langle ij \rangle} := D_{ij} - \frac{1}{3} D_{kk} \delta_{ij},$$

and  $T_{,i} := \partial T / \partial x_i$  (cf. Appendix A of Part I). Additionally, incompressibility ( $D_{kk} = 0$ ) implies  $D_{ij} = D_{\langle ij \rangle}$ . Clearly, (3.2) is still too difficult to deal with.

**Hypothesis 3.1.** Aiming at a simpler theory, we impose on (3.2) the assumptions:

1. *Fore-aft symmetry*: anti-parallel  $c$  axes are assumed to be indistinguishable. This condition applied to (2.2)–(2.6) implies that spatial fluxes are even functions of  $n_i$  ( $t_{ij}^*(-n_k) = t_{ij}^*(n_k)$ ,  $q_i^*(-n_j) = q_i^*(n_j)$ , etc.) while on the other hand interspecies fluxes are odd functions of  $n_i$  ( $\tau_{ij}^*(-n_k) = -\tau_{ij}^*(n_k)$ ,  $\xi_i^*(-n_j) = -\xi_i^*(n_j)$ , etc.);
2. *Replacement of  $H_{ij}^\circ$  by  $H_{ij}^*$  in (3.2)*: the constitutive dependence on the relative spin velocity of disparate  $c$  axes is negligible. This expresses the trivial fact that the material response depends only upon the current fabric of the medium;
3. *Linearization of (3.2) with respect to  $T_{,i}$  and  $H_{ij}^*$* . Notice, however, that this assumption cannot be applied to the entropy deviation rate  $\delta^*$ : from proposition 3.1 of Part I it follows that  $\delta^*$  stands for a difference between entropy production rates that *must* be non-linear functions of their arguments, on account of dissipative effects.

Even after the simplifications above, the generic functionals  $\mathfrak{H}_\sigma$  in (3.2) still contain unknown integrals over  $\mathcal{S}^2$  involving  $\varrho^*$ ,  $\rho_\circ^*$ ,  $n_i$ , and  $p_j \in \mathcal{S}^2$  that are rather difficult to determine. This intricate dependence on multiple orientations can nevertheless be simplified by constraining such integrals to have a few *pre-defined forms*. Thus, after Edelen (1976) we define a set of  $\tilde{\varkappa} + 1$  independent scalar<sup>†</sup> fields  $B_\varkappa^*$  into which *all such integrals are subsumed* ( $\varkappa = 1, 2, \dots, \tilde{\varkappa}, \tilde{\varkappa} + 1$ ):

$$B_\varkappa^*(x_i, t, n_j) := \int_{\mathcal{S}^2} \mathfrak{B}_\varkappa \left( \varrho^*(x_k, t, p_l), \rho_\circ^*(x_m, t, p_q), n_r, p_s \right) d^2 p, \quad (3.3)$$

<sup>†</sup> In principle, one could introduce also tensor-valued fields, but such a generalization would render the constitutive equations much more intricate without noticeable benefit.

where the functions  $\mathfrak{B}_\varkappa$  are not necessarily continuous (though integrable) with respect to  $p_i \in \mathcal{S}^2$ . The *microstructure parameters*  $B_\varkappa^*$  are dimensionless variables, complementary to  $\varrho^*$  and  $\rho_\mathfrak{d}^*$ , the purpose of which is to provide a rough description of the fabric and dislocation distribution over all species within a polycrystalline particle. Owing to this, the quantities  $B_\varkappa^*$  can be classified into two categories: the *fabric (texture) parameters*, which contain integrals involving  $\varrho^*$  but not  $\rho_\mathfrak{d}^*$ ; and the *dislocation parameters*, which necessarily involve  $\rho_\mathfrak{d}^*$  (and occasionally also  $\varrho^*$ ).

**Remark 3.1.** For the sake of simplicity (see §3c), we will suppose from now on that the set  $\{B_\varkappa^* : \varkappa = 1, \dots, \tilde{\varkappa} + 1\}$  comprises just one dislocation parameter, viz.  $B_{\tilde{\varkappa}+1}^* =: \gamma^*$ . All other  $\tilde{\varkappa}$  elements of the set are thus fabric parameters, i.e.  $\{B_\varkappa^* =: \beta_\varkappa^* : \varkappa = 1, \dots, \tilde{\varkappa}\}$ . Explicit forms of  $\beta_\varkappa^*$  and  $\gamma^*$  are not needed in the sequel of this work, further details are left to the third part of this series (Faria 2005b).

Under the restrictions above, (3.2) reduces to the more conventional form

$$F_\sigma^*(x_i, t, n_j) = \mathfrak{J}_\sigma(n_j; \varrho^*, \rho_\mathfrak{d}^*, \beta_\varkappa^*, \gamma^*, H_{lm}^*; T, D_{(pq)}, T, r), \quad (3.4)$$

where  $\mathfrak{J}_\sigma$  are now constitutive *functions* (not functionals), free of any cumbersome integral dependence on multiple orientations. It is this last general form of the constitutive relations which will be considered in the ensuing thermodynamic analysis.

(b) *Exploitation of the second law of thermodynamics*

To exploit the restrictions imposed by the entropy inequality (2.9) we employ the *method of Lagrange multipliers* proposed by Liu (2002), which asserts that, for the case in hand, the following inequality must be valid for *arbitrary values* of the basic fields (2.1), even when external supplies are absent† (cf. (2.2)–(2.9))

$$\begin{aligned} & (\varrho^* \eta^*)' + \frac{\partial \varphi_i^*}{\partial x_i} + \partial_i (\varrho^* \eta^* S_{ij}^* n_j + \varphi_i^*) - \varrho^* \delta^* - \Lambda^* \left\{ \varrho^* + \partial_i (\varrho^* S_{ij}^* n_j) \right. \\ & \left. - \varrho^* \Gamma^* \right\} - \Lambda_\mathfrak{d}^* \left\{ \rho_\mathfrak{d}^* + \partial_i (\rho_\mathfrak{d}^* S_{ij}^* n_j + j_{\mathfrak{d}i}^*) - \Pi_\mathfrak{d}^* \right\} - \Lambda_i^* \left\{ (\varrho^* I s_i^*)' - \frac{\partial m_{ij}^*}{\partial x_j} \right. \\ & \left. + \partial_j (\varrho^* I s_i^* S_{jk}^* n_k - \varpi_{ij}^*) + \epsilon_{ijk} t_{jk}^* - \varrho^* \nu_i^* \right\} - \lambda_i^* \left\{ (\varrho^* v_i)' - \frac{\partial t_{ij}^*}{\partial x_j} \right. \\ & \left. + \partial_j (\varrho^* v_i S_{jk}^* n_k - \tau_{ij}^*) - \varrho^* \kappa_i^* \right\} - \lambda^* \left\{ (\varrho^* e^*)' + \frac{\partial q_i^*}{\partial x_i} + \partial_i (\varrho^* e^* S_{ij}^* n_j + \xi_i^*) \right. \\ & \left. - t_{ij}^* \frac{\partial v_i}{\partial x_j} - m_{ij}^* \frac{\partial s_i^*}{\partial x_j} - \varpi_{ij}^* \partial_j s_i^* + t_{ij}^* S_{ij}^* - \varrho^* \varepsilon^* \right\} \geq 0. \end{aligned} \quad (3.5)$$

As usual, we assume that the Lagrange multipliers  $\Lambda^*$ ,  $\Lambda_\mathfrak{d}^*$ ,  $\Lambda_i^*$ ,  $\lambda_i^*$ ,  $\lambda^*$  are functions of the same variables listed in (3.4), and in addition also of  $v_i$ ,  $S_{ij}^*$ , and  $W_{ij}$ , since objectivity of the multipliers is not taken for granted a priori (Müller 1985; Liu 2002).

After application of the chain rule to the derivatives occurring in (3.5), we obtain an inequality that is explicitly linear in the following quantities:

† Within the frames of a constitutive theory, the neglect of external supplies is based on the assumption that external sources should not influence the material response (Müller 1985; Liu 2002).

$$\begin{aligned} \frac{\partial v_i}{\partial t}, \frac{\partial \varrho^*}{\partial t}, \frac{\partial \rho_{\text{D}}^*}{\partial t}, \frac{\partial \beta_{\mathcal{X}}^*}{\partial t}, \frac{\partial \gamma^*}{\partial t}, \frac{\partial S_{ij}^*}{\partial t}, \frac{\partial T}{\partial t}, \frac{\partial^2 v_i}{\partial x_j \partial t}, \frac{\partial^2 T}{\partial x_i \partial t}, \frac{\partial \varrho^*}{\partial x_i}, \frac{\partial \rho_{\text{D}}^*}{\partial x_i}, \\ \frac{\partial \beta_{\mathcal{X}}^*}{\partial x_i}, \frac{\partial \gamma^*}{\partial x_i}, \frac{\partial S_{ij}^*}{\partial x_k}, \frac{\partial^2 v_i}{\partial x_j \partial x_k}, \frac{\partial^2 T}{\partial x_i \partial x_j}, \partial_i \varrho^*, \partial_i \rho_{\text{D}}^*, \partial_i \beta_{\mathcal{X}}^*, \partial_i \gamma^*, \partial_i S_{jk}^*. \end{aligned}$$

Since the basic fields (2.1) are arbitrary in (3.5), so are the derivatives above. Hence, in order to preserve the inequality (3.5), their respective coefficients must vanish:

$$\lambda_i^* = 0, \quad \Lambda_i^* = 0, \quad \frac{\partial \phi_{(i}^*}{\partial T_{,j)}^*} - \lambda^* \frac{\partial q_{(i}^*}{\partial T_{,j)}^*} = 0, \quad (3.6)$$

$$\frac{\partial \varrho^* \eta^*}{\partial \varrho^*} - \lambda^* \frac{\partial \varrho^* e^*}{\partial \varrho^*} = \Lambda^*, \quad \frac{\partial \varrho^* \eta^*}{\partial \rho_{\text{D}}^*} - \lambda^* \frac{\partial \varrho^* e^*}{\partial \rho_{\text{D}}^*} = \Lambda_{\text{D}}^*, \quad (3.7)$$

$$\frac{\partial \phi_{(i}^*}{\partial D_{(j)k)}^*} - \lambda^* \frac{\partial q_{(i}^*}{\partial D_{(j)k)}^*} + \frac{\partial \phi_{(i}^*}{\partial H_{j)k}^*} - \lambda^* \frac{\partial q_{(i}^*}{\partial H_{j)k}^*} = 0, \quad (3.8)$$

$$\frac{\partial \phi_i^*}{\partial H_{jk}^*} - \lambda^* \frac{\partial q_i^*}{\partial H_{jk}^*} = \frac{1}{2} \lambda^* \epsilon_{kjl} m_{li}^*, \quad (3.9)$$

$$\frac{\partial \varphi_i^*}{\partial H_{jk}^*} - \lambda^* \frac{\partial \xi_i^*}{\partial H_{jk}^*} = \Lambda_{\text{D}}^* \frac{\partial j_{\text{D}i}^*}{\partial H_{jk}^*} + \frac{1}{2} \lambda^* \epsilon_{kjl} \varpi_{li}^* - \varrho^* \left( \eta^* - \Lambda^* - \lambda^* e^* - \Lambda_{\text{D}}^* \frac{\rho_{\text{D}}^*}{\varrho^*} \right) \delta_{i[jn_k]}, \quad (3.10)$$

$$\frac{\partial \eta^*}{\partial A_{\mu}^*} - \lambda^* \frac{\partial e^*}{\partial A_{\mu}^*} = 0, \quad \text{where } A_{\mu}^* = \{ \beta_{\mathcal{X}}^*, \gamma^*, H_{ij}^*, T, D_{(ij)}, T_{,i} \}, \quad (3.11)$$

$$\frac{\partial \phi_i^*}{\partial B_{\tau}^*} - \lambda^* \frac{\partial q_i^*}{\partial B_{\tau}^*} = 0, \quad \text{where } B_{\tau}^* = \{ \varrho^*, \rho_{\text{D}}^*, \beta_{\mathcal{X}}^*, \gamma^* \}, \quad (3.12)$$

$$\frac{\partial \varphi_i^*}{\partial B_{\tau}^*} - \lambda^* \frac{\partial \xi_i^*}{\partial B_{\tau}^*} = \Lambda_{\text{D}}^* \frac{\partial j_{\text{D}i}^*}{\partial B_{\tau}^*}, \quad (3.13)$$

with  $\mu = 1, \dots, \tilde{\mu}$  and  $\tau = 1, \dots, \tilde{\tau}$ ; given  $\tilde{\mu} = 13 + \tilde{\varkappa}$  and  $\tilde{\tau} = 3 + \tilde{\varkappa}$ .

The remainder of the inequality (3.5) reads

$$\begin{aligned} \left( \frac{\partial \phi_i^*}{\partial T} - \lambda^* \frac{\partial q_i^*}{\partial T} \right) \frac{\partial T}{\partial x_i} + \lambda^* \left( t_{(ij)}^* D_{(ij)} - t_{[ij]}^* H_{ij}^* \right) + \lambda^* \varrho^* \varepsilon^* - \varrho^* \delta^* + \Lambda^* \varrho^* \Gamma^* \\ + \Lambda_{\text{D}}^* \Pi_{\text{D}}^* + \varrho^* \left( \hat{\partial}_i \eta^* - \lambda^* \hat{\partial}_i e^* \right) S_{ij}^* n_j + \hat{\partial}_i \varphi_i^* - \lambda^* \hat{\partial}_i \xi_i^* - \Lambda_{\text{D}}^* \hat{\partial}_i j_{\text{D}i}^* \geq 0, \end{aligned} \quad (3.14)$$

with  $\hat{\partial}_i$  denoting the *constrained orientational gradient*, which acts exclusively upon the *explicit* dependence on  $n_i$  (in the present case,  $\hat{\partial}_i$  corresponds to the orientational gradient  $\partial_i$  with  $\varrho^*$ ,  $\rho_{\text{D}}^*$ ,  $\beta_{\mathcal{X}}^*$ ,  $\gamma^*$  and  $H_{kl}^*$  kept constant).

As stated in hypothesis 3.1, we are interested in a linearized theory on the gradient of temperature and the relative  $c$ -axis spin velocity. Subjected to these constraints, the most general representations of  $\phi_i^*$  and  $q_i^*$  read (see e.g. Liu 2002)

$$\phi_i^* = -\Phi_{ij}^* \frac{\partial T}{\partial x_j}, \quad \text{and} \quad q_i^* = -k_{ij}^* \frac{\partial T}{\partial x_j}, \quad (3.15)$$

where we have already exploited the fore–aft symmetry discussed in hypothesis 3.1 (the negative signs in (3.15) come from usual convention). The coefficients  $\Phi_{ij}^*$  and  $k_{ij}^*$  are functions of  $\varrho^*$ ,  $\rho_{\text{D}}^*$ ,  $\beta_{\mathcal{X}}^*$ ,  $\gamma^*$ ,  $T$ ,  $D_{(ij)}$ , and the dyadic  $n_i n_j$ . Supposing that  $\lambda^*$

cannot be merely zero, it follows from (3.9) and (3.15) that the Voigt couple stress must vanish, viz.

$$m_{ij}^* = 0. \quad (3.16)$$

Further, (3.6)<sub>3</sub> and (3.15) imply

$$\lambda^* = \lambda^*(n_i n_j; \varrho^*, \rho_D^*, \beta_{\mathcal{X}}^*, \gamma^*, T, D_{\langle np \rangle}) \quad \text{and} \quad \Phi_{\langle ij \rangle}^* = \lambda^* k_{\langle ij \rangle}^*, \quad (3.17)$$

which combined with (3.8) and (3.12) yield

$$k_{\langle li \rangle}^* \frac{\partial \lambda^*}{\partial D_{\langle jk \rangle}} + k_{\langle lj \rangle}^* \frac{\partial \lambda^*}{\partial D_{\langle ik \rangle}} = 0 \quad \text{and} \quad k_{\langle ij \rangle}^* \frac{\partial \lambda^*}{\partial B_\tau^*} = 0, \quad (3.18)$$

with  $B_\tau^*$  defined in (3.12). Equation (3.18)<sub>1</sub> can still be simplified as follows: by cyclic permutation of the indices  $i, j$  and  $k$  we obtain two variants of this equation, the sum of which can be subtracted from the original form (3.18)<sub>1</sub> to give

$$k_{\langle lk \rangle}^* \frac{\partial \lambda^*}{\partial D_{\langle ij \rangle}} = 0, \quad \text{implying, together with (3.18)<sub>2</sub>, that} \quad \lambda^* = \lambda(T). \quad (3.19)$$

A possible dependence of  $\lambda^*$  upon  $n_i n_j$  drops out since the only scalar invariant of  $n_i n_j$  is  $n_i n_i = 1$ . Hence, (3.8) and (3.12) can be rewritten as

$$\frac{\partial}{\partial D_{\langle ij \rangle}} (\phi_k^* - \lambda q_k^*) = 0 \quad \text{and} \quad \frac{\partial}{\partial B_\tau^*} (\phi_i^* - \lambda q_i^*) = 0, \quad (3.20)$$

where (3.20)<sub>1</sub> is derived from (3.8) following exactly the same procedure of indices permutation already used in the derivation of (3.19)<sub>1</sub>. From (3.15) and (3.20) we infer that the difference  $\Phi_{\langle ij \rangle}^* - \lambda k_{\langle ij \rangle}^*$  can be a function only of  $T$  and the dyadic  $n_i n_j$ , implying that  $\Phi_{\langle ij \rangle}^* = \lambda k_{\langle ij \rangle}^*$ , since it is impossible to build an absolute skew-symmetric tensor by using solely the variables  $T$  and  $n_i n_j$ . Hence, from (3.15), (3.17)<sub>2</sub> and the rationale above, we finally conclude that

$$\phi_i^* = \lambda q_i^*. \quad (3.21)$$

On the other hand, (3.11) and (3.19)<sub>2</sub> lead to

$$\frac{\partial (\eta^* - \lambda e^*)}{\partial C_\kappa^*} = 0, \quad \text{where} \quad C_\kappa^* = \{\beta_{\mathcal{X}}^*, \gamma^*, H_{ij}^*, D_{\langle ij \rangle}, T, i\}, \quad (3.22)$$

with  $\kappa = 1, \dots, \tilde{\kappa}$ ; given  $\tilde{\kappa} = 12 + \tilde{\mathcal{X}}$ , and also

$$\frac{\partial (\eta^* - \lambda e^*)}{\partial T} = -e^* \frac{d\lambda}{dT}. \quad (3.23)$$

Refusing the possibility that  $\lambda$  be a mere constant, (3.22) and (3.23) result in

$$e^* = e^*(\varrho^*, \rho_D^*, T), \quad \eta^* = \eta^*(\varrho^*, \rho_D^*, T). \quad (3.24)$$

In order to identify  $\lambda(T)$  properly, we recall that the normal components of the spatial fluxes of heat and entropy are continuous across an impermeable ideal wall<sup>†</sup> separating two different materials, so that we must have

$$[[\phi_i]] e_i^{\mathcal{W}} = 0, \quad \text{and} \quad [[q_i]] e_i^{\mathcal{W}} = 0, \quad (3.25)$$

<sup>†</sup> Roughly, an ideal wall is defined as a wall that does not contribute to the thermodynamic process, e.g. the wall of a perfect thermometer (Müller 1985; Hutter & Jöhnk 2004).

where  $e_i^{\mathcal{W}}$  is the unit normal vector of the impermeable ideal wall  $\mathcal{W}$ , and the double brackets denote the difference between the observed values of the enclosed quantity on both sides of the wall (Faria & Hutter 2002). After integration of (3.21) over all orientations we get just (cf. §3d of Part I; see also Faria 2001; Faria *et al.* 2003)

$$\phi_i = \lambda(T) q_i. \quad (3.26)$$

Thus, by assuming that the material at one side of the wall is precisely the polycrystal under study, while the medium at the other side is any of the many materials which obey (3.26), it follows from (3.25) and (3.26) that  $[[\lambda(T)]] = 0$ , i.e.  $\lambda(T)$  is continuous across the wall. Further, since the material at the other side of the wall is left unspecified, we conclude that  $\lambda(T)$  cannot be a constitutive property, i.e. it is a *universal function* of the absolute temperature. Consequently, either by assuming that the unspecified material is an ideal gas, or simply by dimensional analysis, we identify  $\lambda(T)$  as the reciprocal of the temperature, viz.

$$\lambda(T) = \frac{1}{T}. \quad \text{Hence, from (3.23) we have} \quad \frac{\partial \psi^*}{\partial T} = -\eta^*, \quad (3.27)$$

which is the well-known relation between the specific entropy  $\eta^*$  and the derivative of the specific Helmholtz free energy,  $\psi^* := e^* - T\eta^*$ , with respect to temperature.

Finally, the identification of  $\Lambda^*$  and  $\Lambda_{\text{D}}^*$  follows from (3.7), viz.

$$\Lambda^*(\varrho^*, \rho_{\text{D}}^*, T) = -\frac{1}{T} \frac{\partial \varrho^* \psi^*}{\partial \varrho^*}, \quad \Lambda_{\text{D}}^*(\varrho^*, \rho_{\text{D}}^*, T) = -\frac{1}{T} \frac{\partial \varrho^* \psi^*}{\partial \rho_{\text{D}}^*}. \quad (3.28)$$

Hence, by introducing the abbreviation

$$\iota_i^* := \varphi_i^* - \frac{\xi_i^*}{T} + \frac{\varrho^*}{T} \frac{\partial \psi^*}{\partial \rho_{\text{D}}^*} J_{\text{D}i}^* \quad (3.29)$$

we obtain from (3.10), (3.13), (3.27)<sub>1</sub>, and (3.28)

$$\frac{\partial \iota_i^*}{\partial \beta_{\varkappa}^*} = \frac{\partial \iota_i^*}{\partial \gamma^*} = 0 \quad \text{and} \quad \varpi_{ij}^* = \varpi^* \epsilon_{ijk} n_k + \pi_{ij}^*, \quad (3.30)$$

$$\text{with} \quad \varpi^* := \varrho^* \left( \varrho^* \frac{\partial \psi^*}{\partial \varrho^*} + \rho_{\text{D}}^* \frac{\partial \psi^*}{\partial \rho_{\text{D}}^*} \right), \quad \pi_{ij}^* := T \epsilon_{ikl} \frac{\partial \iota_j^*}{\partial H_{kl}^*}. \quad (3.31)$$

Clearly,  $\varpi^* = \varpi^*(\varrho^*, \rho_{\text{D}}^*, T)$ , while  $\pi_{ij}^* = \pi_{ij}^*(n_k; \varrho^*, \rho_{\text{D}}^*, T, D_{\langle pq \rangle})$ .

### (c) Analysis of equilibrium

It is an acknowledged fact that, rigorously, real polycrystals can never achieve a state of *absolute thermodynamic equilibrium*.<sup>†</sup> Indeed, dislocations could not exist under such a state (Suzuki *et al.* 1991; Weertman & Weertman 1992) and there is no three-dimensional structure of grain boundaries sufficiently stable to sustain absolute equilibrium (Humphreys & Hatherly 2004; Gottstein & Shvindlerman 1999).

Notwithstanding, we can conceive a ‘steady state’ of the microstructure which corresponds to a sort of equilibrium on the macroscale. Such a situation is not without precedents in nature. For instance, when a reactive mixture achieves chemical

<sup>†</sup> By ‘absolute thermodynamic equilibrium’ we mean the usual notion of equilibrium, viz. the state of maximum entropy achieved by the material under the conditions of: (1) rigid-body motion, (2) rigid microstructure, (3) uniform temperature field, (4) vanishing internal productions.

equilibrium, its constituents do not necessarily stop reacting: rather, the chemical reactions must proceed at the same rate in both directions (dissociation and formation of compounds), maintaining so the concentration of each substance constant.

A similar picture can be set up for polycrystals. Roughly, we introduce the idea of *pseudo-equilibrium* of a polycrystal as the thermodynamic state in which the material satisfies the conditions of absolute thermodynamic equilibrium *on the large scale* only, whereas on the grain scale there prevails a quasi-static process in which grain boundaries still can migrate and dislocations may persist —provided that fabric, dislocation density, and grain size distribution remain invariant within a reasonable time interval— so that  $\varrho^*$  and  $\rho_D^*$  can be regarded as time-independent fields during some appreciable period. We can formalize these ideas as follows:

**Hypothesis 3.2.** Dissipative processes tend to drive polycrystals towards a thermodynamic state of *pseudo-equilibrium*, defined by the following steps:

1. *Identification of the sources of dissipation.* Despite the great variety of dissipative processes taking place in a polycrystal, their sources are limited and easily identifiable. In this theory, the four fundamental sources of dissipation are:

- (a) deformation —described by  $D_{\langle ij \rangle}$  and responsible, e.g., for the production of dislocations and viscous effects;
- (b) lattice rotation —described by  $H_{ij}^*$  and responsible, e.g., for the bending of crystallites and the formation of subgrain boundaries;
- (c) temperature inhomogeneity —described by  $\partial T / \partial x_i$  and responsible, e.g., for heat and entropy fluxes;
- (d) grain boundary migration —described by  $\Gamma^*$  and responsible, e.g., for grain growth and dynamic recrystallization.

2. *Physical interpretation of production terms.* We recognize that the production of dislocations, momenta, internal energy and entropy describe non-equilibrium processes and must therefore vanish when the sources of dissipation disappear:

$$\lim_{X_\chi^* \rightarrow 0} \{ \Pi_D^*, \kappa_i^*, \nu_i^*, \varepsilon^*, \zeta^*, \delta^* \} = 0, \quad X_\chi^* = \{ \Gamma^*, H_{ij}^*, D_{\langle kl \rangle}, T, p \}. \quad (3.32)$$

3. *Definition of pseudo-equilibrium.* A state of pseudo-equilibrium is achieved when all sources of dissipation vanish, i.e.

$$\Gamma^*|_{\mathbb{E}} = H_{ij}^*|_{\mathbb{E}} = D_{\langle ij \rangle}|_{\mathbb{E}} = T, i|_{\mathbb{E}} = 0, \quad (3.33)$$

where  $|_{\mathbb{E}}$  denotes the (pseudo-)equilibrium value of the respective quantity.

**Remark 3.2.** The requirement that fabric, dislocation density, and grain size distribution be steady in pseudo-equilibrium imposes a stringent constraint on the migration of grain boundaries, viz.  $\Gamma^*|_{\mathbb{E}} = 0$ , which demands in turn corresponding restrictions upon the arrangement of dislocations in the polycrystal (otherwise we could fancy a special distribution of dislocations that violates pseudo-equilibrium). Thus, in contrast to other scalar variables (viz.  $\varrho^*$ ,  $\rho_D^*$ ,  $\beta_\varepsilon^*$ ,  $T$ ), the equilibrium values of the dislocation parameter  $\gamma^*$  are strictly limited. Now, by availing ourselves of the arbitrariness left in the definition of  $\gamma^*$ , we can assume from now on that  $\gamma^*|_{\mathbb{E}} = 0$ .

Conditions (3.32) and (3.33) clearly suggest that it may be advantageous taking the recrystallization rate  $\Gamma^*$  as an independent variable, instead of a constitutive

function. To accomplish this change, we explore the fact that the migration of grain boundaries is mainly driven by a favourable arrangement of dislocations, expressed by the parameter  $\gamma^*$ , as discussed in the remark above. Thus, by assuming that  $\Gamma^*(n_i n_j; \varrho^*, \rho_D^*, \beta_{\mathcal{X}}^*, \gamma^*, H_{lm}^*; T, D_{\langle pq \rangle}, T, r)$  is invertible with respect to  $\gamma^*$ , we can perform the change of variables  $\gamma^* \rightarrow \Gamma^*$  and redefine the general relation (3.4) as

$$\mathbf{G}_\sigma^* = \mathfrak{K}_\sigma(n_j; \varrho^*, \rho_D^*, \beta_{\mathcal{X}}^*, \Gamma^*, H_{lm}^*; T, D_{\langle pq \rangle}, T, r), \quad (3.34)$$

where  $\mathbf{G}_\sigma^*$  is similar to  $\mathbf{F}_\sigma^*$ , defined in (2.11), but with  $\Gamma^*$  replaced by  $\gamma^*$ . Further,

$$\mathbf{G}_\sigma^*|_{\mathbb{E}} = \mathfrak{K}_\sigma(n_j; \varrho^*, \rho_D^*, \beta_{\mathcal{X}}^*, 0, 0; T, 0, 0). \quad (3.35)$$

An important consequence of the pseudo-equilibrium hypothesis stated above is that fluxes of dislocations, heat, and entropy vanish at that state, i.e.

$$j_{D_i}^*|_{\mathbb{E}} = q_i^*|_{\mathbb{E}} = \phi_i^*|_{\mathbb{E}} = \xi_i^*|_{\mathbb{E}} = \varphi_i^*|_{\mathbb{E}} = \iota_i^*|_{\mathbb{E}} = 0. \quad (3.36)$$

Indeed, for the spatial fluxes  $q_i^*$  and  $\phi_i^*$  this result follows immediately from (3.15) and (3.33), whereas for the interspecies fluxes  $j_{D_i}^*$ ,  $\xi_i^*$ ,  $\varphi_i^*$  and  $\iota_i^*$  we must also take (2.10) into account: choosing  $\iota_i^*$  as example, the general representation of this vector which is linear in  $H_{ij}^*$  and  $T_{,i}$  reads (cf. e.g. Liu 2002)

$$\iota_i^* = \iota^* n_i + \iota_{ij}^{*(1)} H_{jk}^* n_k + \iota_{ij}^{*(2)} D_{\langle jk \rangle} n_k. \quad (3.37)$$

Owing to (3.30)<sub>1</sub>, we find that  $\iota^*$  and  $\iota_{ij}^{*(\zeta)}$  (with  $\zeta = 1, 2$ ) are functions of  $\varrho^*$ ,  $\rho_D^*$ ,  $T$ ,  $D_{\langle pq \rangle}$ , and the dyadic  $n_k n_l$ . With the help of (2.10), we can rewrite (3.37) as

$$\iota_i^* = \left[ (\delta_{ik} - n_i n_k) \iota_{kj}^{*(1)} \right] H_{jl}^* n_l + \left[ (\delta_{ik} - n_i n_k) \iota_{kj}^{*(2)} \right] D_{\langle jl \rangle} n_l, \quad (3.38)$$

which automatically satisfies (3.36). By using identical arguments we can derive similar representations for  $j_{D_i}^*$ ,  $\xi_i^*$ , and  $\varphi_i^*$ , keeping in mind that these fluxes may depend also on  $\beta_{\mathcal{X}}^*$  and  $\Gamma^*$ , since no restriction analogous to (3.30)<sub>1</sub> applies to them.

In order to exploit properly the residual inequality (3.14) we decompose the symmetric part of the stress tensor,  $t_{(ij)}^*$ , into three terms: one corresponding to the negative of an equilibrium isotropic pressure,  $p^*(\varrho^*, \rho_D^*, \beta_{\mathcal{X}}^*; T)$ , another one defining an equilibrium anisotropic stress,  $\vartheta^*(\varrho^*, \rho_D^*, \beta_{\mathcal{X}}^*; T) n_i n_j$ , and a third one which is related to dissipative effects,  $\sigma_{ij}^*(n_k n_s; \varrho^*, \rho_D^*, \beta_{\mathcal{X}}^*, \Gamma^*, H_{lm}^*; T, D_{\langle pq \rangle}, T, r)$ , i.e.

$$t_{(ij)}^* = -p^* \delta_{ij} + \vartheta^* n_i n_j + \sigma_{ij}^* \quad \text{with} \quad \sigma_{ij}^* = \sigma_{ji}^* \quad \text{and} \quad \sigma_{ij}^*|_{\mathbb{E}} = 0. \quad (3.39)$$

By collecting the results derived so far, the residual inequality (3.14) reduces to

$$\begin{aligned} \varrho^* \zeta^{*P} &= -\frac{q_i^*}{T^2} \frac{\partial T}{\partial x_i} + \frac{1}{T} \left( \sigma_{\langle ij \rangle}^* D_{\langle ij \rangle} - t_{[ij]}^* H_{ij}^* + \vartheta^* n_i D_{\langle ij \rangle} n_j \right) \\ &+ \frac{\varrho^*}{T} \left( \varepsilon^* - T \delta^* - \psi^* \Gamma^* - \varrho^* \frac{\partial \psi^*}{\partial \varrho^*} \Gamma^* - \frac{\partial \psi^*}{\partial \rho_D^*} \Pi_D^* \right) + \hat{\partial}_i \iota_i^* \geq 0, \end{aligned} \quad (3.40)$$

where  $\zeta^{*P} = \zeta^* - \delta^*$  (see proposition 3.1 of Part I).

Another crucial outcome of (3.32) and (3.33) is that the inequality (3.40) attains its minimum value, namely zero, at equilibrium. In other words,

$$\begin{aligned} \zeta^{*P}|_{\mathbb{E}}(n_k n_s; \varrho^*, \rho_D^*, \beta_{\mathcal{X}}^*, \Gamma^*, H_{lm}^*; T, D_{\langle pq \rangle}, T, r) \\ = \zeta^{*P}(n_k n_s; \varrho^*, \rho_D^*, \beta_{\mathcal{X}}^*, 0, 0, T, 0, 0) = 0. \end{aligned} \quad (3.41)$$

Necessary conditions for the occurrence of this minimum are (cf. (3.32))

$$\left. \frac{\partial \zeta^{*P}}{\partial \Gamma^*} \right|_{\mathbb{E}} = 0, \quad \left. \frac{\partial \zeta^{*P}}{\partial H_{ij}^*} \right|_{\mathbb{E}} = 0, \quad \left. \frac{\partial \zeta^{*P}}{\partial D_{\langle ij \rangle}} \right|_{\mathbb{E}} = 0, \quad \left. \frac{\partial \zeta^{*P}}{\partial T_{,i}} \right|_{\mathbb{E}} = 0, \quad (3.42)$$

and also that the Hessian matrix  $\left. \frac{\partial^2 \zeta^{*P}}{\partial X_\xi \partial X_\chi} \right|_{\mathbb{E}}$  be positive semi-definite. (3.43)

In effect, (3.42) exclude those terms in (3.40) that are linear in the dissipative variables  $X_\chi^* = \{\Gamma^*, H_{ij}^*, D_{\langle kl \rangle}, T_{,p}\}$ . A short analysis of (3.15) and (3.39) reveals that all terms in the first line of (3.40) are non-linear in  $X_\chi^*$ , but the last one, which is linear in  $D_{\langle ij \rangle}$ . The situation is not so trivial in the second line of (3.40), since the identification of its linear terms depends on the explicit representations of  $\varepsilon^*$ ,  $\delta^*$ ,  $\Pi_D^*$  and  $\iota_i^*$ . Concerning the latter, we observe from (3.38) that a *linear* dependence of the coefficients  $\iota_{kj}^{*(1)}$  and  $\iota_{kj}^{*(2)}$  upon  $n_k n_j$  is dispensable, because it is already included in the projector tensor  $(\delta_{ik} - n_i n_k)$ . Hence, it suffices to write ( $\zeta = 1, 2$ )

$$\iota_{kj}^{*(\zeta)} = \iota^{*(\zeta)} \delta_{kj} + \iota_{kj}^{*(\zeta)} \Big|_{\mathbb{E}}, \quad \text{with} \quad \iota_{kj}^{*(\zeta)} \Big|_{\mathbb{E}} = \iota^{*(\zeta)} \delta_{kj}, \quad (3.44)$$

where  $\iota^{*(\zeta)}(\varrho^*, \rho_D^*; T)$  and  $\iota_{kj}^{*(\zeta)} \Big|_{\mathbb{E}}(n_i n_l; \varrho^*, \rho_D^*; T, D_{\langle pq \rangle})$  denote, respectively, the equilibrium and non-equilibrium parts of the tensor coefficients  $\iota_{kj}^{*(\zeta)}$ . By inserting (3.44) into (3.38), the derivative in the second line of (3.40) can be computed:

$$\hat{\partial}_i \iota_i^* = -3\iota^{*(2)} n_i D_{\langle ij \rangle} n_j + (\hat{\partial}_i \iota_i^*)_{\text{NL}}, \quad \text{with} \quad (\hat{\partial}_i \iota_i^*)_{\text{NL}} \Big|_{\mathbb{E}} = 0, \quad (3.45)$$

where  $(\cdot)_{\text{NL}}$  indicates that the respective function is strictly non-linear in the sources of dissipation —for (3.45) this means non-linear in  $D_{\langle ij \rangle}$  and its products with  $H_{ij}^*$ — cf. (3.30)<sub>1</sub> and (3.38); see also Appendix A of Part I.

Finally, since the general representations of the production rates  $\varepsilon^*$ ,  $\delta^*$  and  $\Pi_D^*$  have all the same form, it suffices to present here just one of them, viz.

$$\varepsilon^* = \varepsilon^{*(1)} \Gamma^* + \varepsilon^{*(2)} n_i D_{\langle ij \rangle} n_j + \varepsilon_{\text{NL}}^*, \quad \text{with} \quad \varepsilon_{\text{NL}}^* \Big|_{\mathbb{E}} = 0, \quad (3.46)$$

where  $\varepsilon^{*(\zeta)} = \varepsilon^{*(\zeta)}(\varrho^*, \rho_D^*, \beta_{\varkappa}^*; T)$ ,  $\zeta = 1, 2$ , while  $\varepsilon_{\text{NL}}^*$  is a function of all variables listed in (3.34) but  $T_{,i}$ , and it depends non-linearly on  $\Gamma^*$ ,  $H_{ij}^*$  and  $D_{\langle ij \rangle}$ . Identical relations hold also for  $\Pi_D^*$  and  $\delta^*$  —keeping in mind that  $\delta_{\text{NL}}^*$  may depend non-linearly upon all dissipative variables, including  $T_{,i}$ — cf. hypothesis 3.1.

We are now ready to exploit (3.42). From (3.15), (3.39), (3.40), (3.45) and (3.46) we infer that (3.42)<sub>2,4</sub> are identically satisfied, while (3.42)<sub>1,3</sub> imply, respectively,

$$\begin{aligned} \varepsilon^{*(1)} - T\delta^{*(1)} - \Pi_D^{*(1)} \frac{\partial \psi^*}{\partial \rho_D^*} &= \psi^* + \varrho^* \frac{\partial \psi^*}{\partial \varrho^*}, \\ \varepsilon^{*(2)} - T\delta^{*(2)} - \Pi_D^{*(2)} \frac{\partial \psi^*}{\partial \rho_D^*} &= \frac{3T}{\varrho^*} \iota^{*(2)} - \frac{\vartheta^*}{\varrho^*}. \end{aligned} \quad (3.47)$$

To proceed with the analysis of (3.47), we must go beyond mathematics to postulate, on physical grounds, reasonable (though restrictive) interpretations of the coefficients  $\varepsilon^{*(\zeta)}$ ,  $\delta^{*(\zeta)}$ ,  $\Pi_D^{*(\zeta)}$ ,  $\vartheta^*$  and  $\iota^{*(2)}$  ( $\zeta = 1, 2$ ). This will be done in §3d. Thus, we conclude that inequality (3.40) reduces to the form

$$\begin{aligned} \varrho^* \zeta^{*P} &= -\frac{q_i^*}{T^2} \frac{\partial T}{\partial x_i} + \frac{1}{T} \left( \sigma_{\langle ij \rangle}^* D_{\langle ij \rangle} - t_{[ij]}^* H_{ij}^* \right) \\ &+ \frac{\varrho^*}{T} \left( \varepsilon_{\text{NL}}^* - T\delta_{\text{NL}}^* - \frac{\partial \psi^*}{\partial \rho_D^*} \Pi_{\text{DNL}}^* \right) + (\hat{\partial}_i \iota_i^*)_{\text{NL}} \geq 0, \end{aligned} \quad (3.48)$$



which is strictly non-linear in the dissipative variables  $\Gamma^*$ ,  $H_{ij}^*$ ,  $D_{\langle ij \rangle}$  and  $T_{,i}$ . Once explicit representations for all constitutive functions appearing in (3.48) are postulated, the (non-)positivity of transport coefficients could be examined via (3.43). We will refrain, however, from dwelling longer upon general non-linear representations.

(d) *Gibbs equation and recrystallization pressure*

Recrystallization effects modelled by  $\Gamma^*$ ,  $\Pi_{\text{D}}^*$ ,  $\varepsilon^*$  and  $\delta^*$  are in practice very intricate and non-linear. Nevertheless, for a modest understanding of the physics behind (3.47) it may suffice to consider an oversimplified, hypothetical annealing process in a polycrystalline *unit volume* (figure 3). We focus attention on the migration of a single grain boundary, that moves inwards a crystallite with  $c$  axis directed to  $n_i$ . In such an artless situation,  $\varrho^* \Gamma^* < 0$  represents the mass lost by the shrinking crystallite during grain boundary migration, per unit time.† The rate of dislocation loss of such a contracting grain is  $\rho_{\text{D}}^* \Gamma^*$ : the total length of dislocation lines, within a unit volume, that is swept by the moving grain boundary, per unit time. Of course, the loss of dislocations implies a corresponding loss of stored energy and entropy, expressed by the release of latent heat. According to the first and second laws of thermodynamics (Kittel & Krömer 2000), this latent heat can be related to the enthalpy change, or alternatively to the product of the entropy change and temperature. Thus, we can write the energy loss rate as  $\varrho^* h^* \Gamma^*$ , and the entropy loss rate as  $\varrho^* \eta^* \Gamma^*$ , with  $h^* := e^* + p^*/\varrho^*$  denoting the *specific species enthalpy*.

Owing to (3.46) and the corresponding expressions for  $\delta^*$  and  $\Pi_{\text{D}}^*$ , the example illustrated in figure 3 motivates the identifications

$$\varepsilon^{*(1)} = h^* , \quad \delta^{*(1)} = \eta^* , \quad \Pi_{\text{D}}^{*(1)} = \rho_{\text{D}}^* , \quad (3.49)$$

in such a way that (3.47)<sub>1</sub> leads to the notion of *species pressure*

$$p^* = \varrho^* \left( \varrho^* \frac{\partial \psi^*}{\partial \varrho^*} + \rho_{\text{D}}^* \frac{\partial \psi^*}{\partial \rho_{\text{D}}^*} \right) . \quad (3.50)$$

This result is a compelling evidence for interpreting  $\rho_{\text{D}}^*$  as the species dislocation density. Indeed, if  $\rho_{\text{D}}^*$  has the meaning of a dislocation density, then  $c_{\text{D}}^* := \rho_{\text{D}}^*/\varrho^*$  defines the *species concentration of dislocations* (per unit mass, i.e. with dimension of length/mass). Now, if we perform the change of variables  $\rho_{\text{D}}^* \rightarrow c_{\text{D}}^*$  and redefine the Helmholtz free energy as  $\Psi^*(\varrho^*, c_{\text{D}}^*; T) := \psi^*(\varrho^*, \varrho^* c_{\text{D}}^*; T)$ , we find

$$p^* = \varrho^{*2} \frac{\partial \Psi^*}{\partial \varrho^*} , \quad (3.51)$$

which is the habitual definition of pressure, as a function of  $\varrho^*$ ,  $c_{\text{D}}^*$ , and  $T$ . Further, using  $c_{\text{D}}^*$  as variable, we can derive from (3.27)<sub>2</sub>, (3.28) and (3.51) the differential

$$d\Psi^* = -\eta^* dT + \frac{p^*}{\varrho^{*2}} d\varrho^* + \frac{\mu_{\text{D}}^*}{c_{\text{D}}^*} dc_{\text{D}}^* , \quad (3.52)$$

where

$$\mu_{\text{D}}^* := c_{\text{D}}^* \frac{\partial \Psi^*}{\partial c_{\text{D}}^*} = \rho_{\text{D}}^* \frac{\partial \psi^*}{\partial \rho_{\text{D}}^*} \quad (3.53)$$

† Certainly, crystallites surrounding the shrinking grain have a corresponding mass gain, but we are not interested in neighbouring grains at this moment, since they belong to other species.



Figure 3. Hypothetical annealing process. *Left*: unit volume containing a shrinking crystallite (gray). *Right*: after a unit time interval, the gray crystallite has lost the mass indicated by the dashed region, viz.  $\varrho^* \Gamma^* < 0$ . Accordingly, the dislocation loss is given by  $\rho_{\text{D}}^* \Gamma^*$ .

defines the orientation-dependent ‘chemical’ potential of dislocations, or shortly the *species dislocation potential*. Then, returning to  $\rho_{\text{D}}^*$  as variable and using the definition  $\psi^* := e^* - T\eta^*$ , we can rewrite (3.52) in the form of the *Gibbs equation*

$$d\eta^* = \frac{1}{T} \left( de^* - \frac{p^*}{\varrho^{*2}} d\varrho^* - \frac{\mu_{\text{D}}^*}{c_{\text{D}}^*} dc_{\text{D}}^* \right). \quad (3.54)$$

Finally, from the definitions of  $c_{\text{D}}^*$  and  $\mu_{\text{D}}^*$  it is easy to rearrange (3.50) in the form of the specific *Gibbs free energy* (or *free enthalpy*) of a species, viz.

$$g^* := h^* - T\eta^* = \psi^* + \frac{p^*}{\varrho^*} = \frac{\partial \varrho^* \psi^*}{\partial \varrho^*} + \mu_{\text{D}}^* = g_{\text{id}}^* + \mu_{\text{D}}^*. \quad (3.55)$$

In this sense,  $\mu_{\text{D}}^*$  can be interpreted as the part of the specific Gibbs free energy due to dislocations, whereas  $g_{\text{id}}^* := g^* - \mu_{\text{D}}^*$  is the specific Gibbs free energy of *ideal crystallites*, i.e. crystallites without line defects.

In contrast to (3.47)<sub>1</sub>, there is no strong motivation for a physical interpretation of (3.47)<sub>2</sub>. There are, however, some faint hints. Firstly, we rewrite (3.47)<sub>2</sub> as

$$\varrho^* \varepsilon^{*(2)} - \varrho^* T \delta^{*(2)} + \vartheta^* - c_{\text{D}}^{*-1} \mu_{\text{D}}^* \Pi_{\text{D}}^{*(2)} = 3T\iota^{*(2)}. \quad (3.56)$$

According to (3.30)<sub>1</sub> and (3.44), the left-hand side of (3.56) is expected to be a function of  $\varrho^*$ ,  $\rho_{\text{D}}^*$ ,  $\beta_{\text{z}}^*$  and  $T$ , whereas the right-hand side of (3.56) is a function solely of  $\varrho^*$ ,  $\rho_{\text{D}}^*$  and  $T$ . Secondly, it is not difficult to recognize in (3.56) that its right-hand side is related to shear along basal planes (cf. (3.38) and (3.44)), while its left-hand side is linked to extension in the  $c$ -axis direction, i.e. orthogonal to the basal planes. These remarks, though feeble, serve as incentive to simplify (3.56) by supposing that its both sides are equal to the same constant, namely zero. Thus, by assuming in addition that  $\vartheta^*$  vanishes,<sup>†</sup> we obtain

$$T\delta^{*(2)} - \varepsilon^{*(2)} + \rho_{\text{D}}^{*-1} \mu_{\text{D}}^* \Pi_{\text{D}}^{*(2)} = 0, \quad \vartheta^* = 0, \quad \iota^{*(2)} = 0. \quad (3.57)$$

Further, it seems reasonable to assume, in a first approximation, that the production of internal energy by straining along the  $c$ -axis direction should be proportional to the production of dislocations. Now, the density of energy stored in dislocations can be estimated by  $\bar{c}\rho_{\text{D}}^* G b^2$ , where  $b$  denotes the magnitude of the *Burgers vector* (a material constant),  $\bar{c} \sim 0.7$  is a fitting parameter, and  $G(T)$  is the *shear modulus* of the material (Suzuki *et al.* 1991; Humphreys & Hatherly 2004). Thus, we propose

$$\varepsilon^{*(2)} = \bar{c} G b^2 \Pi_{\text{D}}^{*(2)}, \quad \text{so that} \quad \delta^{*(2)} = (\bar{c}\rho_{\text{D}}^* G b^2 - \mu_{\text{D}}^*) \frac{\Pi_{\text{D}}^{*(2)}}{\rho_{\text{D}}^* T}. \quad (3.58)$$

<sup>†</sup> A brief analysis of (3.39)<sub>1</sub> reveals that  $\vartheta^*$  represents an equilibrium tension along the  $c$  axis that must vanish by definition, as long as creep is concerned (i.e., vanishing yield stress).

**Remark 3.3.** Clearly, the production of dislocations by straining along the  $c$ -axis direction should be strongly dependent on the slip activity in pyramidal planes. In this sense, the coefficient  $\Pi_{\text{D}}^{*(2)}$  might be relevant when considerable pyramidal slide occurs, but it is expected to be negligibly small for materials whose pyramidal slip systems are hardly active (which is normally the case). Therefore, in most common situations  $\Pi_{\text{D}}^{*(2)}$  may be neglected, in a first approximation.

Lastly, it remains to notice that the sum of the non-linear production rates in the second line of (3.48) can be interpreted as the time rate of a kind of ‘non-equilibrium pressure’, which we can write as

$$\varrho^* \left( \varepsilon_{\text{NL}}^* - T \delta_{\text{NL}}^* - \frac{\mu_{\text{D}}^*}{\rho_{\text{D}}^*} \Pi_{\text{D NL}}^* \right) = P^* \Gamma^*, \quad \text{with} \quad P^*|_{\text{E}} = 0. \quad (3.59)$$

We may call  $P^*(n_k n_s; \varrho^*, \rho_{\text{D}}^*, \beta_{\mathcal{X}}^*, \Gamma^*, H_{lm}^*; T, D_{\langle pq \rangle}, T, r)$  the *driving pressure for grain boundary migration*, or shortly the *recrystallization pressure*. Actually, the quantity  $P^*$  expresses markedly the duality of the theory: by invoking the polycrystalline nature of the material,  $P^*$  does represent the pressure acting on the grain boundaries due to the stored deformation energy (Gottstein & Shvindlerman 1999; Humphreys & Hatherly 2004); on the other hand, by viewing the material as a ‘mixture of crystallites’, the quantity  $P^*$  can be understood as the *affinity* of a species, while the mass production rate  $\Gamma^*$  plays the role of a ‘reaction rate’ (Atkins 1998). Indeed, in both interpretations  $P^*$  may be associated to differences in the dislocation potentials (i.e., the Gibbs free energies due to dislocations) of crystallites with distinct  $c$ -axis orientations (see Part III, Faria 2005b).

Subjected to the above simplifications, the residual inequality (3.48) reduces to

$$T \varrho^* \varsigma^{*\text{P}} = - \frac{q_i^*}{T} \frac{\partial T}{\partial x_i} + \sigma_{\langle ij \rangle}^* D_{\langle ij \rangle} - t_{[ij]}^* H_{ij}^* + P^* \Gamma^* \geq 0. \quad (3.60)$$

#### (e) *Résumé of the general constitutive relations*

For further reference, we collect here the main results of the general constitutive theory for a class of incompressible polycrystalline media characterized by a single crystallographic axis (the  $c$  axis).

⇒ fundamental scalar relations:

$$\begin{aligned} e^* &= e^*(\varrho^*, \rho_{\text{D}}^*, T), & \eta^* &= \eta^*(\varrho^*, \rho_{\text{D}}^*, T), & \psi^* &:= e^* - T \eta^*, \\ c_{\text{D}}^* &:= \frac{\rho_{\text{D}}^*}{\varrho^*}, & \Psi^*(\varrho^*, c_{\text{D}}^*, T) &:= \psi^*(\varrho^*, \varrho^* c_{\text{D}}^*, T), & \eta^* &= - \frac{\partial \Psi^*}{\partial T} = - \frac{\partial \psi^*}{\partial T}, \\ p^* &= \varrho^{*2} \frac{\partial \Psi^*}{\partial \varrho^*} = \varrho^* \left( \varrho^* \frac{\partial \psi^*}{\partial \varrho^*} + \rho_{\text{D}}^* \frac{\partial \psi^*}{\partial \rho_{\text{D}}^*} \right), & \mu_{\text{D}}^* &:= c_{\text{D}}^* \frac{\partial \Psi^*}{\partial c_{\text{D}}^*} = \rho_{\text{D}}^* \frac{\partial \psi^*}{\partial \rho_{\text{D}}^*}, \\ h^* &:= e^* + p^* / \varrho^*, & g^* &:= h^* - T \eta^* = \frac{\partial \varrho^* \psi^*}{\partial \varrho^*} + \mu_{\text{D}}^*, \\ d\eta^* &= \frac{1}{T} \left( de^* - \frac{p^*}{\varrho^{*2}} d\varrho^* - \frac{\mu_{\text{D}}^*}{c_{\text{D}}^*} dc_{\text{D}}^* \right), \end{aligned} \quad (3.61)$$

⇒ dislocation parameter:

$$\gamma^* = \gamma^*(n_k n_s; \varrho^*, \rho_{\text{D}}^*, \beta_{\mathcal{X}}^*, \Gamma^*, H_{lm}^*; T, D_{\langle pq \rangle}, T, r), \quad (3.62)$$

⇒ fluxes and stresses:

$$\begin{aligned}
t_{ij}^* &= -p^* \delta_{ij} + \sigma_{ij}^* + t_{[ij]}^*, & \sigma_{ij}^* &= \sigma_{ji}^*, & m_{ij}^* &= 0, \\
\phi_i^* &= \frac{q_i^*}{T}, & q_i^* &= -k_{ij}^* \frac{\partial T}{\partial x_j}, & \iota_i^* &:= \varphi_i^* - \frac{1}{T} \left( \xi_i^* - \frac{\mu_D^*}{c_D^*} j_{Di}^* \right), \\
\varphi_i^* &= (\delta_{ik} - n_i n_k) \left( \varphi_{kj}^{*(1)} H_{jl}^* + \varphi_{kj}^{*(2)} D_{\langle jl \rangle} \right) n_l, \\
\xi_i^* &= (\delta_{ik} - n_i n_k) \left( \xi_{kj}^{*(1)} H_{jl}^* + \xi_{kj}^{*(2)} D_{\langle jl \rangle} \right) n_l, \\
j_{Di}^* &= (\delta_{ik} - n_i n_k) \left( j_{Dkj}^{*(1)} H_{jl}^* + j_{Dkj}^{*(2)} D_{\langle jl \rangle} \right) n_l, \\
\iota_i^* &= (\delta_{ik} - n_i n_k) \left( \iota_{kj}^{*(1)} \Big|_{\mathfrak{P}} H_{jl}^* + \iota_{kj}^{*(2)} \Big|_{\mathfrak{P}} D_{\langle jl \rangle} \right) n_l, \\
\varpi_{ij}^* &= p^* \epsilon_{ijk} n_k + \pi_{ij}^*, & \pi_{ij}^* &:= T \epsilon_{ikl} \frac{\partial \iota_j^*}{\partial H_{kl}^*} = T \epsilon_{ikl} n_l (\delta_{jp} - n_j n_p) \iota_{pk}^{*(1)} \Big|_{\mathfrak{P}}, \\
\tau_{ij}^* &= (\delta_{ik} - n_i n_k) \left( \tau^{*(1)} \delta_{jl} + \tau^{*(2)} D_{\langle jl \rangle} \right) \frac{\partial T}{\partial x_k} n_l,
\end{aligned} \tag{3.63}$$

⇒ production rate terms:

$$\begin{aligned}
\varepsilon^* &= h^* \Gamma^* + \bar{c} G b^2 \Pi_D^{*(2)} n_i D_{\langle ij \rangle} n_j + \varepsilon_{\text{NL}}^*, \\
\Pi_D^* &= \rho_D^* \Gamma^* + \Pi_D^{*(2)} n_i D_{\langle ij \rangle} n_j + \Pi_{\text{D NL}}^*, \\
\delta^* &= \eta^* \Gamma^* + (\bar{c} \rho_D^* G b^2 - \mu_D^*) \frac{\Pi_D^{*(2)}}{\rho_D^* T} n_i D_{\langle ij \rangle} n_j + \delta_{\text{NL}}^*, \\
\varrho^* &\left( \varepsilon_{\text{NL}}^* - T \delta_{\text{NL}}^* - \frac{\mu_D^*}{\rho_D^*} \Pi_{\text{D NL}}^* \right) = P^* \Gamma^*, \\
\kappa_i^* &= \kappa_{ij}^* \frac{\partial T}{\partial x_j}, & \nu_i^* &= \epsilon_{ijk} \left( \nu_{lj}^{*(1)} H_{kl}^* + \nu_{lj}^{*(2)} D_{\langle kl \rangle} \right).
\end{aligned} \tag{3.64}$$

In the equations above,

- $\sigma_{ij}^*$  and  $t_{[ij]}^*$  are non-equilibrium functions of all variables listed in (3.34), with strictly linear dependence upon  $H_{ij}^*$  and  $T_{,i}$ , cf. (3.33), (3.39)<sub>3</sub> and (3.41);
- $\delta_{\text{NL}}^*$  is a non-equilibrium function of all variables listed in (3.34), with strictly non-linear dependence upon the sources of dissipation  $\Gamma^*$ ,  $H_{ij}^*$ ,  $D_{\langle ij \rangle}$  and  $T_{,i}$ ;
- $P^*$  is a non-equilibrium function of all variables listed in (3.34), with eventual non-linear dependence upon the sources of dissipation  $\Gamma^*$ ,  $H_{ij}^*$ ,  $D_{\langle ij \rangle}$  and  $T_{,i}$ ;
- $\varepsilon_{\text{NL}}^*$  and  $\Pi_{\text{D NL}}^*$  are non-equilibrium functions of  $n_i n_j$ ,  $\varrho^*$ ,  $\rho_D^*$ ,  $\beta_{\varkappa}^*$ ,  $T$ , as well as  $\Gamma^*$  and  $D_{\langle ij \rangle}$ , with strictly non-linear dependence upon these last two variables;
- $\kappa_{ij}^*$  and  $\nu_{ij}^{*(\zeta)}$  (with  $\zeta = 1, 2$ ) are functions of all variables listed in (3.34);
- $k_{ij}^*$ ,  $\varphi_{ij}^{*(\zeta)}$ ,  $\xi_{ij}^{*(\zeta)}$ ,  $j_{Dkj}^{*(\zeta)}$  and  $\tau^{*(\zeta)}$  (with  $\zeta = 1, 2$ ) are functions of  $n_i n_j$ ,  $\varrho^*$ ,  $\rho_D^*$ ,  $\beta_{\varkappa}^*$ ,  $T$ ,  $\Gamma^*$  and  $D_{\langle ij \rangle}$ ;
- $\iota_{ij}^{*(\zeta)} \Big|_{\mathfrak{P}}$  (with  $\zeta = 1, 2$ ) are non-equilibrium functions of  $T$ ,  $D_{\langle ij \rangle}$  and  $n_i n_j$ ;
- $\Pi_D^{*(2)}$  depends solely upon  $\varrho^*$ ,  $\rho_D^*$ ,  $\beta_{\varkappa}^*$  and  $T$ ;
- $G$  is simply a function of  $T$ , while  $b$  and  $\bar{c}$  are constants.

Once we know the explicit forms of the microstructure parameters  $\gamma^*$  and  $\beta_{\mathcal{Z}}^*$ , as well as all quantities listed above, insertion of (3.61)–(3.64) into (2.2)–(2.6) provides a closed set of field equations for the basic fields  $\varrho^*$ ,  $\rho_{\mathcal{D}}^*$ ,  $s_i^*$ ,  $v_i$ ,  $T$  and  $\Gamma^*$ .

#### 4. Conclusion

By combining the theory of mixtures with continuous diversity (Faria 2001) with the celebrated method of Lagrange multipliers (Liu 2002), we were able to derive a thermodynamically consistent constitutive theory for large polycrystalline masses made of transversely isotropic grains, with regard of incompressibility, strain-induced anisotropy and recrystallization, under the constraint of negligible grain shifting (i.e. no ‘superplastic flow’, cf. remark 3.2 of Part I and remark 2.1 of Part III). Owing to the fabric (texture) changes by lattice rotation, as well as the bending/twisting of crystallites by polygonization, the polycrystal and its composing grains were modelled as polar media (Truesdell & Noll 1965; Faria & Hutter 2002).

Relevant results of the constitutive theory include the vanishing of the Voigt couple stress  $m_{ij}^*$ , viz. (3.63)<sub>3</sub>, and the validity of the usual Clausius–Duhem hypothesis  $\phi_i^* = q_i^*/T$  (see (3.63)<sub>4,5</sub>) relating heat and entropy fluxes.† In contrast, a similar hypothesis does not hold for the interspecies fluxes of heat and entropy,  $\xi_i^*$  and  $\varphi_i^*$ , cf. (3.63)<sub>6</sub>. We found also that all thermodynamic potentials, viz.  $e^*$ ,  $\psi^*$ ,  $g^*$  and  $h^*$ , depend solely on the temperature  $T$  and the species densities of mass  $\varrho^*$  and dislocations  $\rho_{\mathcal{D}}^*$ . This is a welcome result, because it renders the construction of equations of state a relatively easy task. Further, we discovered that dislocations contribute to the Gibbs free energy of the grains through the dislocation potential  $\mu_{\mathcal{D}}^*$ . This quantity is for polycrystalline media the counterpart to the chemical potential of physical chemistry (Atkins 1998), being therefore essential for the equilibrium thermodynamics of the polycrystal, as evidenced by the Gibbs equation (3.54). Additionally, there exists a non-equilibrium ‘pressure’ responsible for the migration of grain boundaries, called recrystallization pressure  $P^*$ . It is a constitutive function, given by (3.59). Finally, polygonization is expressed by the orientational dependence of the  $c$ -axis spin velocity  $s_i^*$  (cf. (2.8); see also Faria & Kipfstuhl 2004). Such a dependence is caused by bending and twisting torques modelled by the interspecies couple stress  $\varpi_{ij}^*$  (cf. (2.4) and §3b of Part I; see Placidi *et al.* 2004). In this sense,  $\varpi_{ij}^*$  may also be called the *polygonization tensor*.

The results derived so far are rather general and suit to a whole class of polycrystals. Several simplifications can still be brought into effect by selecting a particular material. An example of such simplifications is given in Part III of this series (Faria 2005*b*) where this constitutive theory is applied to the dynamics of ice sheets.

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† The vanishing of the Voigt couple stress is partially caused by the neglect of a constitutive dependence upon  $\partial s_i^*/\partial x_j$  (cf. (3.1)), which is a reasonable assumption in a first order gradient theory as long as the spin velocity  $S_{ij}^*$  is of same order as the vorticity  $W_{ij}$ . Also the validity of the Clausius–Duhem hypothesis is a consequence of the vanishing of grain shifting (§2a) and the constraints assumed in hypothesis 3.1. None of these results are expected to hold in general.

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