

Nonlinear Field Theory of Stress Induced Diffusion in Crystalline Solids

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Abstract Two different mathematical descriptions of the material drift based respectively on the concept of mass- and molar-averaged velocities are presented. In this way two different material derivatives over time are introduced: mass and molar, respectively. The first approach based on the overall mass motion is used mainly in the traditional continuum thermodynamics of deformable solids while the second approach developed here comes back to the constitutive modelling used mainly in the chemical physics. The problem of the stress induced diffusion is situated on the border of the two different approaches developed often separately. In this paper, taking into account the standard balance laws for molar motion, the driving forces for diffusion are determined. The forces obtained for diffusion of chemical components depend not only on gradients of chemical potentials (osmotic force) but also on some additional forces controlling the stress induced diffusion process. The driving forces derived for dislocation field comprise the Peach-Koehler force as well as an additional term resulting from the effect of dislocation movement on the concentration of vacancies.

Mass balance vs. molar balance

Mass balance for each component of solid structure satisfies the following balance law

$$\dot{\rho}_i + \rho_i \operatorname{div} \dot{\mathbf{x}}_i = 0, \quad (1)$$

where ρ_i and $\dot{\mathbf{x}}_i$ denote the mass density and velocity of the i -th material particle while $\dot{\rho}_i$ denotes the material derivative of mass density of the i -th component, i.e.

$$\dot{\rho}_i = \frac{\partial \rho_i}{\partial t} + \operatorname{grad} \rho_i \dot{\mathbf{x}}_i. \quad (2)$$

Dividing the first equation by the molar mass of the i -th component, $M_i = \text{const}$, it is easy to prove that the molar concentration also satisfies the master balance law

$$\dot{c}_i + c_i \operatorname{div} \dot{\mathbf{x}}_i = 0, \quad (3)$$

where $\rho_i = M_i c_i$ and

$$\dot{c}_i = \frac{\partial c_i}{\partial t} + \operatorname{grad} c_i \dot{\mathbf{x}}_i. \quad (4)$$

This means that to determine an overall motion function for a material as a whole we can use alternatively the mass densities or molar concentrations. Namely, let us define two mutually different overall material velocities

$$\mathbf{u} \stackrel{df}{=} \frac{1}{\rho} \sum_{i=1}^N \rho_i \dot{\mathbf{x}}_i, \quad \mathbf{v} \stackrel{df}{=} \frac{1}{c} \sum_{i=1}^N c_i \dot{\mathbf{x}}_i, \quad (5)$$

where

$$\rho \stackrel{df}{=} \sum_{i=1}^N \rho_i, \quad c \stackrel{df}{=} \sum_{i=1}^N c_i. \quad (6)$$

Using such defined two different material derivatives we can rewrite (1) and (3) in the following form

$$\overset{u}{\rho}_i + \rho_i \operatorname{div} \mathbf{u} + \operatorname{div} (\rho_i \mathbf{u}_i) = 0, \quad \overset{v}{c}_i + c_i \operatorname{div} \mathbf{v} + \operatorname{div} (c_i \mathbf{v}_i) = 0, \quad (7)$$

where

$$\overset{u}{\rho}_i \stackrel{df}{=} \frac{\partial \rho_i}{\partial t} + \operatorname{grad} \rho_i \cdot \mathbf{u}, \quad \overset{v}{c}_i \stackrel{df}{=} \frac{\partial c_i}{\partial t} + \operatorname{grad} c_i \cdot \mathbf{v}, \quad (8)$$

$$\mathbf{u}_i \stackrel{df}{=} \dot{\mathbf{x}}_i - \mathbf{u}, \quad \mathbf{v}_i \stackrel{df}{=} \dot{\mathbf{x}}_i - \mathbf{v}. \quad (9)$$

The local velocities, \mathbf{u}_i and \mathbf{v}_i , called here respectively the mass and molar diffusion rates, satisfy the conditions

$$\sum_{i=1}^N \rho_i \mathbf{u}_i = \mathbf{0}, \quad \sum_{i=1}^N c_i \mathbf{v}_i = \mathbf{0}. \quad (10)$$

Summing (7) over all components it is easy to show that the respective material derivatives of ρ and c satisfy the master balance law, namely

$$\overset{u}{\rho} + \rho \operatorname{div} \mathbf{u} = 0, \quad \overset{v}{c} + c \operatorname{div} \mathbf{v} = 0, \quad (11)$$

cf. (11a) with (1.2.10) and (1.1.43) in [1], respectively.

Mass vs. molar fractions

The mass and molar fractions can be defined as

$$\omega_i \stackrel{df}{=} \frac{\rho_i}{\rho}, \quad n_i \stackrel{df}{=} \frac{c_i}{c}, \quad (12)$$

which means that the fractions satisfy

$$\rho_i = \rho \omega_i, \quad c_i = c n_i. \quad (13)$$

Differentiating the last relations over time it can be shown that the respective material rates satisfy

$$\overset{u}{\rho}_i = \overset{u}{\rho} \omega_i + \rho \overset{u}{\omega}_i, \quad \overset{v}{c}_i = \overset{v}{c} n_i + c \overset{v}{n}_i. \quad (14)$$

Substituting into (7) and using (11) we find, cf. (1.2.15) in [1],

$$\boxed{\overset{u}{\omega}_i = -\frac{1}{\rho} \operatorname{div} (\rho \omega_i \mathbf{u}_i)}, \quad \boxed{\overset{v}{n}_i = -\frac{1}{c} \operatorname{div} (c n_i \mathbf{v}_i)}. \quad (15)$$

Molar concentration of vacancies

Similarly to molar concentration of chemical components we can determine the molar concentrations of crystal defects, e.g. vacancies. A trouble with crystal defects is that many of them cannot be described uniquely by means of scalar functions but often it is indispensable to employ tensorial variables, e.g. dislocation distribution. The evolution of such fields is governed by balance laws complicated more than the master balance law [2]. Due to limited size of this paper we concentrate here on migration that defects which take the crucial role in the stress induced diffusion. For example, in the known Smigelskas Kirkendall's experiment [3] the significant part of molar fraction of material dissolves in lattice in one region (brass) by climbing down of edge dislocations, and next, such dissolved material (zink) is carried out by vacancy movement to other regions where the crystal lattice grows up again by climbing up of other dislocations operating in that regions (copper). The gradient of zink concentration induces the main driving force for vacancy movement. Our aim is to show an example of constitutive equations for modelling of such problem, see (54-59). Before that, according to the state-of-the-art of the nonlinear field theory, we first should balance all thermodynamic driving forces. To this aim, let us introduce: the molar concentration of vacancies c_0 , its molar fraction according to (12), and assume the following balance law for vacancies

$$\boxed{n_0^v = -\frac{1}{c} \operatorname{div}(c n_0^v \mathbf{v}_0) + \operatorname{tr} \mathbf{d}_{\text{pl}}}, \quad (16)$$

where $\operatorname{tr} \mathbf{d}_{\text{pl}}$ is the trace of plastic deformation rate tensor. Our assumption means nothing more as only that the whole volume effect of plastic deformation is coupled with the nucleation and/or annihilation of vacancies.

Reference configuration

The material velocities, \mathbf{u} and \mathbf{v} , determine two mutually different functions of material motion

$$\mathbf{x}(\mathbf{X}, t) \stackrel{df}{=} \int_0^t \mathbf{u} dt + \mathbf{X} \quad \text{or} \quad \mathbf{x}(\mathbf{X}, t) \stackrel{df}{=} \int_0^t \mathbf{v} dt + \mathbf{X}. \quad (17)$$

where \mathbf{x} and \mathbf{X} denote the current and reference positions of material particle. As yet, in theories developed in terms of thermodynamics of large deformations the first approach based on the mass movement was used mainly. Nevertheless, the stress induced diffusion is situated on the border of mechanics and chemistry, while in chemistry the molar concentrations and molar fractions take the crucial role in constitutive modelling. Therefore in this paper a brief comparison of thermodynamic consequences for two alternative descriptions are shown. Independently of which description we chose we have to determine the elastic strain. Let us assume that the total deformation gradient can be decomposed into thermodynamically reversible deformation \mathbf{F}_e and thermodynamically irreversible one \mathbf{F}_{pl} . Making the polar decomposition of the reversible (lattice) deformation into rotation tensor \mathbf{R} and left or right stretch tensors, \mathbf{V} and \mathbf{U} , the mentioned method leads to the following relations for the total deformation gradient

$$\mathbf{F} = \frac{\partial \mathbf{x}}{\partial \mathbf{X}} = \underbrace{\mathbf{R}\mathbf{U}}_{\mathbf{F}_e} \mathbf{F}_{\text{pl}} = \underbrace{\mathbf{V}\mathbf{R}}_{\mathbf{F}_e} \mathbf{F}_{\text{pl}}, \quad (18)$$

where $\mathbf{V} = \mathbf{R}\mathbf{U}\mathbf{R}^T$. The strain tensors can be defined as the logarithm function of the respective stretch tensor, see among others [4, 5],

$$\widehat{\boldsymbol{\varepsilon}} \stackrel{df}{=} \ln \mathbf{U} = \frac{1}{2} \ln (\mathbf{F}_e^T \mathbf{F}_e), \quad (19)$$

$$\boldsymbol{\varepsilon} \stackrel{df}{=} \ln \mathbf{V} = \frac{1}{2} \ln (\mathbf{F}_e \mathbf{F}_e^T) = \mathbf{R} \widehat{\boldsymbol{\varepsilon}} \mathbf{R}^T. \quad (20)$$

In order to determine the stress conjugate with strains, we need to know the material derivatives of the strain tensors. Taking into account two material motion functions we find alternatively

$$\overset{u}{\widehat{\boldsymbol{\varepsilon}}} = \widehat{\boldsymbol{\mathcal{A}}}: [\mathbf{R}^T (\text{grad } \mathbf{u} - \mathbf{d}_{pl}) \mathbf{R}], \quad \overset{v}{\widehat{\boldsymbol{\varepsilon}}} = \widehat{\boldsymbol{\mathcal{A}}}: [\mathbf{R}^T (\text{grad } \mathbf{v} - \mathbf{d}_{pl}) \mathbf{R}], \quad (21)$$

where $\mathbf{d}_{pl} = \mathbf{F}_e \overset{u}{\mathbf{F}}_{pl} \mathbf{F}^{-1}$ or $\mathbf{d}_{pl} = \mathbf{F}_e \overset{v}{\mathbf{F}}_{pl} \mathbf{F}^{-1}$. Decomposing the fourth order tensor $\widehat{\boldsymbol{\mathcal{A}}}$ in the basis spanned on strain eigenvectors it can be shown [4] that all non-vanishing components are

$$\widehat{\mathcal{A}}_{ijij} = \widehat{\mathcal{A}}_{ijji} = \begin{cases} \delta_{ij} & \text{for } \widehat{\varepsilon}_i = \widehat{\varepsilon}_j, \\ \frac{2(\widehat{\varepsilon}_i - \widehat{\varepsilon}_j)}{e^{\widehat{\varepsilon}_i - \widehat{\varepsilon}_j} - e^{\widehat{\varepsilon}_j - \widehat{\varepsilon}_i}} & \text{for } \widehat{\varepsilon}_i \neq \widehat{\varepsilon}_j. \end{cases} \quad (22)$$

Overall molar mass

An overall molar mass is defined here as follows $M \stackrel{df}{=} \rho/c$. It is easy to show that

$$\frac{1}{M} = \sum_{i=1}^N \frac{1}{M_i} \omega_i, \quad M = \sum_{i=1}^N M_i n_i. \quad (23)$$

Taking into account (15) it can be proved that their respective material derivatives vanish, i.e.

$$\overset{u}{\frac{1}{M}} = 0 \quad \text{and} \quad \overset{v}{M} = 0. \quad (24)$$

Momentum balance

Before we draw the constitutive relations for the free energy let us recall the fundamental relations for momentum and moment of momentum used in the theory of mixture

$$\text{div } \boldsymbol{\sigma}_i + \rho_i \mathbf{f}_{bi} - \rho_i \ddot{\mathbf{x}}_i = \mathbf{0}, \quad (25)$$

$$\boldsymbol{\sigma}_i - \boldsymbol{\sigma}_i^T = \mathbf{0}. \quad (26)$$

where $\boldsymbol{\sigma}_i$, \mathbf{f}_{bi} and $\ddot{\mathbf{x}}_i$ denote the partial Cauchy stress, body force and acceleration of particles of i th component.

Summing (25) over all components and using (5a-11a) we find (27a-29a). On the other hand, diving (25) by molar mass M_i , next summing over all constituents, using (5b-11b), and multiplying by overall molar mass M we find (27b-29b).

$$\text{div } \boldsymbol{\sigma} + \rho \mathbf{f} - \rho \overset{u}{\dot{\mathbf{u}}} = \mathbf{0}, \quad \text{div } \boldsymbol{\sigma} + c \mathbf{f} - c M \overset{v}{\dot{\mathbf{v}}} = \mathbf{0}, \quad (27)$$

where, alternatively

$$\boldsymbol{\sigma} = \sum_{i=1}^N \left(\boldsymbol{\sigma}_i - \rho_i \mathbf{u}_i \otimes \mathbf{u}_i \right), \quad \boldsymbol{\sigma} = \sum_{i=1}^N \frac{M}{M_i} \left(\boldsymbol{\sigma}_i - \rho_i \mathbf{v}_i \otimes \mathbf{v}_i \right), \quad (28)$$

$$\mathbf{f} \stackrel{df}{=} \sum_{i=1}^N \omega_i \mathbf{f}_{bi}, \quad \mathbf{f} \stackrel{df}{=} \sum_{i=1}^N n_i \mathbf{f}_{bi} - \left(\boldsymbol{\sigma}_i - \rho_i \mathbf{v}_i \otimes \mathbf{v}_i \right) \text{grad} \frac{M}{M_i}, \quad (29)$$

cf. (28a) and (52a) with eqn. (215.1) in [6]. These two different averaging techniques shown above, cf. (28a) and (28b), can not be used simultaneously. To state a constitutive equation for an overall stresses we must take a decision first, which approach to the overall motion will be employed: mass or molar? It is worth to mention that the problem of homogenisation of stresses, e.g. a problem of their upper and lower bounds, makes a very wide problem itself. Our aim is to show two mutually different continuum approaches based respectively on the overall mass and overall molar movement functions. The first approach based on the overall mass motion is used mainly in the traditional continuum thermodynamics of deformable solids while the second approach developed here in terms of continuum mechanics comes back to the constitutive modelling used mainly in the chemical physics. The problem of the stress induced diffusion is situated on the border of the two different approaches developed often separately.

Balance laws based on mass movement

Let us assume the following form of the integral balance equations for solid structure

$$\frac{d_u}{dt} \int_{\mathcal{B}} \rho dv = 0, \quad (30)$$

$$\frac{d_u}{dt} \int_{\mathcal{B}} \rho \mathbf{u} dv = \int_{\partial \mathcal{B}} \boldsymbol{\sigma} ds + \int_{\mathcal{B}} \rho \mathbf{f} dv, \quad (31)$$

$$\frac{d_u}{dt} \int_{\mathcal{B}} \mathbf{x} \times \rho \mathbf{u} dv = \int_{\partial \mathcal{B}} \mathbf{x} \times \boldsymbol{\sigma} ds + \int_{\mathcal{B}} \mathbf{x} \times \rho \mathbf{f} dv, \quad (32)$$

$$\frac{d_u}{dt} \int_{\mathcal{B}} \rho e + \sum_{i=1}^N \frac{1}{2} \rho_i (\mathbf{u} + \mathbf{u}_i)^2 dv = \int_{\partial \mathcal{B}} \mathbf{u} \boldsymbol{\sigma} ds + \int_{\partial \mathcal{B}} \mathbf{q} ds + \int_{\mathcal{B}} \rho \mathbf{f} u dv - \int_{\partial \mathcal{B}} \mathbf{q}_T ds + \int_{\mathcal{B}} \rho h dv, \quad (33)$$

$$\frac{d_u}{dt} \int_{\mathcal{B}} \rho \eta dv \geq - \int_{\partial \mathcal{B}} \frac{\mathbf{q}_T}{T} ds + \int_{\mathcal{B}} \frac{\rho h}{T} dv, \quad (34)$$

where $\frac{d_u}{dt}$ denotes the material derivative determined in relation to the mass velocity \mathbf{u} , cf. (7a). In equations mentioned above the symbols e , \mathbf{q} , \mathbf{q}_T , h , η , T denote the specific internal energy, vector of its transfer, vector of heat transfer, density of energy production and temperature. The integral equations lead to the following differential equation set

$$\overset{u}{\rho} + \rho \text{div} \mathbf{u} = 0, \quad (35)$$

$$\text{div} \boldsymbol{\sigma} + \rho \mathbf{f} - \rho \overset{u}{\mathbf{u}} = \mathbf{0}, \quad (36)$$

$$\boldsymbol{\sigma} - \boldsymbol{\sigma}^T = \mathbf{0}, \quad (37)$$

$$-\rho \overset{u}{e} + \boldsymbol{\sigma} : \text{grad} \mathbf{u} - \text{div} \mathbf{q} - \text{div} \mathbf{q}_T + \rho h = 0, \quad (38)$$

$$-\rho \overset{u}{\psi} - \rho \eta \overset{u}{T} + \boldsymbol{\sigma} : \text{grad} \mathbf{u} - \text{div} \mathbf{q} - \frac{\mathbf{q}_T}{T} \text{grad} T \geq 0, \quad (39)$$

where the specific free energy is determined as $\psi = e - \eta T$.

Balance laws based on molar movement

Similarly as for mass movement we assume here, cf.(11) and (27),

$$\frac{d_v}{dt} \int_{\mathcal{B}} c dv = 0, \quad (40)$$

$$\frac{d_v}{dt} \int_{\mathcal{B}} c M \mathbf{v} dv = \int_{\partial \mathcal{B}} \boldsymbol{\sigma} ds + \int_{\mathcal{B}} c \mathbf{f} dv, \quad (41)$$

$$\frac{d_v}{dt} \int_{\mathcal{B}} \mathbf{x} \times c M \mathbf{v} dv = \int_{\partial \mathcal{B}} \mathbf{x} \times \boldsymbol{\sigma} ds + \int_{\mathcal{B}} \mathbf{x} \times c \mathbf{f} dv, \quad (42)$$

$$\begin{aligned} \frac{d_v}{dt} \int_{\mathcal{B}} c M e + \sum_{i=1}^N \frac{1}{2} c_i M_i (\mathbf{v} + \mathbf{v}_i)^2 dv &= \int_{\partial \mathcal{B}} \mathbf{v} \boldsymbol{\sigma} ds + \int_{\mathcal{B}} c \mathbf{f} \mathbf{v} dv - \int_{\partial \mathcal{B}} \mathbf{q}_T ds - \int_{\partial \mathcal{B}} \mathbf{q} ds \\ &+ \int_{\mathcal{B}} c h dv, \end{aligned} \quad (43)$$

$$\frac{d_v}{dt} \int_{\mathcal{B}} c \eta dv \geq - \int_{\partial \mathcal{B}} \frac{\mathbf{q}_T}{T} ds + \int_{\mathcal{B}} \frac{c h}{T} dv, \quad (44)$$

where $\frac{d_v}{dt}$ denotes the material derivative determined in relation to the molar drift rate \mathbf{v} , cf. (8) where $\frac{d_v c_i}{dt} \equiv \dot{c}_i$. It is easy to show that the above integral equations lead to the following differential equation set

$$\dot{c} + c \operatorname{div} \mathbf{v} = 0, \quad (45)$$

$$\operatorname{div} \boldsymbol{\sigma} + c \mathbf{f} - c M \dot{\mathbf{v}} = \mathbf{0}, \quad (46)$$

$$\boldsymbol{\sigma} - \boldsymbol{\sigma}^T = \mathbf{0}, \quad (47)$$

$$-c \dot{e} + \boldsymbol{\sigma} : \operatorname{grad} (M \mathbf{v}) - \operatorname{div} \mathbf{q} - \operatorname{div} \mathbf{q}_T + c h = 0, \quad (48)$$

$$-c \dot{\psi} - c \eta \dot{T} + \boldsymbol{\sigma} : \operatorname{grad} (M \mathbf{v}) - \operatorname{div} \mathbf{q} - \frac{\mathbf{q}_T}{T} \operatorname{grad} T \geq 0, \quad (49)$$

where $\psi = e - \eta T$.

Constitutive equations for molar free energy can be assumed here in the following general form

$$\psi = \psi(\widehat{\boldsymbol{\varepsilon}}, n_0, n_1, \dots, n_{n-1}, T). \quad (50)$$

Substituting into (49) and taking into account the equations for rates of thermodynamic variables, see (21b,15b,16b), we obtain

$$\sum_{i=0}^{n-1} \mathbf{f}_i \mathbf{j}_i + (\boldsymbol{\sigma} - \boldsymbol{\sigma}_\mu) : \mathbf{d}_{pl} - \frac{\mathbf{q}_T}{T} \operatorname{grad} T \geq 0 \quad (51)$$

under the following resultant identities

$$\boldsymbol{\sigma} = c \mathbf{R}(\widehat{\boldsymbol{\mathcal{A}}} : \frac{\partial \psi}{\partial \widehat{\boldsymbol{\varepsilon}}}) \mathbf{R}^T - \sum_{i=1}^N c_i M \mathbf{v}_i \otimes \mathbf{v}_i, \quad \boldsymbol{\sigma}_\mu = \frac{\partial \psi}{\partial n_0} \mathbf{1}, \quad \eta = - \frac{\partial \psi}{\partial T}, \quad (52)$$

$$\mathbf{f}_i = - \operatorname{grad} \frac{\partial \psi}{\partial n_i}, \quad \mathbf{q} = \sum_{i=0}^{n-1} \frac{\partial \psi}{\partial n_i} \mathbf{j}_i, \quad \mathbf{j}_i = c n_i \mathbf{v}_i. \quad (53)$$

Example Let us consider

$$\psi = \frac{1}{2\hat{c}}(\hat{\boldsymbol{\epsilon}} - \hat{\boldsymbol{\epsilon}}_{\text{ch}}) : \hat{\mathbf{c}} : (\hat{\boldsymbol{\epsilon}} - \hat{\boldsymbol{\epsilon}}_{\text{ch}}) + \psi_{\text{ch}}, \quad (54)$$

where the chemical strain $\hat{\boldsymbol{\epsilon}}_{\text{ch}}$, elastic stiffness $\hat{\mathbf{c}}$ and ψ_{ch} are independent of $\hat{\boldsymbol{\epsilon}}$, i.e. they depend only on $n_0, n_1, \dots, n_{n-1}, T$ while the molar concentration \hat{c} is referred to the volume element in the local reference configuration, i.e. $\hat{c} = c \det \mathbf{F}_e^{-1}$. The constitutive relation for the chemical strain $\hat{\boldsymbol{\epsilon}}_{\text{ch}}$ (cf. Vegard law) takes the key role in modelling of the coupled stress-diffusion effect while ψ_{ch} denotes here the chemical part of free energy responsible for the osmotic diffusion. In our case the elastic strain can be identified with $\hat{\boldsymbol{\epsilon}}_e \stackrel{df}{=} \hat{\boldsymbol{\epsilon}} - \hat{\boldsymbol{\epsilon}}_{\text{ch}}$, cf. [7, 8]. To determine the thermodynamic forces let us assume that the plastic deformation is governed by the movement of the self-balancing dislocation distribution tensor fields, namely

$$\mathbf{d}_{\text{pl}} = \sum_{\mathbf{d}} \boldsymbol{\alpha}_{\mathbf{d}} \times \mathbf{v}_{\mathbf{d}} \quad (55)$$

where $\sum_{\mathbf{d}} \boldsymbol{\alpha}_{\mathbf{d}} = 0$ and \times means the cross product, $\mathbf{v}_{\mathbf{d}}$ is the velocity of the \mathbf{d} -th dislocation distribution tensor field $\boldsymbol{\alpha}_{\mathbf{d}}$. Substituting (54) and (55a) into (51) and neglecting the inertial term in (52a) we find

$$\sum_{i=0}^{n-1} \mathbf{f}_i \mathbf{j}_i + \sum_{\mathbf{d}} \mathbf{f}_{\mathbf{d}} \mathbf{v}_{\mathbf{d}} - \frac{\mathbf{q}_T}{T} \text{grad } T \geq 0, \quad (56)$$

where,

$$\boldsymbol{\sigma} = \mathbf{c} : (\boldsymbol{\epsilon} - \boldsymbol{\epsilon}_{\text{ch}}), \quad \mathbf{f}_i = -\text{grad}(\mu_i - \mu_{ei}), \quad \mu_i = \frac{\partial \psi_{\text{ch}}}{\partial n_i}, \quad (57)$$

$$\mathbf{f}_{\mathbf{d}} = (\boldsymbol{\sigma} - \boldsymbol{\sigma}_{\mu}) \dot{\times} \boldsymbol{\alpha}_{\mathbf{d}}, \quad \mathbf{q} = \sum_{i=0}^{n-1} (\mu_i - \mu_{ei}) \mathbf{j}_i, \quad \mu_{ei} = \boldsymbol{\sigma} : \mathbf{a}_i, \quad (58)$$

see also (52b) and (53c), the sign $\dot{\times}$ denotes a double scalar-cross product carried out over two sequential indexes, see [5]. Due to configuration changes $\mathbf{c} = \mathbf{R}(\hat{\mathbf{A}} : \hat{\mathbf{c}})\mathbf{R}^T \det \mathbf{F}_e^{-1}$ and $\mathbf{a} = \mathbf{R}\hat{\mathbf{a}}\mathbf{R}^T$ where $\hat{\mathbf{a}} = \partial \hat{\boldsymbol{\epsilon}}_{\text{ch}} / \partial n_i$. To complete constitutive equations we must state equations for the interdiffusion of chemical components, dislocation velocity and heat flux, e.g.

$$\mathbf{j}_i = \sum_{j=0}^N \mathbf{l}_{ij}(\mathbf{f}_i - \mathbf{f}_j), \quad \mathbf{v}_{\mathbf{d}} = \boldsymbol{\theta}_{\mathbf{d}} \mathbf{f}_{\mathbf{d}}, \quad \mathbf{q}_T = -\mathbf{k} \text{grad } T. \quad (59)$$

where \mathbf{l}_{ij} , $\boldsymbol{\theta}_{\mathbf{d}}$ and \mathbf{k} denote the material tensors.

Final Remarks

In this paper it has been shown in brief that it is possible to build up a nonlinear thermodynamic system for material motion based on two different approaches to material motion: mass and molar. The mathematical consequences have been shown for material derivatives, balance equations, and partially for driving forces and constitutive equations. As yet, see [6, 1, 8, 2], the mathematical description of stress induced diffusion was developed mainly in terms of nonlinear continuum thermodynamics based on the overall mass movement. On the other hand, usually, in the chemical physics the constitutive modelling is based on molar description. To balance such chosen molar thermodynamic system a quite different description of material drift is needed.

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