THERMODYNAMIC EXTREMAL PRINCIPLE
AND ITS APPLICATION TO DUFOUR AND
SORET EFFECTS AND PLASTICITY

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Abstract. An extremal principle is formulated for thermodynamic systems near equilibrium subjected to various external conditions. It is shown that the principle describes unambiguously the kinetics of the thermodynamic system and replaces classical phenomenological equations. Thus the principle can be considered as an effective tool for the treatment of non-equilibrium thermodynamic systems. In two examples the principle is used for the description of Dufour and Soret effects and plasticity.

1. Introduction

Linear thermodynamics of irreversible processes introduces linear relations between generalized thermodynamic fluxes and generalized thermodynamic forces called phenomenological equations with coefficients depending on material properties and state variables like temperature $\theta$ [1]–[3]. This concept is suitable for the description of evolution of systems not too far from the equilibrium, e.g. for modeling of material processing and properties at elevated temperatures. The classical way of determining the evolution of a system is represented by the solution of phenomenological equations, complemented by conservation laws and proper boundary and contact as well as initial conditions.

In 1931 Onsager [4] showed that the linear phenomenological equations for heat conduction in an anisotropic system can be derived from the requirement of the maximum of a functional having a close relation to the total entropy production in the system and formulated the Thermodynamic Extremal Principle (TEP). Then Onsager applied the TEP to multicomponent diffusion in 1945 in a more or less forgotten paper [5]. During the following 60 years the field of extremal principles in thermodynamics has spread in several directions. The Lagrangian [6], [7] and Hamiltonian [8], [9] structures of the principle as well as the method of path integrals [10] have been developed. Furthermore, extremal principles have been formulated for steady-state and transient non-linear systems or systems far from equilibrium [7], [11], [12]. The important role of entropy production with respect to the proper formulation of constitutive laws in a wide field of applications can be recognized in [13]–[15]. It was also demonstrated that the principle can be generalized to arbitrary processes obeying the laws of linear non-equilibrium thermodynamics [16]–[18]. During the last 15 years the TEP has been applied to the development of models in materials science [19]–[29]. The authors have demonstrated that the TEP seems to be a handy tool for the solution of practical problems of thermodynamics of irreversible processes.
The aim of the present paper is to show the reader how the TEP can be introduced in a rational way and to derive the well-known equations for the Dufour and Soret effects and for the plasticity from the TEP.

2. Thermodynamic Extremal Principle (TEP)

Let us consider a body and define in its interior a system occupying the domain $V$ with the surface $\partial V$ and the surface outer normal $\nu$ in its actual configuration at time $t$. The Cartesian coordinates $x_1, x_2, x_3$ are represented by a vector $\mathbf{x}$. Scalar quantities like the temperature $\theta$ are functions of $\mathbf{x}$ and $t$. Three-component column vectors are denoted by e.g. $\mathbf{a}$, square matrices of order 3 are denoted by e.g. $R$; superscript $^T$ refers to a transposed vector or matrix. We use the Einstein summation convention for double indices: the expression $b_k^T J_k$ means the sum of scalar products of the vectors $b_k$ and $J_k$ over all $k$. The product $a^T R a$ is a quadratic form in $a_1, a_2, a_3$.

Let the thermodynamic system be near the thermodynamic equilibrium. The evolution of the system is caused by irreversible processes in the system. These processes are represented by fluxes, by the motion of interfaces in polycrystalline and/or multiphase systems and finally by the rates of eigenstrain components. For simplification we consider only the fluxes as kinetic variables in the system. Let $J_k(\mathbf{x}, t), \ k \in \{0, \ldots, n\}$, be the fluxes occurring in the system where $J_0$ is the heat flux and $J_k$ for $k > 0$ are other kinds of fluxes, e.g. diffusive fluxes of components, the electric current etc.

The total entropy production $P$ in the system is a functional of the fluxes $J_k$ and in general can be expanded in a Taylor series with respect to the origin of the space of $J_k$-fluxes as

$$ P = \int_V (A + B_k^T J_k + J_k^T R_{kl} J_l + \text{higher-order terms}) \, dV. \quad (1) $$

From the requirement that the entropy production $P$ in any part of the system must be zero in the state of thermodynamic equilibrium, $J_k \equiv 0$, it follows that $A \equiv 0$. Since for systems not in thermodynamic equilibrium the total entropy production $P$ must be positive for arbitrary fluxes (Second Law of Thermodynamics), also the second term in the expansion (1) must not appear, $B_k \equiv 0$, and the third term must be a positive definite quadratic form of the components of the fluxes $J_k$. For the state near the thermodynamic equilibrium the first non-zero term of the Taylor-expansion is considered. Then $P$ is given by the truncated Taylor series after three terms as

$$ P = \int_V J_k^T R_{kl} J_l \, dV \equiv 2 \int_V \phi(J, \bar{J}) \, dV \equiv 2 \Phi(J, \bar{J}) \geq 0. \quad (2) $$

The symbol $\bar{J}$ in (2) represents a column vector $(J_0^T, J_1^T, \ldots, J_n^T)^T$ and $\phi(J, \bar{J})$ denotes the quadratic form of components of local values of the flux $\bar{J}$. Moreover, we can introduce a matrix $R$, compound from submatrices $R_{kl}$ with $k, l \in \{0, \ldots, n\}$. Then

$$ R_{klij} = \frac{1}{2} \frac{\partial^2 \phi}{\partial J_{kl} \partial J_{ij}} = \frac{1}{2} \frac{\partial^2 \phi}{\partial J_{lj} \partial J_{ki}} = R_{lkji}, \quad \text{i.e.} \quad R_{kl} = R_{lk}^T \quad (3) $$

describe the local material properties. The equation (2) represents the mathematical expression of the Second Law of Thermodynamics for systems near the thermodynamic equilibrium being a positive definite quadratic form in the fluxes.
The rate of the total entropy, $\dot{S}$, of an open system is given by

$$\dot{S} = P + \dot{S}_{\text{ext}},$$

(4)

where $\dot{S}_{\text{ext}}$ is the total flow of the entropy into the system. The rate of the total entropy can then be expressed according to [2] as

$$\dot{S} = \int_V \frac{\mu_k}{\theta} \text{div} \ J_k \, dV,$$

(5)

where $\mu_k(x, t)$, $k \in \{1, \ldots, n\}$, are the chemical potentials of the components $k$; $\mu_0 = -1$. The total flow of the entropy into the system follows according to [2] as

$$\dot{S}_{\text{ext}} = \int_{\partial V} \frac{\mu_k}{\theta} J^T_k \nu \, dA,$$

(6)

($dA$ is a surface element on $\partial V$). By the application of the Gauss theorem the combination of (5) and (6) yields

$$P = \dot{S} - \dot{S}_{\text{ext}} = -\int_V J^T_k \text{grad} \frac{\mu_k}{\theta} \, dV \equiv \int_V \psi(J) \, dV \equiv \Psi(J).$$

(7)

The quantity $\psi(J)$ in (7), coming from balancing the local rate of entropy in the system, is obviously a linear form in the fluxes.

A comparison of (2) and (7) furnishes the necessary equivalence condition

$$2\Phi(J, J) = \Psi(J).$$

(8)

Both functionals in (8), $2\Phi$ and $\Psi$, represent the total entropy production in the system. They have, however, a different physical meaning. As outlined above, $2\Phi$ is a positive definite quadratic form of the components of fluxes and reflects the material properties of the system. As a simple example it corresponds to the heat produced in a resistor due to an electric current. On the other hand, $\Psi$ is a linear form of the components of fluxes and reflects the driving forces in the system. In the a.m. simple example it corresponds to the energy released by the motion of electrons in an electric field caused by the voltage applied on the resistor.

Now the Thermodynamic Extremal Principle (TEP) is formulated as follows: From all admissible fluxes $J$, constrained by some conservation and boundary/contact conditions, those are selected in an irreversible process in a thermodynamic system near the equilibrium, which maximize the total entropy production in the system, expressed either by $2\Phi(J, J)$ or by $\Psi(J)$ and subjected to the equivalence condition (8).

3. Derivation of phenomenological equations

The requirement of an extremum of the functional $\Psi$ with respect to the fluxes $J$, constrained by condition (8), leads to the variation

$$\delta(\Psi + \alpha(2\Phi - \Psi)) = 0$$

(9)

with $\alpha$ being a Lagrange multiplier. Using relations (2) and (7) the variation (9) leads to the Euler/Lagrange equations

$$-\text{grad} \frac{\mu_k}{\theta} + \alpha \left( 2R_{kl} J_l + \text{grad} \frac{\mu_k}{\theta} \right) = 0$$

(10)
with \( k \in \{0, 1, \ldots, n\} \). Multiplication of all (10) by \( J_T^k \) from the left side, their summation with respect to \( k \), integration over the volume \( V \) of the system and comparison with (8) yield the value of \( \alpha = -1 \). Then (10) can be rewritten as

\[
R_{kl}J_l = -\text{grad} \frac{\mu_k}{\theta} .
\]

(11)

Relations (11), representing 3 linear equations for each \( k \) and altogether \( 3(n+1) \) linear equations for the \( 3(n+1) \) unknown components of the fluxes \( J_0, J_1, \ldots, J_n \), can formally be assembled into a matrix equation \( \overline{R}J = \overline{f} \), where \( \overline{R} \) is a square matrix of order \( 3(n+1) \) and both \( \overline{J} \) and \( \overline{f} \) are column vectors with \( 3(n+1) \) components; \( \overline{f} \) consists of the subvectors \( f_k = -\text{grad} \frac{\mu_k}{\theta} \).

(12)

\( \overline{R} \) is symmetric due to \( R_{kl} = R_{lk}^T \).

The integrand of (2) can now be rewritten as \( J_T^R \overline{R}J \). Since \( P \) must be positive for any volume \( V \), this fact leads directly to the positive definiteness of \( \overline{R} \), allowing an inversion of the matrix relation \( \overline{R}J = \overline{f} \) to \( J = \overline{L}f \) where \( \overline{L} \) is also positive definite and symmetric and can be disassembled into its submatrices \( L_{kl} \). Then the kinetic equations can be written in the form

\[
J_k = -L_{kl} \text{grad} \frac{\mu_l}{\theta} .
\]

(13)

which are the linear, phenomenological equations.

Since the properties of the matrices \( \overline{R} \) and \( \overline{L} \) are the same, the properties of \( R_{kl} \) can be identically addressed to \( L_{kl} \). Thus the symmetry relation for \( L_{kl} \) reads

\[
L_{kl} = L_{lk}^T .
\]

(14)

For the isotropic cases \( L_{kl} \) takes the form \( \omega_{kl}I \), where \( I \) is the unit matrix, and \( \omega_{kl} \) are some material characteristics. The symmetry properties of the coefficients \( \omega_{kl} \) can be addressed as the well-known Onsager’s reciprocal relations. In general, cross-effects are met by (14) in anisotropic materials. It should be emphasized that the symmetry relations are a direct consequence of the application of TEP and they were not a priori assumed, as strongly criticized e.g. by Truesdell [30], Lecture 7. They come from the assumption that the entropy production is a positive definite quadratic form of the kinetic variables for states near the thermodynamic equilibrium.

Insertion of \( \alpha = -1 \) into (9) yields the variation of \( -2\Phi + 2\Psi \), representing the functional \( P \) of the entropy production, constrained by (8), to be extremized. We have introduced \( \Phi \) in (2) and \( \Psi \) in (7); using our simplified notation, we have

\[
-2\Phi(J, \overline{J}) + 2\Psi(\overline{J}) = \int_V (-J_T^R \overline{R}J + 2J_T^f) dV .
\]

(15)

The second variation of the functional \( -2\Phi + 2\Psi \) is characterized by the corresponding Hessian matrix \( -2\overline{R} \); for all details see [31], p. 195. Since \( \overline{R} \) is a positive definite matrix, \( H \) the negative definite Hessian matrix \( -2\overline{R} \) ensures a maximum of the functional \( -2\Phi + 2\Psi \).
4. Thermodynamic potentials

The formulation of the TEP, presented in Section 2, is designed for the most general case of open thermodynamic systems. In practice many thermodynamic systems can be considered as closed systems. In the following it is shown that for closed systems the rate of a thermodynamic potential takes over the role of the total entropy production.

The simplest system cannot exchange the entropy with its surroundings enforcing $\dot{S}_{\text{ext}} = 0$, i.e. an insulated closed system with a fixed volume $V$. Then according to (4) the total entropy production in the system $P$ equals the rate of the total entropy of the system $\dot{S}$

$$P = \dot{S}.$$  \hspace{1cm} (16)

For such a system the TEP can be formulated in terms of $\dot{S}$ replacing $P$. As a direct consequence of the TEP by the rate of entropy $\dot{S} > 0$ for states out of equilibrium, and $S$ achieves its maximum for the equilibrium state of the system.

Systems at a constant temperature $\theta$ are often a better approximation of the reality than insulated ones. Such a condition can be ensured by a constant environment temperature and by a sufficiently high heat conductivity in the system. Assuming a constant volume $V$ of the system, it follows according to the first law of thermodynamics that

$$\dot{E} = \theta \dot{S}_{\text{ext}}$$  \hspace{1cm} (17)

where $E$ is the total internal energy of the system. According to (7)

$$P = \frac{\theta \dot{S} - \dot{E}}{\theta} = -\frac{\dot{F}}{\theta},$$  \hspace{1cm} (18)

where $F$ is the total free energy of the system.

In the case of a constant temperature $\theta$ and a constant external pressure $p$ the first law of thermodynamics reads

$$\dot{E} + p\dot{V} = \theta \dot{S}_{\text{ext}}.$$  \hspace{1cm} (19)

Then according to (7)

$$P = \frac{\theta \dot{S} - \dot{E} - p\dot{V}}{\theta} = -\frac{\dot{G}}{\theta}$$  \hspace{1cm} (20)

where $G$ is the total Gibbs’ energy of the system.

5. Applications of TEP

5.1. The Dufour and Soret effects. We assume $n$ atomic components represented by their molar fractions $x_i$ with $i \in \{1, \ldots, n\}$ and their diffusive fluxes $J_i$ interacting with the heat flux $J_0$ in an one-dimensional system ($z$ is the length coordinate). We assume no coupling between the diffusional fluxes as it is typical for interstitial components. The coupling between the heat flux and the diffusional fluxes is known as Dufour effect, see the recent paper by Lebon et al. [32]. Contrarily, the coupling between the diffusional fluxes and the heat flux is known as Soret effect, see [30] and the recent paper by Platten [33]. Both effects are known since the 19-th century, and their kinetic laws have a somewhat heuristic origin. We can show that by a direct application of the TEP both evolution equations can be derived in a general way for a multicomponent system.
Using (11) one can write
\[ R_{kl} J_l = -\frac{\partial}{\partial z} \left( \frac{\mu_k}{\theta} \right) \]  
(21)
for \( k \in \{1, \ldots, n\} \). Note that \( R_{kl} \) is now written for convenience as \( R_{kl} \) because we are working only in an one-dimensional setting.

An inversion of (21) with \( L_{kl} = R_{kl}^{-1} \) yields
\[ J_k = -L_{kl} \frac{\partial}{\partial z} \left( \frac{\mu_l}{\theta} \right). \]
(22)
Since we assume that the individual diffusion processes do not interact, it follows that \( L_{kl} = L_{kk} \delta_{kl} \), \( \delta_{kl} = \begin{cases} 1 & \text{for } k = l, \\ 0 & \text{for } k \neq l \end{cases} \)
(23)
no summation for \( k \) is allowed here and \( k, l \in \{1, \ldots, n\} \). The terms \( L_{l0} = L_{0l} \) with \( l \in \{0, 1, \ldots, n\} \) are assumed to be non-zero. To ensure the positive definiteness of the matrix of elements \( L_{kl} \) with \( k, l \in \{0, \ldots, n\} \), all principal minors of these matrix must be positive. This implies directly that \( L_{11}, \ldots, L_{nn} \) are positive, and from the calculation of the determinant of the whole matrix one can derive the relation
\[ \frac{L_{0i}^2}{L_{ii}} < L_{00} \]
(24)
where the summation index \( i \) is restricted to \( \{1, \ldots, n\} \).

An evaluation of (22) under the consideration of the structure of \( L_{kl} \) yields
\[ J_0 = -\left( \frac{L_{00}}{\theta^2} - \frac{L_{0k}}{\theta} \left( \frac{\mu_k}{\theta} - \frac{\partial \mu_k}{\partial \theta} \right) \right) \frac{\partial \theta}{\partial z} \frac{\partial \mu_k}{\partial x_j}, \]
(25)
where the sum indices \( j \) and \( k \) are restricted to \( \{1, \ldots, n\} \) and
\[ J_i = -\left( \frac{L_{0i}}{\theta^2} - \frac{L_{ii}}{\theta} \left( \frac{\mu_i}{\theta} - \frac{\partial \mu_i}{\partial \theta} \right) \right) \frac{\partial \theta}{\partial z} \frac{\partial \mu_i}{\partial x_i}, \]
(26)
without any summation for \( i \in \{1, \ldots, n\} \).

As one can see from (25), the heat flux \( J_0 \) is coupled with the diffusive process. If one expresses the gradient \( \partial \theta/\partial z \) by \( J_0 \) and all gradients \( \partial x_j/\partial z \) by \( J_j \), one can evaluate a relation between the diffusive fluxes and the heat flux.

The coefficients
\[ \frac{L_{00}}{\theta^2} - \frac{L_{0k}}{\theta} \left( \frac{\mu_k}{\theta} - \frac{\partial \mu_k}{\partial \theta} \right), \quad \frac{L_{ii}}{\theta} \frac{\partial \mu_i}{\partial x_i} \]  
(no summation)
(27)
can be calibrated by Fourier’s Law and Fick’s First Law, resp., the first one as the thermal conductivity \( \lambda \) and the second one as the ratio \( D_i/V_m \), where \( D_i \) is the diffusion coefficient of component \( i \) and \( V_m \) is the molar volume.

To obtain an accordance with the dimensions, we introduce Dufour diffusion coefficients \( D_{F,j} \) as
\[ L_{0k} \frac{\partial \mu_k}{\partial x_j} = \frac{\theta}{V_m} D_{F,j} \]
(28)
and thermal diffusion coefficients
\[
\frac{L_{0i}}{\theta^2} - \frac{L_{ii}}{\theta} \left( \frac{\mu_i}{\theta} - \frac{\partial \mu_i}{\partial \theta} \right) = \frac{\theta}{V_m} D_{T,i} \quad \text{(no summation)}.
\] (29)

Note that all diffusion coefficients \( D_i, D_{F,j} \) and \( D_{T,i} \) have the same dimension \( m^2/s \).

Then the fluxes can finally be written as
\[
J_0 = -\lambda \frac{\partial \theta}{\partial z} - \theta \frac{D_{F,j}}{V_m} \frac{\partial x_j}{\partial z} \quad \text{(30)}
\]
and
\[
J_i = -\frac{D_{T,i}}{\theta V_m} \frac{\partial \theta}{\partial z} - \frac{D_i}{V_m} \frac{\partial x_i}{\partial z} \quad \text{(31)}
\]

without summation for \( i \in \{1, \ldots, n\} \). Lebon et al. [32] report with their relations (13), (14) equivalent relations, however, with different dimensions of their diffusion coefficients. Platten [33] starts with relation (1) of [33] for the Soret effect, however using the expression \( D_T c_0 (1 - c_0) \) instead of \( D_{T,i} \) with \( c_0 \) being a constant and ignoring the second contribution on the left side of (26).

What shall be finally mentioned is that the TEP delivers evolution equations for both effects, being simultaneously active for a multicomponent system in strict accordance with the Second Law, see the restrictions on the coefficients \( L_{ij} \), outlined by (24). For the case of any constraints between the fluxes the TEP can be applied, too, with proper formulations of these side conditions, as e. g. in [25] and [34]. A typical case of such a side condition may be that the sum of the fluxes \( J_i \) with \( i \in \{1, \ldots, n\} \) is equal to zero.

5.2. Plasticity. The TEP has proved to be an excellent tool to understand rate-independent plastic, irreversible straining. We restrict in the following context on a small strain setting with a stress tensor \( \sigma \) and its deviator \( s = \sigma - \frac{1}{3} (\text{tr } \sigma) I \); here \( \text{tr } \sigma \) means the trace of \( \sigma \) and \( I \) the unity matrix. The tensor \( \varepsilon_p \) is the plastic strain yielding \( \varepsilon = \varepsilon_p + \varepsilon_e \) with \( \varepsilon \) being the total strain and \( \varepsilon_e \) the elastic strain tensor. The storage of energy due to the isotropic hardening of the material is described by the equivalent plastic strain \( \varepsilon_{pv} \) whose rate is defined as
\[
\dot{\varepsilon}_{pv} = \sqrt{\frac{2}{3} \varepsilon_{\varepsilon_p} : \dot{\varepsilon}_{\varepsilon_p}} = \sqrt{\frac{2}{3} ||\dot{\varepsilon}_{\varepsilon_p}||} ;
\] (32)
with \( || \cdot || \) we denominate the norm of a vector or tensor. In the case of kinematic hardening also a backstress tensor may appear as a further set of internal variables. For sake of simplicity we assume that no energy is stored due to any hardening which means only the elastic strain energy is stored and the rest is dissipated. Finally we have only \( \varepsilon_{\varepsilon_p} \) as the set of internal variables with \( s \) playing the role of forces and \( \dot{s}_{\varepsilon_p} \) that of fluxes. We keep the temperature \( \theta \) constant and have for \( \Psi \) according to (7)
\[
\Psi = -\int_V \frac{1}{\theta} \frac{\partial G}{\partial \varepsilon_{\varepsilon_p}} : \dot{s}_{\varepsilon_p} \ dV = \frac{1}{\theta} \int_V s : \dot{s}_{\varepsilon_p} \ dV .
\] (33)

Plastification takes place, if the so-called yield condition is fulfilled; otherwise we have an elastic loading or unloading process,
\[
\frac{3}{2} s : s = r^2 (\varepsilon_{pv}) .
\] (34)
The quantity \( r \) is the yield stress and is usually a function of \( \varepsilon_{pv} \). During plastification the deviator must keep to the yield condition, so this condition becomes an identity and leads to the so-called consistency condition being the rate of (34) as
\[
\frac{3}{2} \frac{\dot{s}}{s} = \hat{\gamma} r .
\]

The value of \( \dot{r} \) can be calculated as
\[
(d r / d \varepsilon_{pv}) \dot{\varepsilon}_{pv} \text{ with } r = \frac{d r}{d \varepsilon_{pv}} \text{ denominated as hardening modulus } E_i .
\]
The modulus \( E \) can be taken from a \( r-\varepsilon_{pv} \) diagram providing \( r \) as function of \( \varepsilon_{pv} \) by a uniaxial tension/compression test.

Let us study now several cases with respect to the application of the TEP. Generally the local dissipation function \( Q = 2 \phi \theta \) can be introduced and the entropy production \( s : \dot{\varepsilon}_{pv} / \theta \) corresponds to \( \psi \). Then for constant \( \theta \) we have to extremize
\[
Q + \alpha (Q - s : \dot{\varepsilon}_{pv}) \quad \text{or} \quad s : \dot{\varepsilon}_{pv} + \alpha (Q - s : \dot{\varepsilon}_{pv})
\]
with respect to \( \dot{\varepsilon}_{pv} \). Both formulations yield according to Sect. 3 the same result
\[
s = \frac{Q}{\partial Q / \partial \dot{\varepsilon}_{pv} : \dot{\varepsilon}_{pv}} .
\]
We start with a quadratic function \( Q \) defined as
\[
C \dot{\varepsilon}_{pv} : \dot{\varepsilon}_{pv}
\]
with \( C \) being a positive constant. Applying (37) yields immediately
\[
s = C \dot{\varepsilon}_{pv} .
\]
We can insert (38) into the yield condition (34) and find
\[
\frac{3}{2} C^2 \| \dot{\varepsilon}_{pv} \|^2 = r^2
\]
and
\[
s = \sqrt{\frac{2}{3}} \frac{r}{\| \dot{\varepsilon}_{pv} \|} , \quad \dot{\varepsilon}_{pv} = \sqrt{\frac{3}{2}} \frac{r}{\| \dot{\varepsilon}_{pv} \|} \frac{A \| \dot{\varepsilon}_{pv} \|}{\| \dot{\varepsilon}_{pv} \|} .
\]

The second expression (40) represents the “classical” normality rule of plasticity.

Note that we have started with a dissipation function \( Q \) of homogeneity degree 2. However, often as dissipation function a function of homogeneity degree 1, namely \( Q = A \| \dot{\varepsilon}_{pv} \| \), is used with \( A \) being a positive constant. Since the norm of \( \dot{\varepsilon}_{pv} \) is always positive, \( Q \geq 0 \). We apply now our concept to \( Q \) being a function of homogeneity degree 1 with \( \partial \| \dot{\varepsilon}_{pv} \| / \partial \dot{\varepsilon}_{pv} = \| \dot{\varepsilon}_{pv} \| / \dot{\varepsilon}_{pv} \) and \( d \| \dot{\varepsilon}_{pv} \| / dt = \dot{\varepsilon}_{pv} / \| \dot{\varepsilon}_{pv} \| \) and find from (37) with the both relations listed
\[
s = \frac{A \| \dot{\varepsilon}_{pv} \|}{A \dot{\varepsilon}_{pv} / \| \dot{\varepsilon}_{pv} \|} : \dot{\varepsilon}_{pv} \| \dot{\varepsilon}_{pv} \| .
\]

With the yield condition we can calibrate \( A \) and find immediately the same relation between \( \dot{\varepsilon}_{pv} \) and \( s \) as that given by (40).

Since plasticity can be dealt with either in the strain space or in the stress space, we study as next case the maximum of the first relation (36) with respect to \( s \).
A similar calculation as above yields
\[
\dot{\varepsilon}_p = \frac{Q}{\partial Q / \partial s : s} \frac{\partial Q}{\partial s}.
\]
(42)

We engage a dissipation function
\[
Q = B \dot{s} : \dot{s}
\]
with \( B \) being a positive constant and find with (42)
\[
\dot{\varepsilon}_p = B \dot{s}.
\]
(43)

The plastic strain rate \( \dot{\varepsilon}_p \) is now in a normality relation with \( Q \). Details with respect to the normality structure can be taken from [35] and a set of papers by Yang et al., referenced there. The quantity \( B \) can be calibrated by applying the yield condition (34) and leads to the same result as given by (40). We leave it to the reader to check, if the consistency condition (35) is fulfilled; it can be verified easily.

Finally the reader may ask how relation (40) for \( \dot{\varepsilon}_p \) can be applied in a calculational procedure. One has to start with the consistency relation and multiply both sides by \( \dot{s} \) yielding
\[
\left( \frac{3}{2} \dot{s} : \dot{s} \right) = \frac{3}{2} \left( \dot{s} \otimes \dot{s} \right) \dot{\sigma} = \dot{r} \dot{s}.
\]
(44)

The product \( \dot{s} \otimes \dot{s} \) yields a forth-order tensor equivalent to the dyadic product of vectors. Furthermore, we use the relation \( \dot{s} : \dot{s} = \dot{\sigma} : \dot{s} \). Now we insert in the third term the first expression of (40), namely the relation between \( \dot{s} \) and \( \dot{\varepsilon}_p \), yielding
\[
\dot{\varepsilon}_p = \frac{3}{2} \sqrt{\frac{3}{2} \dot{r}} \frac{1}{\| \dot{\varepsilon}_p \|} \left( \dot{s} \otimes \dot{s} \right) \dot{\varepsilon}_p.
\]
(45)

We use now (32)
\[
\frac{\dot{r}}{\| \dot{\varepsilon}_p \|} = \sqrt{\frac{2}{3} \frac{\dot{r}}{\dot{\varepsilon}_p}} = \sqrt{\frac{2}{3} \frac{d r}{d \dot{\varepsilon}_p}} = \sqrt{\frac{2}{3} E_{p}^{i s}}
\]
and find
\[
\dot{\varepsilon}_p = \frac{9}{4} \frac{1}{\dot{r}^2} \frac{1}{E_{p}^{i s}} \left( \dot{s} \otimes \dot{s} \right) \dot{\sigma}.
\]
(47)

We can learn from (47) that the plastic strain increment depends both on the actual stress state by \( \dot{s} \otimes \dot{s} \) and on the increment of the stress tensor \( \dot{\sigma} \). Although the total plastic strain \( \dot{\varepsilon}_p \) depends on the load (and stress) path, its increment does not depend on any “memory” of the material.

6. Conclusion

Based on the application of TEP, an alternative approach to the treatment of thermodynamic systems near the equilibrium is reported with the following results:

(1) On the basis of purely thermodynamic considerations the Thermodynamic Extremal Principle (TEP) is formulated and can be considered as a generalized form of Onsager’s principle [4], [5].

(2) The classical phenomenological equations describing the system evolution on the local level and including Onsager’s reciprocity relations are derived from the TEP. This is a direct consequence that the dissipation is approximated in the sense of a
truncated Taylor series by a positive definite quadratic form in the thermodynamic fluxes.

(3) Thermodynamic potentials are assigned to closed thermodynamic systems under various external conditions. The rates of the thermodynamic potentials take over the role of entropy production in the closed systems.

(4) The TEP is used for the derivation of equations describing the Dufour and Soret effects and plasticity.

Acknowledgements

Financial support by the Österreichische Forschungsförderungsgesellschaft mbH, the Province of Styria, the Steirische Wirtschaftsförderungsgesellschaft mbH and the Municipality of Leoben under the frame of the Austrian Kplus Programme is gratefully acknowledged. The works have been also supported by the Grant Agency of the Academy of Sciences of the Czech Republic – grant No. A200410601 and by the program Kontakt–Austrian-Czech Scientific Cooperation No. 05/2006.

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Presented: September 29, 2005
Published on line: February 01, 2008