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Constraints in thermodynamic extremal principles for non-local dissipative processes

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Abstract Phenomena treated by non-equilibrium thermodynamics can be very effectively described by thermodynamic variational principles. The remarkable advantage of such an approach consists in possibility to account for an arbitrary number of constraints among state or kinetic variables stemming, e.g., from conservation laws or balance equations. As shown in the current paper, the variational principles can provide original evolution equations for the state variables implicitly respecting the constraints. Moreover, the variational approach allows formulating the problem directly in discrete state variables and deriving their evolution equations without the necessity to solve partial differential equations. The variational approach makes it also possible to use different kinetic variables in formulation of dissipation and dissipation function.

Keywords Variational principles · Thermodynamic extremal principle · Dissipative processes

1 Introduction

Thermodynamic variational principles (later “principles”) are now accepted tools to develop kinetic (evolution) equations in systems with constraints among the state variables. It should be mentioned that already Lord Rayleigh [25] set the first steps in 1871 by introduction of a “dissipation function,” for details see Sect. 2.1 of this paper. For sake of completeness, we would like to add that “dissipation potentials” have been used in mechanics of materials since several decades, for an overview see [4]. However, groundbreaking contributions were published by Onsager [23] and Ziegler [29] and [30]. With respect to relevant contributions to the principles, we refer the reader to Hackl and Fischer [15] published in 2008 and to the overview [12] published in 2014.

From the point of view of applications of the principles, we consider Ziegler’s concept [29,30] as one of the most successful ones for processes not too far from the equilibrium and obeying the laws of linear non-equilibrium thermodynamics, see, e.g., the textbooks by de Groot and Mazur [6], Callen [3] and Gyarmati

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[14]. Ziegler's concept maximizes the dissipation with the constraint that the dissipation D as bilinear form of forces and fluxes is equal to a particular dissipation function Q , a physical quantity, e.g., a quadratic form of the fluxes (for explanation of the terms see the next section). Generally, this extremal principle, supplemented by proper conservation laws as well as boundary and contact conditions, leads to a set of partial differential equations for the evolution of the system, which may be rather difficult to handle even for quite simple systems. However, material science requires models describing the evolution of the material system only by a limited number of the most appropriate time dependent state variables. A straightforward way, how one can obtain the time dependent state variables, has been provided by reformulating Ziegler's concept in terms of discrete state variables as shown by Svoboda and Turek [27].

From this time on, this concept has been denominated as the "Thermodynamic Extremal Principle" (TEP). Since this formulation avoids having to work directly with partial differential equations, the TEP has become an efficient tool to find kinetic equations for the internal variables in a wide variety of fields. Diverse applications to thermodynamic problems from multicomponent diffusion to grain growth have been reported, for references see, e.g., [12]. However, one aspect has not yet been dealt with in detail in the literature, namely the situation, when the sets of kinetic variables in the dissipation D and in the dissipation function Q are not the same ones. Generally, the sets of kinetic variables may be related by functional dependencies, which can be considered as constraints. The goal of this note is now to show how to implement efficiently such functional relations in the maximization procedure.

2 System description

2.1 Variables and Gibbs energy

Remark 1: We use the matrix notation with "T" as superscript meaning a transposed matrix.

Remark 2: All quantities are described in the actual configuration with "div" and "grad" and the Laplace operator Δ as operators there.

First of all, we introduce a representative volume element (RVE) of a multicomponent system. The RVE is supposed to be a sufficiently small part of the system so that it can be considered as homogeneous but large enough to allow a statistical approach (see also Sect. 4.2).

To define the thermodynamic material system the following quantities are introduced:

1. the external state variables, collected for sake of easier writing in a vector \mathbf{X} ,
2. the internal state variables, collected in a vector \mathbf{x} ,
3. the Gibbs thermodynamic potential G as function $G(\mathbf{X}, \mathbf{x}; \mathbf{p})$ defined on the RVE with given material parameters collected in a vector \mathbf{p} .

We would like to mention the definition of internal variables and their appearance in the dissipation D worked out in detail in the seminal paper by Coleman and Gurtin [5] 50 years ago. The term "dissipative structures" was explained by Maugin [20]. Recently this author published also an according very interesting overview (a "saga") [21].

2.2 Dissipation and dissipation function

According to standard continuum thermodynamics, see e.g. [5], the dissipation D per RVE follows, with \mathbf{X} assumed as fixed, from the well established relation

$$D = -\frac{\partial G}{\partial \mathbf{x}} \cdot \dot{\mathbf{x}} = \mathbf{f} \cdot \dot{\mathbf{x}}, \quad (1)$$

where the vector $-\partial G/\partial \mathbf{x}$ is denoted as collection of the thermodynamic forces \mathbf{f} and $\dot{\mathbf{x}}$ as collection of the thermodynamic fluxes. We use the term "collection," since a thermodynamic force can be a scalar or a vectorial quantity. With respect to the terms thermodynamic "forces" and "fluxes," we refer to Onsager [23] and the book by Baluffi et al. [2]. The dissipation D may be considered as a pure mathematical construct, of course, stemming from the physical entity G .

Therefore, to reflect the internal mechanisms of dissipation, the dissipation function Q is introduced which, in a rather general form, is a function $Q(\mathbf{X}, \mathbf{x}, \dot{\mathbf{x}}; \mathbf{p})$ with given material parameters, collected in vector \mathbf{p} (note

that \mathbf{p} and $\tilde{\mathbf{p}}$ need not to be identical). In many practical cases, however, Q depends on a set $\{\mathbf{K}\}$ of kinetic variables, whose members do not appear as components of the vector $\dot{\mathbf{x}}$. The reader may think of diffusion, where the concentrations (or molar fractions) of the components are internal state variables \mathbf{x} and, therefore, their rates appear in D . However, Q includes the set of fluxes \mathbf{j}_k of the components (counting index k) and not the vector $\dot{\mathbf{x}}$. Therefore, let us separate the internal variables in primary ones, \mathbf{x}_p (with M_p members) whose rates $\dot{\mathbf{x}}_p$ appear also in Q and secondary ones, \mathbf{x}_s (with M_s members), whose rates $\dot{\mathbf{x}}_s$ do appear only in D but not in Q . The set of kinetic variables $\{\mathbf{K}\}$ consists of M_w scalar members collected in a vector \mathbf{w} and a subset $\{\mathbf{W}\}$ with M_w vector members \mathbf{W}_k (k is the index; think, e.g., on the a/m fluxes). Then Q follows as $Q(\mathbf{X}, \mathbf{x}, \dot{\mathbf{x}}_p, \{\mathbf{K}\}; \tilde{\mathbf{p}})$. Since both, D and Q , describe the dissipation process, they must be equal, i.e.,

$$D(\mathbf{X}, \mathbf{x}; \dot{\mathbf{x}}_p, \dot{\mathbf{x}}_s; \mathbf{p}) = \mathbf{f} \cdot \dot{\mathbf{x}} = Q(\mathbf{X}, \mathbf{x}, \dot{\mathbf{x}}_p; \{\mathbf{K}\}; \tilde{\mathbf{p}}). \quad (2)$$

The TEP in its original form, see, e.g., [12], involving the same kinetic variables $\dot{\mathbf{x}}$ in both, D and Q , states that the dissipation obtains a maximum subjected to the constraint, Eq. (2). The according Lagrangian L follows as

$$L = D - \lambda(Q - D) \quad (3)$$

with λ being a Lagrange multiplier. Maximizing of L with respect to the kinetic variables $\dot{\mathbf{x}}$ provides a relation between the thermodynamic forces \mathbf{f} and the kinetic variables $\dot{\mathbf{x}}$ as

$$\mathbf{f} = \left(\frac{Q}{(\partial Q / \partial \dot{\mathbf{x}}) \cdot \dot{\mathbf{x}}} \right) \frac{\partial Q}{\partial \dot{\mathbf{x}}}. \quad (4)$$

It should be noted again that Q as dissipation function goes back to Lord Rayleigh [25]. Furthermore, it may be of interest that Onsager [23] introduced a dissipation potential $\phi(\mathbf{X}, \mathbf{x}, \dot{\mathbf{x}}; \mathbf{q})$ with given material parameters, collected in a vector \mathbf{q} , for the thermodynamic forces as

$$\frac{1}{T} \mathbf{f} = \frac{\partial \phi}{\partial \dot{\mathbf{x}}} \quad (5)$$

with T as the temperature.

3 The thermodynamic extremal principle (TEP) and constraints

3.1 Dissipation and constraints

The dissipation D , Eq. (2), can be reformulated as

$$D = \mathbf{f}_p \cdot \dot{\mathbf{x}}_p + \mathbf{f}_s \cdot \dot{\mathbf{x}}_s, \quad (6)$$

with

$$\mathbf{f}_p = -\frac{\partial G}{\partial \mathbf{x}_p}, \quad \mathbf{f}_s = -\frac{\partial G}{\partial \mathbf{x}_s}. \quad (7)$$

The dissipation D_{system} of the total system follows as

$$D_{\text{system}} = \int_{V_{\text{system}}} D \, dV = \int_{V_{\text{system}}} (\mathbf{f}_p \cdot \dot{\mathbf{x}}_p + \mathbf{f}_s \cdot \dot{\mathbf{x}}_s) \, dV. \quad (8)$$

In many cases, a functional relation exists between $\dot{\mathbf{x}}_s$ and $\dot{\mathbf{x}}_p$ and the set $\{\mathbf{K}\}$ in the form

$$\dot{\mathbf{x}}_s = \mathbf{A} \cdot \dot{\mathbf{x}}_p + \mathbf{B} \cdot \mathbf{w} + \mathbf{C} \cdot \text{div}(\{\mathbf{W}\}) \quad (9)$$

with the following definitions:

1. \mathbf{A} is a given matrix A_{ij} with M_s rows and M_p columns;
2. \mathbf{B} is a given matrix B_{ij} with M_s rows and M_w columns;
3. \mathbf{C} is a given matrix C_{ij} with M_s rows and M_w columns;
4. $\{\mathbf{W}\}$ represents a set with M_w vectors \mathbf{W}_k ;
5. $\text{div}(\{\mathbf{W}\})$ represents a vector with M_w elements $\text{div}(\mathbf{W}_k)$.

Finally, $\mathbf{C} \cdot \text{div}(\{\mathbf{W}\})$ represents a vector \mathbf{c} with the elements $c_i = \sum_{k=1}^{M_W} C_{ik} \text{div}(\mathbf{W}_k)$, $i = 1, \dots, M_s$.

Taking into account the above definitions and inserting of Eq. (9) into the integrand on the r.s. of Eq. (8) yield

$$D = \mathbf{f}_p \cdot \dot{\mathbf{x}}_p + \mathbf{f}_s \cdot \dot{\mathbf{x}}_s = (\mathbf{f}_p + \mathbf{A}^T \cdot \mathbf{f}_s) \cdot \dot{\mathbf{x}}_p + (\mathbf{B}^T \cdot \mathbf{f}_s) \cdot \mathbf{w} + \sum_{i=1}^{M_s} f_{s,i} \sum_{k=1}^{M_W} C_{ik} \text{div}(\mathbf{W}_k). \quad (10)$$

If we introduce the vector $\tilde{\mathbf{f}}_s = \mathbf{C}^T \cdot \mathbf{f}_s$ and integrate the last term on the r.s. of Eq. (10)₂ over the total volume V_{system} and apply the Gauss theorem (assuming that $\mathbf{W}_k \cdot \mathbf{n} = 0$ with \mathbf{n} being the normal to $\partial V_{\text{system}}$), then we can reformulate (10)₂ with $\tilde{\mathbf{f}}_p = \mathbf{f}_p + \mathbf{A}^T \cdot \mathbf{f}_s$ as

$$D = \mathbf{f}_p \cdot \dot{\mathbf{x}}_p + \mathbf{f}_s \cdot \dot{\mathbf{x}}_s = \tilde{\mathbf{f}}_p \cdot \dot{\mathbf{x}}_p + (\mathbf{B}^T \cdot \mathbf{f}_s) \cdot \mathbf{w} - \sum_{k=1}^{M_W} \text{grad}(\tilde{f}_{s,k}) \cdot \mathbf{W}_k. \quad (11)$$

We define now $\mathbf{f}_w = \mathbf{B}^T \cdot \mathbf{f}_s$ and $\mathbf{f}_{W,k} = -\text{grad}(\tilde{f}_{s,k})$ and can formulate D as

$$D = \tilde{\mathbf{f}}_p \cdot \dot{\mathbf{x}}_p + \mathbf{f}_w \cdot \mathbf{w} + \sum_{k=1}^{M_W} \mathbf{f}_{W,k} \cdot \mathbf{W}_k. \quad (12)$$

For sake of easier writing, we denominate the rates as $\dot{\boldsymbol{\xi}} = \{\dot{\mathbf{x}}_p, \mathbf{w}, \mathbf{W}_k\}$ ($k = 1, \dots, M_W$), so that we can formulate D , Eq. (2), as $D = \tilde{D}(\mathbf{X}, \mathbf{x}, \dot{\boldsymbol{\xi}}; \mathbf{p})$ and $Q = \tilde{Q}(\mathbf{X}, \mathbf{x}, \dot{\boldsymbol{\xi}}; \tilde{\mathbf{p}})$. Furthermore, the thermodynamic forces are denoted as

$$\mathbf{f}_{\dot{\boldsymbol{\xi}}} = \frac{\partial \tilde{D}}{\partial \dot{\boldsymbol{\xi}}} = \{\tilde{\mathbf{f}}_p, \mathbf{f}_w, \mathbf{f}_{W,1}, \dots, \mathbf{f}_{W,M_W}\}. \quad (13)$$

Finally, we can rewrite Eq. (2) as

$$\tilde{D}(\mathbf{X}, \mathbf{x}, \dot{\boldsymbol{\xi}}; \mathbf{p}) = \tilde{Q}(\mathbf{X}, \mathbf{x}, \dot{\boldsymbol{\xi}}; \tilde{\mathbf{p}}). \quad (14)$$

3.2 The TEP in modified form

The modification of D to \tilde{D} as above allows applying the TEP in its original form given by Eqs. (2) and (3), which will be replaced now by Eq. (14) and the modified Lagrangian

$$\tilde{L} = \tilde{D} - \lambda (\tilde{Q} - \tilde{D}). \quad (15)$$

Maximizing of \tilde{L} with respect to the kinetic variables $\dot{\boldsymbol{\xi}}$ provides a relation between the thermodynamic forces $\mathbf{f}_{\dot{\boldsymbol{\xi}}}$ and the rates of the kinetic variables $\dot{\boldsymbol{\xi}}$ as

$$\mathbf{f}_{\dot{\boldsymbol{\xi}}} = \left(\frac{\tilde{Q}}{(\partial \tilde{Q} / \partial \dot{\boldsymbol{\xi}}) \cdot \dot{\boldsymbol{\xi}}} \right) \frac{\partial \tilde{Q}}{\partial \dot{\boldsymbol{\xi}}}. \quad (16)$$

Since one needs finally the evolution equations for $\dot{\boldsymbol{\xi}}$, it is necessary to invert Eq. (16). If Q is supposed as a homogeneous function in $\dot{\boldsymbol{\xi}}$ of order l , yielding $\partial \tilde{Q} / \partial \dot{\boldsymbol{\xi}} \cdot \dot{\boldsymbol{\xi}} = l \tilde{Q}$, it follows

$$\mathbf{f}_{\dot{\boldsymbol{\xi}}} = \frac{1}{l} \frac{\partial \tilde{Q}}{\partial \dot{\boldsymbol{\xi}}}. \quad (17)$$

If \tilde{Q} is a quadratic function in $\dot{\xi}$, which means $l = 2$, having the form $\tilde{Q} = \dot{\xi} \cdot \mathbf{U}(\mathbf{X}, \mathbf{x}) \cdot \dot{\xi}$ with \mathbf{U} being a positive-definite symmetric matrix involving material and structural parameters, then this yields

$$\dot{\xi} = \mathbf{U}^{-1} \cdot \mathbf{f}_{\xi}. \quad (18)$$

No problem from the mathematical point of view does occur, if the order of homogeneity l is unequal to 2 but equal for all processes. If this is not the case, we refer to the papers by Hackl et al. [16, 17] and the recent paper by Goddard [13] referring to the necessity of introducing a dissipation potential for some distinct problems.

4 Application of the TEP to local and non-local diffusion

One of the most relevant processes in the evolution of material systems is the diffusion process. Let us consider a multicomponent system consisting of M components with the site fractions $y_k, k = 1, \dots, M$. To each component a diffusive flux \mathbf{j}_k is assigned. The diffusion is vacancy-mediated (as it is the case, when K substitutional and $(M - K)$ interstitial components are diffusing). The vacancies occupy a site fraction y_0 and diffuse with a flux \mathbf{j}_0 . Let us assume that $K \leq M$ substitutional components diffuse. As outlined in detail in Svoboda et al. [26] Sects. 2.1 and 2.2 two basic identities exist: one for the site fractions and the other for the fluxes. Both identities lead to two constraints, namely

$$y_0 = 1 - \sum_{k=1}^K y_k, \quad \mathbf{j}_0 = - \sum_{k=1}^K \mathbf{j}_k. \quad (19)$$

Note, that constraint Eq. (19)₁ can directly be inserted into the Gibbs energy G , since the y_k are internal variables. Furthermore, constraint Eq. (19)₂ can also directly be inserted into the dissipation function Q as ‘‘classical’’ function of the squares of the fluxes.

The rate, with which the vacancies are generated or annihilated, is denoted as $\alpha, 0 \leq |\alpha| \leq \infty$, with $\alpha = 0$ for no generation or annihilation and with $|\alpha| \Rightarrow \infty$ for ideal generation or annihilation. The mass balance, also treated in Svoboda et al. [26], is expressed for the site fractions as

$$\dot{y}_k = -y_k \alpha - \bar{\Omega} \operatorname{div} \mathbf{j}_k, \quad k = 1, \dots, M. \quad (20)$$

The quantity $\bar{\Omega}$ is the molar volume of one mole of lattice sites and depends, therefore, on the individual site fractions $y_k, k = 1, \dots, M$. The mass balance activates now a third set of constraints, which will be dealt with below.

Going back to Fick’s work from 1855 one needs a constitutive law for the fluxes $\mathbf{j}_k, k = 1, \dots, M$. Therefore, the TEP is employed to derive such a constitutive (or evolution) law, see again Svoboda et al. [26], Sect. 4 there, and the rather recent paper by Fischer et al. [11].

4.1 Local diffusion

This is the standard case for a deterministic situation, where no stochastic processes are considered. We concentrate only on constraints Eq. (20). The dissipation D , see Eq. (1), has as kinetic variables the \dot{y}_k and α . The dissipation function Q , see Eq. (2), has as kinetic variables the fluxes \mathbf{j}_k and α . Note that we avoid the rate of a diffusion-induced creep strain for sake of an easier formulation. The dissipation D (denoted now as \tilde{D}) is calculated according to Eqs. (9) to (12) by assigning the actual quantities to the symbols in general Eqs. (11) and (12). The flux $\dot{\mathbf{x}}_p$ consists of only one member $\dot{x}_p = \alpha$, \mathbf{x}_s corresponds to the vector \mathbf{y} with $\mathbf{y}^T = (y_1, y_2, \dots, y_M)$ and $\dot{\mathbf{x}}_s$ to $\dot{\mathbf{y}}$. With the notation of Eqs. (9, 10) we have \mathbf{A} degenerating to a (1×1) matrix with the only element -1 , $\mathbf{w} = \mathbf{0}$, $\mathbf{C} = -\bar{\Omega} \mathbf{I}$ (\mathbf{I} is the unity matrix) and $\mathbf{W}_k = \mathbf{j}_k$ with $k = 1, \dots, M$ and $M_W = M_s = M$. Then we find with Eq. (12)

$$\tilde{D} = (f_{\alpha} - \mathbf{f}_s \cdot \mathbf{y}) \alpha + \sum_{k=1}^M (\operatorname{grad}(\bar{\Omega} f_{s,k})) \cdot \mathbf{j}_k. \quad (21)$$

4.2 Non-local diffusion

Non-local concepts in continuum mechanics are already dealt with since the pioneering work of Mindlin on non-local plate theory, more than half a century ago, see, e.g., Mindlin's Collected Works in [18]. A general view on non-local continuum fields was published by Eringen [9]. Here, it shall be mentioned that discrepancies have been detected between the Eringen model in differential and integral form, see, e.g., recent paper [10]. The rather popular gradient approach was related to the non-local field theory by Aifantis [1]. Locally varying material properties as the elastic moduli have motivated to introduce non-local theoretical concepts, see, e.g., recent contributions [7,22]. With respect to an extremal principle recent paper [24] concerning the Principle of Minimum of Potential Energy of an elastic system shall be mentioned. Particularly of increasing relevance are computational algorithms for non-local diffusion, together with constraints as, e.g., volume constraints, taking into account stochastic processes (as jumping of atoms or Brownian motion). Here we refer to papers by Du et al. [8] and Tian et al. [28] and Lehoucq and Rowe [19] concerning the analysis and approximation of non-local diffusion problems.

We offer a problem solution concept for non-local diffusion by an efficient application of the TEP with constraints. For sake of demonstrating the concept in an easy as possible way we consider the case of diffusion of only one interstitial element with the site fraction y , to which a chemical potential $\mu = \mu(y)$ is assigned, and the activity of vacancies represented by their generation/annihilation rate α [since α is involved in the site fraction balance of y , see Eq. (19)₁]. Furthermore, the following (simplifying) assumptions are applied:

1. the molar volume $\bar{\Omega}$ is assumed as constant quantity in space and time;
2. the role of the stress state is considered as negligible; consequently, diffusion-induced creep is not activated;
3. the volume of RVE, denoted as dV , is as a constant quantity; therefore, the material derivative $d(dV)/dt = 0$ or, in other words, $\text{div } \mathbf{v} = \mathbf{0}$ with \mathbf{v} being the material velocity vector;
4. the quantity y and the chemical potential μ (see below) are replaced by

$$\dot{y} \Rightarrow (1 - \theta) \dot{y} + \theta \dot{\bar{y}} = \dot{\bar{y}}, \quad \mu \Rightarrow (1 - \theta) \mu + \theta \bar{\mu} = \bar{\mu}. \quad (22)$$

The quantities \bar{y} and $\bar{\mu}$ are the non-local averages of the local quantities y and μ resp., e.g., over the RVE. Furthermore, a time-independent switcher θ is introduced $0 \leq \theta \leq 1$, which allows investigating the interaction of a pure deterministic behavior (\dot{y}, μ , local) and pure stochastic behavior ($\dot{\bar{y}}, \bar{\mu}$, non-local). A short introduction to the definition of a non-local quantity is presented in the "Appendix".

The dissipation D follows with Eq. (22) as

$$D = -\mu \dot{\bar{y}} = -\mu ((1 - \theta) \dot{y} + \theta \dot{\bar{y}}). \quad (23)$$

The dissipation function Q writes as

$$Q = \mathbf{j}^2/A + K\alpha^2 \quad (24)$$

with A as a given mobility coefficient and K as a given bulk viscosity; for details see [26], Sects. 4 and 5 there.

As constraint the balance for the site fraction y is expressed in \bar{y} and writes with Eq. (20)

$$\dot{\bar{y}} + \bar{y}\alpha + \bar{\Omega} \text{div } \mathbf{j} = 0, \quad (25)$$

and with Eq. (22) as

$$(1 - \theta) \dot{y} + \theta \dot{\bar{y}} + [(1 - \theta) y + \theta \bar{y}] \alpha + \bar{\Omega} \text{div } \mathbf{j} = 0. \quad (26)$$

The TEP is formulated for the system with Eqs. (23–26) as

$$L = \int_{V_{\text{system}}} \left[D - \lambda (D - Q) + 2\eta (\dot{\bar{y}} + \bar{y}\alpha + \bar{\Omega} \text{div } \mathbf{j}) \right] dV. \quad (27)$$

Now two Lagrange multipliers, namely the constants λ and η , appear. Before calculating the Lagrange parameters, it is useful to apply the "duality condition" [Eq. (47) in the "Appendix"] to the expressions $\mu \dot{\bar{y}}$ in D and $\eta \dot{\bar{y}}$ in the constraint in Eq. (27), which can be replaced by $\bar{\mu} \dot{\bar{y}}$ and $\bar{\eta} \dot{\bar{y}}$, resp. Furthermore, the Gauss theorem allows replacing $\eta \text{div } \mathbf{j}$ by $-\text{grad } \eta \cdot \mathbf{j}$ in Eq. (27), since we assume a closed system with a zero normal projection of \mathbf{j} at the surface. These both steps allow to rewrite L , Eq. (27), as

$$L = -(1 - \lambda) \int_{V_{\text{system}}} \bar{\mu} \dot{\bar{y}} dV + \lambda \int_{V_{\text{system}}} (\mathbf{j}^2/A + K\alpha^2) dV + 2 \int_{V_{\text{system}}} (\bar{\eta} \dot{\bar{y}} + \bar{\eta} \bar{y} \alpha - \bar{\Omega} \text{grad } \eta \cdot \mathbf{j}) dV. \quad (28)$$

We perform variations with respect to \dot{y} , \mathbf{j} and α yielding

$$\text{ad } \dot{y}: \quad -(1 - \lambda) \tilde{\mu} + 2\tilde{\eta} = 0, \quad (29)$$

$$\text{ad } \alpha: \quad \lambda K \alpha + \eta \tilde{y} = \lambda K \alpha + \tilde{\eta} y = 0, \quad (30)$$

$$\text{ad } \mathbf{j}: \quad \lambda \mathbf{j} / A - \bar{\Omega} \text{ grad } \eta = 0. \quad (31)$$

After multiplication of Eq. (29) by \dot{y} , of Eq. (30) by α and (31) by \mathbf{j} , integration over the system and keeping in mind $D = Q$, see Eqs. (23, 24), one finds $\lambda = -1$ and from

$$\text{ad (29): } \quad \tilde{\eta} = \tilde{\mu}, \quad (32)$$

$$\text{ad (30): } \quad \alpha = \eta \tilde{y} / K, \quad (33)$$

$$\text{ad (31): } \quad \mathbf{j} = -A \bar{\Omega} \text{ grad } \eta. \quad (34)$$

Obviously, \mathbf{j} depends on the Lagrange parameter η , see Eq. (34), which is related to the chemical potential μ with the non-local relation Eq. (32), $\tilde{\eta} = \tilde{\mu}$.

If $\theta = 0$, which refers to a pure local problem, then immediately the established equation

$$\mathbf{j} = -A \bar{\Omega} \text{ grad } \mu \quad (35)$$

appears.

However, if $\theta \neq 0$, one has to extract η from $\tilde{\eta}$ together with $\tilde{\eta} = \tilde{\mu}$. To separate η from $\tilde{\eta}$ we can use the relation

$$\eta = \beta_0 \tilde{\eta} + \beta_2 \Delta \tilde{\eta} + \text{h.o.t.}, \quad (36)$$

derived in the ‘‘Appendix’’, see Eq. (45). The coefficients β_0 and β_2 are given also in the ‘‘Appendix’’, see Eqs. (44) and (46), respectively. Then Eq. (32), with the assumption of a known function $\tilde{\mu} = (1 - \theta) \mu + \theta \bar{\mu}$, allows formulating a partial differential equation based on Eq. (36) as

$$\beta_2 (1 - \theta) \Delta \tilde{\eta} + (\beta_0 + (1 - \beta_0) \theta) \tilde{\eta} = \tilde{\mu}. \quad (37)$$

The solution of Eq. (37), together with the appropriate boundary condition, see Eqs. (49) or (50) in the ‘‘Appendix’’, gives $\tilde{\eta}$ from which η is obtained by applying Eq. (36). This closes the formulation.

5 Conclusion

The ‘‘Thermodynamic Extremal Principle’’ (TEP), based on Ziegler’s work, can be formulated in the frame of linear thermodynamics as a maximization problem with only one constraint equating the dissipation in the system (bilinear form in fluxes and forces) and the dissipation function (quadratic form in fluxes accounting for material properties like diffusivities and interface mobilities). This concept of the TEP can also be used in a straightforward way, if some further constraints, e.g., as balance or conservation equations meeting specific mechanisms etc., exist. The respective procedure is outlined in this paper. Then the TEP provides in the current form original constitutive laws implicitly respecting the constraints. Moreover, the TEP allows treating systems for which the dissipation and the dissipation function are expressed in different kinetic variables coupled by linear relations representing further constraints. A proper redefinition of the kinetic variables may significantly reduce the number of kinetic variables and constraints and provide the most effective description of the system. One should keep in mind that the redefinition does not influence the dissipation and thus also the system kinetics. The developed concept is demonstrated on an example for local and non-local multicomponent diffusion.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Appendix

Let us define the non-local average of a field f on a domain with radius a as

$$\bar{f}(\mathbf{r}) = \int_{V_{\text{system}}} g_a(\bar{\mathbf{r}} - \mathbf{r}) f(\bar{\mathbf{r}}) d\bar{V}, \quad (38)$$

the integral kernel being of the form

$$g_a(\mathbf{r}) = \frac{1}{a^n} g(|\mathbf{r}|/a), \quad (39)$$

where n is the dimension of V_{system} . The shape function g is supposed to have the properties

$$\int_{V_{\text{system}}} g(\mathbf{r}) dV = 1, \quad g'(0) = 0, \quad \lim_{r \rightarrow \infty} g(r) = 0, \quad (40)$$

the simplest example being given as

$$g(r) = \frac{1}{B_n} \begin{cases} 1 & \text{for } r \leq 1 \\ 0 & \text{for } r > 1 \end{cases}, \quad (41)$$

where B_n is the volume of the unit ball of dimension n .

If a is small in comparison to the diameter of V_{system} , then Eq. (38) can be inverted. Fourier-transformation of Eq. (38) gives

$$\hat{f}(\mathbf{s}) = (2\pi)^{n/2} \hat{g}(a|\mathbf{s}|) \hat{f}(\mathbf{s}). \quad (42)$$

Solving Eq. (42) for $\hat{f}(\mathbf{s})$ and calculating its Taylor-expansion with respect to a yields

$$\hat{f}(\mathbf{s}) = \hat{f}(\mathbf{s}) \left[\beta_0 - \frac{k}{2} a^2 |\mathbf{s}|^2 + \text{h.o.t.} \right], \quad (43)$$

where we have made use of $g'(0) = 0$.

The parameters in Eq. (43) are

$$\beta_0 = \frac{1}{(2\pi)^{n/2} \hat{g}(0)}, \quad k = \frac{\hat{g}''(0)}{(2\pi)^{n/2} \hat{g}(0)^2}. \quad (44)$$

Finally, back-transformation of Eq. (44) gives

$$f(\mathbf{r}) = \beta_0 \bar{f}(\mathbf{r}) + \beta_2 \Delta \bar{f}(\mathbf{r}) + \text{h.o.t.}, \quad (45)$$

where

$$\beta_2 = \frac{k}{2} a^2. \quad (46)$$

Moreover, we would like to remark that in the limit $a \rightarrow 0$ we have the duality condition

$$\int_{V_{\text{system}}} \bar{f}_1 f_2 dV = \int_{V_{\text{system}}} f_1 \bar{f}_2 dV. \quad (47)$$

This holds in either case, whether \bar{f} is defined via Eq. (38) or Eq. (45). In the first case, Eq. (47) follows from a substitution of variables, since contributions from the boundary of V_{system} vanish in the limit. The second case follows applying Green's formula

$$\int_{V_{\text{system}}} [f_1 \Delta f_2 - \Delta f_1 f_2] dV = \int_{\partial V_{\text{system}}} [f_1 (\mathbf{n} \cdot \nabla f_2) - (\mathbf{n} \cdot \nabla f_1) f_2] dS, \quad (48)$$

provided, that both f_1 and f_2 satisfy on $\partial V_{\text{system}}$ the Dirichlet boundary conditions

$$f = 0, \quad (49)$$

or the the Neumann boundary conditions

$$\mathbf{n} \cdot \nabla f = 0. \quad (50)$$

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