ON THE STRUCTURE OF MAXIMUM ENTROPY PRODUCTION PRINCIPLE: FROM NEAR TO FAR-FROM EQUILIBRIUM

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ABSTRACT

In this paper, we investigate the microscopic structure of the maximum entropy production principle (MEPP) from a mathematical point of view. It is shown that a MEPP-governed thermodynamic flux or a Ziegler flux is a subclass of the non-linear Onsager flux that is potential or non-rotational in the constrained affinity space, which means MEPP conditionally holds for near-equilibrium processes. A non-linear Onsager flux can be represented in Maclaurin series of which each term is a Ziegler flux. For a far-from-equilibrium process whose thermodynamic flux is non-potential or rotational, the flux can be represented by a series of weighted non-linear Onsager fluxes using the Darboux theorem. The two levels of representation indicate that Ziegler fluxes can serve as the basic elements to construct any complex thermodynamic flux from near to far-from equilibrium. In other words, any complex phenomena can be described elementally by MEPP.

INTRODUCTION

The maximum entropy production principle (MEPP) is a thermodynamic postulate developed by Ziegler [1], which uniquely determines the "easiest and most accessible" [2] evolution path of a non-equilibrium thermodynamic system. Extensive applications of MEPP have been reported in different sciences (see, e.g., recent reviews by Kleidon & Lorenz [3] and Martyushev & Seleznev [4]), however, in the absence of compelling evidence to support its applicability, whether experimental or theoretical [2, 4]. Martyushev [2] left us with two essential questions around MEPP, "(i) can this principle claim to be the basis of all non-equilibrium physics? and (ii) is it possible to prove MEPP?" In this paper, we make an effort to answer question (i) from a mathematical point of view.

The relationship between MEPP and the second law of thermodynamics has been an issue of long-standing interests. Ziegler [1] and Ziegler & Wehrli [5] suggested that the second law of thermodynamics be covered by MEPP, which gives a positive answer to question (i). However, such idea has not yet been well accepted, because, when applied to different sciences, MEPP definitely involves constrains more than the second law of thermodynamics [4, 6-8]. Thus, the principle should be identified as a postulate, or a reasonable classification of behavior for certain non-equilibrium systems instead of a general thermodynamic law. To have a better understanding of MEPP and its scope of application, we may first "divide" the space of non-equilibrium states into several significant subspaces based on their distance with respect to equilibrium.

Figure 1 shows a sketch of the space of possible non-equilibrium states for a given thermodynamic system. The origin represents the equilibrium point. When the state of the system is infinitely close to equilibrium, the irreversible processes are governed by the well-known Onsager reciprocal relation (Onsager flux in Fig. 1) [9], which is the defining characteristic of the linear subspace. The linear subspace is subsumed in the near-equilibrium subspace, which is characterized in definition by the non-linear Onsager reciprocal relation (non-linear Onsager flux in Fig. 1) by Edelen [10, 11]. The reason why the subspace is labelled "near-equilibrium" will be explained later. In a series of studies by Yang et al. [12-15], it has been proved that MEPP (Ziegler flux in Fig. 1) is a sufficient condition of the non-linear Onsager reciprocal relation, which means MEPP conditionally holds for near-equilibrium processes and thus its scope is not as broad as Ziegler [1] supposed. However, we shall show it in this paper that MEPP can still work as a basic element to describe any near- and far-from-equilibrium processes that do not satisfy the principle itself. The conclusions may help to understand the way MEPP acts in complex phenomena.

From a mathematical point of view, the thermodynamic theories mentioned above including MEPP focus on the dependences of the thermodynamic fluxes on their conjugate thermodynamic forces. To embody rigorous definitions of the thermodynamic flux and force, the theoretical context is formulated in the framework of normality structure. As an internal variable approach, the normality structure proposed by Rice [16, 17] has been an appealing constitutive framework for solids undergoing irreversible thermodynamic processes. Nevertheless, the conclusions might be extended to any well-defined non-equilibrium systems because we do not refer to any special properties of solids at the level of thermodynamic flux and force.
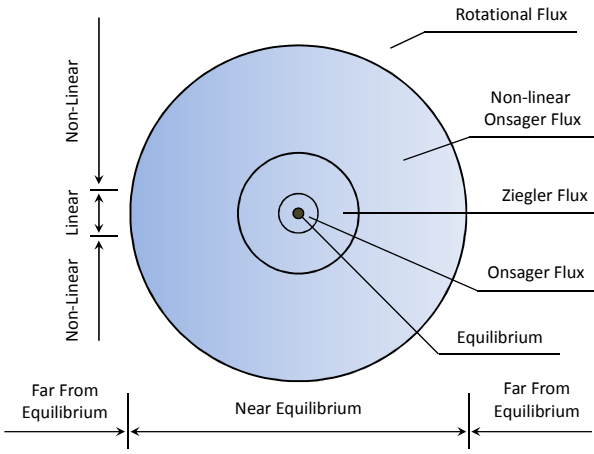
Figure 1 A sketch of the space of non-equilibrium states and its division

PRELIMINARIES

Internal variable approach for solids

Consider a material sample of size V. Introduce the specific free energy ϕ and its Legendre transform ψ with respect to strain,

$$\phi = \phi(\boldsymbol{\varepsilon}, \vartheta, H)$$
$$\psi = \psi(\boldsymbol{\sigma}, \vartheta, H) = \boldsymbol{\varepsilon} : \frac{\partial \phi}{\partial \boldsymbol{\varepsilon}} - \phi \qquad (1)$$

where ϑ denotes temperature; $\boldsymbol{\varepsilon}$ denotes any strain tensor, objective and symmetric, that measures deformation from an arbitrary reference state; $\boldsymbol{\sigma}$ denotes the symmetric conjugate stress such that $\boldsymbol{\sigma} : \delta\boldsymbol{\varepsilon}$ is the work per unit volume of the adopted reference state in any virtual deformation $\delta\boldsymbol{\varepsilon}$; H denotes symbolically the current pattern of microstructural rearrangement of constituent elements of the materials. At fixed H, variations of $\boldsymbol{\sigma}$ and ϑ necessarily induce a purely elastic response. Then the first law of thermodynamics leads to the stress-strain relations,

$$\boldsymbol{\sigma} = \frac{\partial \phi(\boldsymbol{\varepsilon}, \vartheta, H)}{\partial \boldsymbol{\varepsilon}}, \qquad \boldsymbol{\varepsilon} = \frac{\partial \psi(\boldsymbol{\sigma}, \vartheta, H)}{\partial \boldsymbol{\sigma}} \qquad (2)$$

Consider two neighbouring patterns of microstructural rearrangement denoted by H and $H + \mathrm{d}H$, respectively. It is assumed that a set of incremental scalar internal variables $\mathrm{d}\boldsymbol{\xi} = \{\mathrm{d}\xi_1, \mathrm{d}\xi_2, \dots, \mathrm{d}\xi_n\}$ characterizes the specific local rearrangements, which is represented collectively by $\mathrm{d}H$, at sites throughout the material sample. The $\mathrm{d}\boldsymbol{\xi}$ and $\mathrm{d}H$ are related by

$$\frac{1}{V} f_\alpha \mathrm{d}\xi_\alpha = \frac{1}{V} \mathbf{f} \cdot \mathrm{d}\boldsymbol{\xi} = -\mathrm{d}^p \phi = \mathrm{d}^p \psi \qquad (3)$$

where

$$\mathrm{d}^p \phi = \phi(\boldsymbol{\varepsilon}, \vartheta, H + \mathrm{d}H) - \phi(\boldsymbol{\varepsilon}, \vartheta, H)$$
$$\mathrm{d}^p \psi = \psi(\boldsymbol{\sigma}, \vartheta, H + \mathrm{d}H) - \psi(\boldsymbol{\sigma}, \vartheta, H) \qquad (4)$$

Equation (3) also defines a set of scalar thermodynamic forces $\mathbf{f} = \{f_1, f_2, \dots, f_n\}$ conjugate to the internal variables,

$$\mathbf{f} = \mathbf{f}(\boldsymbol{\varepsilon}, \vartheta, H) \ \text{ or } \ \mathbf{f} = \mathbf{f}(\boldsymbol{\sigma}, \vartheta, H) \qquad (5)$$

The corresponding set of total internal variables,

$$\boldsymbol{\xi} = \{\xi_1, \xi_2, \dots, \xi_n\} \qquad (6)$$

generally are not state variables in the sense that thermodynamic state functions are not direct functions of $\boldsymbol{\xi}$, but instead depend on the path history of $\boldsymbol{\xi}$. Only if the $\boldsymbol{\xi}$ is one set of explicit state variables, the conjugate forces can be determined as

$$\mathbf{f} = -V \frac{\partial \phi(\boldsymbol{\varepsilon}, \vartheta, \boldsymbol{\xi})}{\partial \boldsymbol{\xi}} = V \frac{\partial \psi(\boldsymbol{\sigma}, \vartheta, \boldsymbol{\xi})}{\partial \boldsymbol{\xi}} \qquad (7)$$

Kinetic rate law

This paper focuses on the kinetic rate law of the internal variable set $\boldsymbol{\xi}$, namely, the dependence of the thermodynamic flux $\dot{\boldsymbol{\xi}}$ on the thermodynamic force $\mathbf{f}$. In the constrained affinity space $\mathcal{A}^n$ coordinated by $\mathbf{f}$ with fixed external variables, the general kinetic rate law can be written as

$$\dot{\boldsymbol{\xi}} = \dot{\boldsymbol{\xi}}(\mathbf{f}) \qquad (8)$$

The kinetic rate law Eq. (8) is constrained only by the second law of thermodynamics, which leads to the *dissipation inequality*, i.e., the entropy production rate σ should be always non-negative,

$$\sigma = \frac{1}{\vartheta V} \mathbf{f} \cdot \dot{\boldsymbol{\xi}} \geq 0 \qquad (9)$$

The most fundamental form of the kinetic rate law is the well-known Onsager reciprocal relation [9], that is, $\dot{\boldsymbol{\xi}}$ depends linearly on $\mathbf{f}$,

$$\dot{\boldsymbol{\xi}} = \mathbf{L} \cdot \mathbf{f}, \qquad \mathbf{L} = \mathbf{L}^{\mathrm{T}} \qquad (10)$$

where $\mathbf{L}$ is the second order tensor of kinetic coefficients in $\mathcal{A}^n$ that is symmetric and independent of $\dot{\boldsymbol{\xi}}$ and $\mathbf{f}$. As required by the dissipation inequality Eq. (9), $\mathbf{L}$ should be positive semidefinite. A thermodynamic flux is termed an *Onsager flux* if it satisfies Eq. (10).

The number of degrees of freedom (DOFs) of a thermodynamic flux is defined as the number of independent scalar functions in $\mathcal{A}^n$ to determine all its components. Thus, the number of DOFs of a general thermodynamic flux given by Eq. (8) is n. And the number of DOFs of an Onsager flux is 1 because all its components can be derived from a quadratic potential function Q,

$$\dot{\boldsymbol{\xi}} = \nabla_{\mathbf{f}} Q, \qquad Q = Q(\mathbf{f}) = \frac{1}{2} \mathbf{f} \cdot \mathbf{L} \cdot \mathbf{f} \qquad (11)$$

where $\nabla_{\mathbf{f}}$ denotes the gradient operator in $\mathcal{A}^n$, $\nabla_{\mathbf{f}} = \partial / \partial \mathbf{f}$.

NON-LINEAR ONSAGER FLUX AND NEAR-EQUILIBRIUM

Rice flux and normality structure

The theory of normality structure is proposed by Rice [16, 17], who simplified Eq. (8) by assuming that each flux component depends only on its own conjugate force component, as termed the *Rice flux*,

$$\dot{\xi}_\alpha = \dot{\xi}_\alpha(f_\alpha), \qquad (\alpha = 1, 2, \ldots, n) \qquad (12)$$

As a result, the number of DOFs is reduced from n to 1 because a flow potential Q exists such that the flux components are related in the following form

$$\dot{\boldsymbol{\xi}} = \nabla_{\mathbf{f}} Q, \qquad Q = Q(\mathbf{f}) = \int_0^{\mathbf{f}} \dot{\xi}_\alpha d f_\alpha \qquad (13)$$

With the kinetic rate law given by Eq.(13), the normality structure for solids can be easily shown,

$$\frac{d^p \boldsymbol{\varepsilon}}{dt} = \frac{1}{V} \frac{\partial Q}{\partial \boldsymbol{\sigma}} \qquad (14)$$

where $d^p \boldsymbol{\varepsilon}$ denotes the inelastic part of strain, because, known form Eq. (2) and Eq. (3),

$$\frac{d^p \boldsymbol{\varepsilon}}{dt} = \frac{1}{dt} \frac{\partial d^p \psi}{\partial \boldsymbol{\sigma}} = \frac{1}{V} \frac{\partial \mathbf{f}}{\partial \boldsymbol{\sigma}} \cdot \dot{\boldsymbol{\xi}} = \frac{1}{V} \frac{\partial Q}{\partial \boldsymbol{\sigma}} \qquad (15)$$

The Rice flux Eq. (12) is a very strong restriction because the flux components are required to be fully decoupled in $\mathcal{A}^n$. It is only a sufficient condition for the normality structure or the existence of a flow potential Q.

Non-linear Onsager flux

As discussed by Yang et al. [12-15], the sufficient and necessary condition for normality structure is the non-linear Onsager reciprocal relation proposed by Edelen [10, 11],

$$\frac{\partial \dot{\xi}_\alpha}{\partial f_\beta} = \frac{\partial \dot{\xi}_\beta}{\partial f_\alpha} \quad \text{or} \quad \nabla_{\mathbf{f}} \boldsymbol{\xi} = \boldsymbol{\xi} \nabla_{\mathbf{f}} \qquad (16)$$

A thermodynamic flux is termed a *non-linear Onsager flux* if it satisfies Eq. (16), which encompasses both Rice flux and Onsager flux as subclasses. Know from the Green theorem and Stokes theorem, the following four statements are equivalent:
a) the thermodynamic flux is a non-linear Onsager flux as defined by Eq. (16);
b) the flux components can be derived from a flow potential Q,

$$\dot{\boldsymbol{\xi}} = \nabla_{\mathbf{f}} Q, \qquad Q = Q(\mathbf{f}) = \int_0^{\mathbf{f}} \dot{\boldsymbol{\xi}} \cdot d\mathbf{f} \qquad (17)$$

which means the number of DOFs of $\dot{\boldsymbol{\xi}}$ is 1 and the normality structure Eq. (14) holds;
c) the thermodynamic flux is potential or non-rotational,

$$\oint \dot{\boldsymbol{\xi}} \cdot d\mathbf{f} = 0 \quad \text{or} \quad \nabla_{\mathbf{f}} \wedge \dot{\boldsymbol{\xi}} = \mathbf{0} \qquad (18)$$

where $\wedge$ denotes the exterior product in $\mathcal{A}^n$;
d) $\dot{\boldsymbol{\xi}} \cdot d\mathbf{f}$ is a total differential or a differential 1-form of Class 1,

$$\dot{\boldsymbol{\xi}} \cdot d\mathbf{f} = dQ \qquad (19)$$

The non-linear Onsager flux is employed in this paper as the criterion to distinguish between near- and far-from equilibrium processes. That is to say, the behavior of a thermodynamic system in states near equilibrium is dominated by the thermodynamic flux that is potential or non-rotational in a sufficiently small neighborhood of an equilibrium state. The criterion can be formulated by anyone of the conditions from Eq. (16) to Eq. (19). Such criterion was suggested by Edelen [11] who put stress on the existence of a potential function (Eq. (17) or Eq. (19)) that characterizes near-equilibrium states:

"*Thermostatics is based on the assumption that the system under study is always at or sufficiently close to an equilibrium state that the thermodynamic potential functions (internal energy, free energy, etc.) can be defined as functions of the state variables, which are independent of the time and independent of the history of the system.*"

In a few studies, the Onsager flux Eq. (10) was taken as the criterion, which, however, is somewhat narrow because Onsager fluxes occur only in an infinitesimal neighborhood of equilibrium and thus it is not convincing to conclude that a process violating Eq. (10) is far from equilibrium. Figure 1 shows a clearer vision: the linear subspace is subsumed in the near-equilibrium subspace.

MEPP NEAR EQUILIBRIUM

Ziegler flux and its scope

Let $\dot{\boldsymbol{\xi}}$ be continuously differentiable with respect to $\mathbf{f}$, the MEPP can be written in the form of orthogonality condition [1, 5],

$$\dot{\boldsymbol{\xi}} = \lambda \nabla_{\mathbf{f}} \sigma \qquad (20)$$

where σ denotes the entropy production rate and λ is a Lagrangian multiplier required by MEPP. Substituted with Eq. (9), Eq. (20) becomes

$$\nabla_{\mathbf{f}} \dot{\boldsymbol{\xi}} \cdot \mathbf{f} = q \dot{\boldsymbol{\xi}} \qquad (21)$$

where

$$q = \frac{1}{\lambda \vartheta V} - 1 \qquad (22)$$

Known from the Euler's homogeneous function theorem, Eq. (21) shows that $\dot{\boldsymbol{\xi}}$ should be a homogeneous function of degree q in its conjugate force $\mathbf{f}$. A thermodynamic flux satisfying Eq. (21) is termed a *Ziegler flux*. Obviously, Onsager flux is a subclass of Ziegler flux when $q = 1$.

Taking the derivative of Eq. (21) with respect to $\mathbf{f}$, one obtains

$$\dot{\xi}\nabla_{\mathbf{f}} + \nabla_{\mathbf{f}}^2\dot{\xi} \cdot \mathbf{f} = q\nabla_{\mathbf{f}}\dot{\xi} \qquad (23)$$

Noting that the second order tensor $\nabla_{\mathbf{f}}^2\dot{\xi} \cdot \mathbf{f}$ is symmetric, Eq. (23) minus its transpose yields

$$\nabla_{\mathbf{f}}\dot{\xi} = \dot{\xi}\nabla_{\mathbf{f}} \qquad (24)$$

Equation (24) means Ziegler flux is a subclass of non-linear Onsager flux, as indicated by Fig. 1. Therefore, the scope of application of MEPP is limited to near equilibrium processes.

Representation of a Non-linear Onsager flux in a series of Ziegler fluxes

Consider a generic non-linear Onsager flux $\dot{\xi}$ that is determined by the flow potential Q in the form of Eq. (17). Let Q be expanded in Maclaurin series at the equilibrium point $Q(\mathbf{0}) = 0$,

$$Q(\mathbf{f}) = \sum_{i=0}^{\infty} \frac{1}{i!}\mathbf{f}^i \circ \nabla_{\mathbf{f}}^i Q(\mathbf{0}) \qquad (25)$$

where $\circ$ denotes the complete inner product and the i-th order tensor $\nabla_{\mathbf{f}}^i Q(\mathbf{0})$ is full symmetric and constant. Note that the zeroth and the first terms vanish, i.e.,

$$\frac{1}{0!}\mathbf{f}^0 \circ \nabla_{\mathbf{f}}^0 Q(\mathbf{0}) = Q(\mathbf{0}) = 0$$

$$\frac{1}{1!}\mathbf{f}^1 \circ \nabla_{\mathbf{f}}^1 Q(\mathbf{0}) = \mathbf{f} \cdot \left.\frac{\partial Q}{\partial \mathbf{f}}\right|_{\mathbf{f}=0} = \mathbf{f} \cdot \dot{\xi}(\mathbf{0}) = 0 \qquad (26)$$

Substituting Eq. (25) to Eq. (17), $\dot{\xi}$ is represented as

$$\dot{\xi} = \nabla_{\mathbf{f}}Q = \dot{\xi}^{\langle 2 \rangle} + \dot{\xi}^{\langle 3 \rangle} + \cdots = \sum_{i=2}^{\infty} \dot{\xi}^{\langle i \rangle} \qquad (27)$$

where $\dot{\xi}^{\langle i \rangle}$ is the i-th term of the Maclaurin series,

$$\dot{\xi}^{\langle i \rangle} = \frac{1}{(i-1)!}\mathbf{f}^{i-1} \circ \nabla_{\mathbf{f}}^i Q(\mathbf{0}) \qquad (28)$$

Obviously, $\dot{\xi}^{\langle i \rangle}$ $(i = 2,3,\dots,n)$ is a series of Ziegler fluxes of degree $i-1$, because

$$\nabla_{\mathbf{f}}\dot{\xi}^{\langle i \rangle} \cdot \mathbf{f} = (i-1)\dot{\xi} \qquad (29)$$

And the first term $\dot{\xi}^{\langle 2 \rangle}$ is an Onsager flux,

$$\dot{\xi}^{\langle 2 \rangle} = \mathbf{L} \cdot \mathbf{f}, \qquad \mathbf{L} = \left.\frac{\partial^2 Q}{\partial \mathbf{f}^2}\right|_{\mathbf{f}=0} = \mathbf{L}^{\mathrm{T}} \qquad (30)$$

Equation (27) shows that, any non-linear Onsager flux can be represented in a series of Ziegler fluxes and the classical Onsager reciprocal relation holds strictly when and only when the current state is in an infinitesimal neighborhood of equilibrium. Therefore, any near-equilibrium processes can be approximately described using such representation, where the number of the terms can be arbitrary and determined by the required accuracy of the description.

Prigogine's minimum entropy production principle

One may refer to Martyushev & Seleznev [4] and Rajagopal & Srinivasa [7] for thorough discussions on the significance of the Prigogine's minimum entropy production principle [18] and its relationship between MEPP. Here we simply prove that the Prigogine's principle is an inevitable result of the second law of thermodynamics for a given Ziegler flux with $q \geq 0$.

The Prigogine's principle states that, if some of the thermodynamic forces are fixed at zero, i.e.,

$$f_\alpha = 0, \qquad \alpha = 1,2,\dots,\chi \ (\chi < n) \qquad (31)$$

the entropy production reaches the minimum if and only if the remained thermodynamic fluxes vanish, namely,

$$\dot{\xi}_\alpha = 0, \qquad \alpha = \chi + 1, \chi + 2, \dots, n \qquad (32)$$

is the sufficient and necessary condition of

$$\sigma = \frac{1}{\vartheta V}\mathbf{f} \cdot \dot{\xi} \to \min \qquad (33)$$

The proof goes as follows. Equation (33) equals to

$$\nabla_{\mathbf{f}}(\sigma) = \frac{1}{\vartheta V}\left(\dot{\xi} + \nabla_{\mathbf{f}}\dot{\xi} \cdot \mathbf{f}\right) = \frac{1+q}{\vartheta V}\dot{\xi} = \mathbf{0}$$

$$\mathbf{f} \cdot \nabla_{\mathbf{f}}^2(\sigma) \cdot \mathbf{f} = \frac{1+q}{\vartheta V}\mathbf{f} \cdot \nabla_{\mathbf{f}}\dot{\xi} \cdot \mathbf{f} = (1+q)q\sigma \geq 0 \qquad (34)$$

Obviously, Eq. (34a) is exactly Eq. (32) and Eq. (34b) is the second law of thermodynamics as long as the degree q is positive.

MEPP FAR FROM EQUILIBRIUM

Representation of a rotational flux in a series of non-linear Onsager fluxes

In this section, we consider thermodynamic fluxes far away from equilibrium. The fluxes are rotational and cannot be derived from a potential function. Let $\dot{\xi}(\mathbf{f})$ be a generic rotational flux. Using the $n$dimensional generalization of the Helmholtz representation theorem [19], $\dot{\xi}$ can be decomposed into two parts,

$$\dot{\xi}(\mathbf{f}) = \dot{\xi}_p(\mathbf{f}) + \dot{\xi}_r(\mathbf{f}) \qquad (35)$$

where $\dot{\xi}_p(\mathbf{f})$ is the potential part that is curl free and can be determined by the potential function Q,

$$\dot{\xi}_p = \nabla_{\mathbf{f}}Q, \qquad Q = Q(\mathbf{f}) = \int_0^1 \dot{\xi}(\tau\mathbf{f}) \cdot \mathbf{f}\,\mathrm{d}\tau \qquad (36)$$

and $\dot{\xi}_r(\mathbf{f})$ is the purely rotational part

$$\dot{\xi}_r = \int_0^1 \tau\left(\nabla_{\mathbf{f}}\dot{\xi}(\tau\mathbf{f}) - \dot{\xi}(\tau\mathbf{f})\nabla_{\mathbf{f}}\right) \cdot \mathbf{f}\,\mathrm{d}\tau \qquad (37)$$

which also satisfies

$$\dot{\boldsymbol{\xi}}_r \cdot \mathbf{f} = 0 \qquad (38)$$

The properties of $\dot{\boldsymbol{\xi}}_p$ have been discussed in the previous two sections and here we only have to focus on $\dot{\boldsymbol{\xi}}_r$.

Consider the differential 1-form $\dot{\boldsymbol{\xi}}_r(\mathbf{f}) \cdot d\mathbf{f}$. Known from the Darboux theorem [19], it should be of Class $2m$ with $m \geq 1$ and can be represented as

$$\dot{\boldsymbol{\xi}}_r(\mathbf{f}) \cdot d\mathbf{f} = \sum_{i=1}^{m} P^{\langle i \rangle}(\mathbf{f}) dQ^{\langle i \rangle}(\mathbf{f}) \qquad (39)$$

where $P^{\langle i \rangle}$ and $Q^{\langle i \rangle}$ are independent scalar functions of total number $2m$. Thus, the $\dot{\boldsymbol{\xi}}_r$ is determined as

$$\dot{\boldsymbol{\xi}}_r = \sum_{i=1}^{m} P^{\langle i \rangle}(\mathbf{f}) \nabla_{\mathbf{f}} Q^{\langle i \rangle}(\mathbf{f}) \qquad (40)$$

which indicates that the number of DOFs of $\dot{\boldsymbol{\xi}}_r$ is $2m$. It should be noted that the representation of $\dot{\boldsymbol{\xi}}_r$ by Darboux theorem is totally different from the representation of $\dot{\boldsymbol{\xi}}_p$ in Maclaurin series as given by Eq. (27). First, the number of terms of Eq. (27) is arbitrary while in Eq. (40) m is a nature of the given flux: m increases as the flux removes from equilibrium. Second, in Eq. (27), each term is a high-level minimal of its preceding term, but in Eq. (40) all terms are of equal status.

Combining Eq. (40) with Eq. (35), a generic flux $\dot{\boldsymbol{\xi}}(\mathbf{f})$ that is far from equilibrium can be represent by a series of weighted non-linear Onsager fluxes in the following form

$$\dot{\boldsymbol{\xi}} = \dot{\boldsymbol{\xi}}_p + P^{\langle 1 \rangle} \dot{\boldsymbol{\xi}}_p^{\langle 1 \rangle} + P^{\langle 2 \rangle} \dot{\boldsymbol{\xi}}_p^{\langle 2 \rangle} + \cdots + P^{\langle m \rangle} \dot{\boldsymbol{\xi}}_p^{\langle m \rangle} \qquad (41)$$

where $\dot{\boldsymbol{\xi}}_p^{\langle i \rangle}$ $(i = 1,2,\ldots,m)$ denote m non-linear Onsager fluxes determined by the potential $Q^{\langle i \rangle}(\mathbf{f})$ and weight functions are force-dependent, $P^{\langle i \rangle} = P^{\langle i \rangle}(\mathbf{f})$. On the other hand, any non-linear Onsager flux can be represented by a series of Ziegler fluxes, so we can conclude that any flux far from equilibrium can be finally represented by a series of weighted Ziegler fluxes through the two levels of representation. This might be the way MEPP acts in far-from-equilibrium processes. Finally, we may answer the question (i) proposed by Martyushev [2]: MEPP could be a basis of all non-equilibrium physics, but not in a straightforward way.

An example: the non-Darcy flow

Take the Darcy's law for example, which is a constitutive equation for the flow of a fluid through a porous medium. The Darcy's law establishes the linear relation between the pressure gradient and the velocity. For one-dimensional flow, it can be written as

$$-\nabla p = \frac{\mu}{K} v \qquad (42)$$

where ∇p denotes the pressure gradient, v the velocity, μ the fluid viscosity and K the permeability of the porous medium. A well-known non-linear extension of the Darcy's law is the Forchheimer equation [20], which is quadratic,

$$-\nabla p = \frac{\mu}{K} v + \rho \beta v^2 \qquad (43)$$

where ρ and β denote respectively the fluid density and the non-Darcy coefficient. In general, the non-Darcy effect can be presented in the polynomial form [21],

$$-\frac{K}{\mu} \nabla p = v + \frac{1}{v} f(v,v) + \frac{1}{v^2} g(v,v,v) + \cdots \qquad (44)$$

where f and g are bilinear and trilinear functions, respectively. The nonlinear extensions can be supported in thermodynamics with the proposed representation theorems.

CONCLUSIONS

In this paper, a non-equilibrium process is considered as near equilibrium if there exists a potential function from which all components of the thermodynamic flux can be derived. Such flux is termed non-linear Onsager flux. By contrast, a process is considered as far from equilibrium if the flux is non-potential or rotational.

The maximum entropy production principle (MEPP) by Ziegler is a reasonable classification of behavior for certain non-equilibrium systems instead of a general thermodynamic law. A MEPP-governed thermodynamic flux or a Ziegler flux is actually a homogenous non-linear Onsager flux. Thus, the scope of application of MEPP is not universe but limited to near-equilibrium processes.

Any non-linear Onsager flux can be represented in Maclaurin series of which each term is a Ziegler flux. Therefore, any near-equilibrium processes can be approximately described using such representation, where the number of the terms of the representation can be arbitrary and determined by the required accuracy of the description.

For a far-from-equilibrium process, the rotational flux can be represented by a series of weighted non-linear Onsager fluxes using the Darboux theorem. The number of the terms of the representation is a nature of the rotational flux: the number increases as the flux removes from equilibrium.

The two levels of representation indicate that Ziegler fluxes can serve as the basic elements to construct any complex thermodynamic flux from near to far-from equilibrium. In other words, any complex phenomena can be described elementally by MEPP.

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