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Gyarmati's principle and Edelen representation of thermodynamic forces in the maximum entropy formalism

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HIGHLIGHTS

- A brief review of the maximum entropy formalism (MEF) due to Jaynes is provided.
- Gyarmati's principle is extended to nonlinear irreversible processes in the MEF.
- Edelen representation of thermodynamic forces is found to be derivable from the MEF.

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ABSTRACT

Gyarmati's variational principle is generalized to nonlinear cases in the maximum entropy formalism of Jaynes by basing it on a statistical mechanical expression involving the partition function. The force representation for the general solution of the Clausius–Duhem inequality due to Edelen, which is expressed as the sum of the dissipative and non-dissipative parts of the thermodynamic forces, is also found to be derivable from within the maximum entropy formalism.

1. Introduction

Edelen's construct of dissipation potentials is mathematically rigorous and requires virtually no special assumptions [1–3]. Being motivated by a well-known theorem called "Poincare's lemma" that any closed differential form defined on a star-shaped domain is an exact differential form, Edelen developed the decomposition theorem for general vector-valued functions. In his decomposition theorem, any mapping $\boldsymbol{J}(\boldsymbol{X}, \boldsymbol{\omega})$ of the product space $E_M \times E_p$ of an M–dimensional vector space E_M and a p–dimensional vector space $E_p$into E_M that is of class C^1 in $\boldsymbol{X}$ and continuous in $\boldsymbol{\omega}$ can be represented as the sum of the gradient of a scalar-valued function $\psi(\boldsymbol{X}, \boldsymbol{\omega})$ and vector-valued function $\boldsymbol{U}(\boldsymbol{X}, \boldsymbol{\omega})$ that is orthogonal to the radial vector $\boldsymbol{X}$, namely, $\boldsymbol{J}(\boldsymbol{X}, \boldsymbol{\omega}) = \nabla_{\boldsymbol{X}}\psi(\boldsymbol{X}, \boldsymbol{\omega}) + \boldsymbol{U}(\boldsymbol{X}, \boldsymbol{\omega})$with $\boldsymbol{X} \cdot \boldsymbol{U}(\boldsymbol{X}, \boldsymbol{\omega}) = \boldsymbol{0}$. $\psi(\boldsymbol{X}, \boldsymbol{\omega})$ is called the dissipation potential or more appropriately the flux potential. All vector-valued functions $\boldsymbol{J}(\boldsymbol{X}, \boldsymbol{\omega})$ that satisfy the second law of thermodynamics will be obtained by applying the decomposition theorem to the second law. In thermodynamics, $\boldsymbol{X}$ and $\boldsymbol{J}(\boldsymbol{X}, \boldsymbol{\omega})$ are identified respectively with the thermodynamic forces and the conjugate thermodynamic fluxes, with $\boldsymbol{\omega}$ denoting the thermostatic state variables. $\nabla_{\boldsymbol{X}}\psi(\boldsymbol{X}, \boldsymbol{\omega})$ and $\boldsymbol{U}(\boldsymbol{X}, \boldsymbol{\omega})$ correspond to the dissipative and non-dissipative parts of the thermodynamic fluxes $\boldsymbol{J}(\boldsymbol{X}, \boldsymbol{\omega})$, respectively.

Edelen [3] showed that the non-dissipative part of the thermodynamic fluxes is not a consequence of any of the laws of thermodynamics and causes the generalized Onsager symmetry to fail. It is also worth noting that the violation of the

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generalized Onsager symmetry is now well-established in the field of mesoscopic or quantum transport theories (see Leturcq et al. [4] for example) and that the thermodynamic orthogonality is a special case of the decomposition theorem (Ostoja-Starzewski and Zubelewicz [5]). In order to point out the physical relevance of the non-dissipative part of the thermodynamic fluxes and its role in nonlinear irreversible processes, Okada [6] took a brief look at the quantum Hall effect to show that in an integral quantum Hall regime the Hall current exists as the non-dissipative part of the electric current.

It was suggested by Ostoja-Starzewski and Zubelewicz [5] that while attempting to develop new theories in continuum physics, there are physical situations where it becomes more advantageous to represent thermodynamic forces $\boldsymbol{X}$ as the sum of the gradient of the force potential $\phi\left(\boldsymbol{J},\boldsymbol{\omega}\right)$ and vector-valued function $\boldsymbol{U}\left(\boldsymbol{J},\boldsymbol{\omega}\right)$ that is orthogonal to the conjugate thermodynamic fluxes $\boldsymbol{J}$, namely, $\boldsymbol{X}\left(\boldsymbol{J},\boldsymbol{\omega}\right)=\nabla_{\boldsymbol{X}}\phi\left(\boldsymbol{J},\boldsymbol{\omega}\right)+\boldsymbol{U}\left(\boldsymbol{J},\boldsymbol{\omega}\right)$ with $\boldsymbol{J}\cdot\boldsymbol{U}\left(\boldsymbol{J},\boldsymbol{\omega}\right)=\boldsymbol{0}$ in a manner dual to the flux potential referred to above. It was also mentioned in the same paper that it is not possible to decompose $\boldsymbol{X}$ as above by retracing the result of Dewar's work [7] based on the maximum entropy formalism.

In this paper, in order to represent the thermodynamic forces $\boldsymbol{X}$ as the sum of their dissipative and non-dissipative components, we take an alternative approach, within the framework of the maximum entropy formalism of Jaynes [8], based on the method that Verhas [9] employed to generalize the reciprocal relations and the universal form of Gyarmati's principle. In Section 2, we will provide a brief review of the maximum entropy formalism for easy reference in the subsequent sections. In Section 3, Gyarmati's principle will be extended to nonlinear cases using the method of Verhas [9] in the maximum entropy formalism. We will show in Section 4 how the Edelen representation of thermodynamic forces is re-derived by the procedure developed in Section 3. We conclude by remarking on some ramifications of the results of Sections 3 and 4.

2. Review of the maximum entropy formalism

In this section, we provide a brief review of the maximum entropy formalism due to Jaynes [8] for the reader to refer to in the subsequent sections. It was proposed by Jaynes that for problems of statistical inference the probabilities p_i should be assigned so as to maximize the Shannon information entropy

$$H=-\sum_{i}^{n}p_i\ln p_i \tag{1}$$

subject to

$$\sum_{i=1}^{n}p_i=1 \tag{2}$$

and a set of m given constraints

$$F_k=\langle f_k\rangle=\sum_{i=1}^{n}p_if_k\left(i\right),\ 1\leq k\leq m, \tag{3}$$

where $\{F_k\}$ are the results of various macroscopic measurements and the quantities measured are represented by the random variables $\{f_k\}$. $f_k\left(i\right)$ is the value of f_k in microstate i and n is the number of microstates with $n>m$.

The resulting probability distribution is the minimally prejudiced one given by

$$p_i=\left(1/Z\left(\boldsymbol{\lambda}\right)\right)exp\left\{-\sum_{k=1}^{m}\lambda_kf_k\left(i\right)\right\}, \tag{4}$$

where $\boldsymbol{\lambda}=\{\lambda_k\}\left(k=1\sim m\right)$ are Lagrange multipliers that appear in the derivation of the maximum entropy probability distribution (4) from a variational principle. The maximum attainable value of the information entropy is given by

$$H_{max}=\ln Z\left(\boldsymbol{\lambda}\right)+\sum_{k=1}^{m}\lambda_kF_k, \tag{5}$$

where $Z\left(\boldsymbol{\lambda}\right)$ is the partition function defined by

$$Z\left(\boldsymbol{\lambda}\right)=\sum_{i=1}^{n}exp\left\{-\sum_{k=1}^{m}\lambda_kf_k\left(i\right)\right\}. \tag{6}$$

The Lagrange multipliers $\boldsymbol{\lambda}$ are related to the given constraints $\boldsymbol{F}$ by the equations

$$F_k=\langle f_k\rangle=-\frac{\partial\ln Z\left(\boldsymbol{\lambda}\right)}{\partial\lambda_k},\quad 1\leq k\leq m. \tag{7}$$

The constraints $\boldsymbol{F}$ are coupled into the maximum entropy probability distribution through the Lagrange multipliers $\boldsymbol{\lambda}$, which can be determined in terms of $\boldsymbol{F}$ from solving the set of m nonlinear equations [10]

$$\sum_{i=1}^{n}p_if_k\left(i\right)-F_k=0,\quad 1\leq k\leq m. \tag{8}$$

For example, applying the maximum entropy formalism to a closed system in thermal equilibrium with a heat bath at absolute temperature T yields a very important formula in statistical mechanics, namely, the microscopic expression of Helmholtz free energy $\mathcal{F}$ in terms of the partition function

$$\mathcal{F} = -\beta^{-1} \ln Z(\beta), \tag{9}$$

where $\beta = 1/k_B T$ (k_B: Boltzmann's constant). Once the partition function $Z(\beta)$ is given, macroscopic predictions can be made for the mean energy and thermodynamic entropy of the system as well as for the Helmholtz free energy. This is a summary of the maximum entropy formalism.

3. Generalization of Gyarmati's principle to nonlinear cases

It is shown below that $\boldsymbol{F}$ in non-equilibrium states can be represented in terms of the second- and third-order statistics for the random vector $\boldsymbol{f} = \{f_k\}$ in equilibrium. Starting with Eq. (7), we expand it in a neighborhood of the origin $\boldsymbol{\lambda} = 0$ by a Taylor series up to and including the second-order term under the assumption that the constraint vector $\boldsymbol{F}$ is of class C^2 in $\boldsymbol{\lambda}$, to obtain

$$\begin{aligned} F_k(\boldsymbol{\lambda}) &= F_k(\mathbf{0}) + D_{\boldsymbol{\lambda}} F_k(\mathbf{0}) + \frac{1}{2} D^2_{\boldsymbol{\lambda}} F_k(\mathbf{0}) + \cdots \\ &= F_k(\mathbf{0}) + \sum_i^m \frac{\partial F_k}{\partial \lambda_i}\bigg|_{\boldsymbol{\lambda}=\mathbf{0}} \lambda_i + \frac{1}{2} \sum_{i,j}^m \frac{\partial^2 F_k}{\partial \lambda_i \partial \lambda_j}\bigg|_{\boldsymbol{\lambda}=\mathbf{0}} \lambda_i \lambda_j + \cdots, \quad 1 \le k \le m. \end{aligned} \tag{10}$$

We note that the origin $\boldsymbol{\lambda} = 0$ corresponds to equilibrium states without loss of generality. For if $\boldsymbol{\lambda^{eq}}$ should occur which do not vanish in equilibrium, a transformation of variables $\boldsymbol{\lambda} = \boldsymbol{\lambda^{eq}} + \boldsymbol{\sigma}$ will then convert the problem to one in which the new variables $\boldsymbol{\sigma}$ vanish in equilibrium. Using Eq. (7) in Eq. (10), we obtain the following expression

$$F_k(\boldsymbol{\lambda}) = F_k(\mathbf{0}) - \sum_i^m \frac{\partial^2 \ln Z}{\partial \lambda_k \partial \lambda_i}\bigg|_{\boldsymbol{\lambda}=\mathbf{0}} \lambda_i - \frac{1}{2} \sum_{i,j}^m \frac{\partial^3 \ln Z}{\partial \lambda_k \partial \lambda_i \partial \lambda_j}\bigg|_{\boldsymbol{\lambda}=\mathbf{0}} \lambda_i \lambda_j + \cdots, \quad 1 \le k \le m. \tag{11}$$

The first, second and third coefficients on the right-hand side of Eq. (11) correspond to the first-, second- and third-order cumulants for the random vector $\boldsymbol{f}$, respectively. The first coefficients represent the mean (i.e., measured) values of f_k in equilibrium. The second coefficients represent the covariance matrix of the random vector $\boldsymbol{f}$ in equilibrium, as given by

$$\frac{\partial^2 \ln Z}{\partial \lambda_k \partial \lambda_i}\bigg|_{\mathbf{0}} = (\langle f_k f_i \rangle - \langle f_k \rangle \langle f_i \rangle)_{\mathbf{0}} = B_{ik} = \frac{\partial^2 \ln Z}{\partial \lambda_i \partial \lambda_k}\bigg|_{\mathbf{0}} \equiv B_{ki}, \quad 1 \le k,\ i \le m, \tag{12}$$

which is a real-valued symmetric positive definite matrix. As can easily be seen, the diagonal elements of B_{ki} are fluctuations of the components of $\boldsymbol{f}$ in equilibrium, whereas the other off-diagonal elements give the pairwise correlations between any two different components f_k and f_i in equilibrium. The third coefficients represent the third-order cumulant in equilibrium, as shown below.

$$\begin{aligned} -\frac{\partial^3 \ln Z}{\partial \lambda_k \partial \lambda_i \partial \lambda_j}\bigg|_{\mathbf{0}} &= \left(\langle f_k f_i f_j \rangle - \langle f_k \rangle \langle f_i f_j \rangle - \langle f_i \rangle \langle f_k f_j \rangle - \langle f_j \rangle \langle f_k f_i \rangle + 2 \langle f_k \rangle \langle f_i \rangle \langle f_j \rangle \right)_{\mathbf{0}} \\ &\equiv 2 b_{kji}, \quad 1 \le k, j, i \le m. \end{aligned} \tag{13}$$

The third- and higher-order cumulants measure the departure of the random vector $\boldsymbol{f}$ from a Gaussian random vector with an identical mean vector and covariance matrix, namely a measure of nonlinearity beyond the linear response regime. To look at it from the other side of the coin, if $\boldsymbol{f}$ is Gaussian, then its third- and higher-order cumulants will all become zero and thus the correspondence between $\boldsymbol{F}$ and $\boldsymbol{\lambda}$ will be a linear transformation. As for F_k, we set it equal to zero in consideration of the well-known condition in thermodynamics that thermodynamic fluxes obeying the second law of thermodynamics vanish with vanishing thermodynamic forces. This simplifies Eqs. (12) and (13) accordingly.

Now, we assume the extent of the norm $\|\boldsymbol{\lambda}\|$ to be such that only the linear and quadratic terms in $\boldsymbol{\lambda}$ will be used in Eq. (10). Eq. (10) can thus be approximated by

$$F_k(\boldsymbol{\lambda}) = \sum_i^m \frac{\partial F_k}{\partial \lambda_i}\bigg|_{\boldsymbol{\lambda}=\mathbf{0}} \lambda_i + \frac{1}{2} \sum_{i,j}^m \frac{\partial^2 F_k}{\partial \lambda_i \partial \lambda_j}\bigg|_{\boldsymbol{\lambda}=\mathbf{0}} \lambda_i \lambda_j, \quad 1 \le k \le m. \tag{14}$$

Since the upper and lower limits of summation are always equal to m and 1 respectively for the rest of the paper, we omit them for brevity from here onwards. Using Eqs. (12) and (13), we can express Eq. (14) as

$$F_k(\boldsymbol{\lambda}) = -\sum_i B_{ki} \lambda_i + \sum_{j,i} b_{kji} \lambda_j \lambda_i. \tag{15}$$

It follows from relation (11) that $b_{kji} = b_{kij}$, i.e., symmetric with respect to the indices j and i. Noting that for fixed k

$$\sum_{j,i} \left(b_{ijk} - b_{jki}\right) \lambda_j \lambda_i = 0, \tag{16}$$

we construct a coefficient matrix

$$L_{ki}\left(\boldsymbol{\lambda}\right) = -B_{ki} + \sum_{j} \left(b_{kji} + b_{ijk} - b_{jki}\right) \lambda_j \tag{17}$$

so that Eq. (15) can be recovered. The term $b_{kji} + b_{ijk} - b_{jki}$ inside the parenthesis in the second term on the right-hand side of Eq. (17) can be shown to be symmetric with respect to the indices k and i for each j by simply comparing it with the counterpart that results from interchanging k with i. Taking the specified sum over the index j and adding the resultant to the symmetric matrix B_{ki} gives the symmetry of L_{ki}. Since $L_{ki} = -B_{ki}$ at $\boldsymbol{\lambda} = \mathbf{0}$ and B_{ki} is a symmetric positive definite matrix, it is implied that $det\left(L_{ki}\right) > 0$at equilibrium. This determinant remains positive at near-equilibrium and beyond (up to the assumed extent of $\|\boldsymbol{\lambda}\|$) owing to the smoothness requirement that $F_k = F_k\left(\boldsymbol{\lambda}\right)$ is of class C^2 in $\boldsymbol{\lambda}$ and therefore L_{ki} should be invertible in a wider range around equilibrium than the range of validity of linear response laws. Repeating the similar argument for each principal submatrix of L_{ki} (i.e., those submatrices that give rise to the principal minors of L_{ki}), we find that the principal minors of the determinant of L_{ki} are positive. Therefore, it can be concluded from a result of linear algebra that the matrix L_{ki} remains positive definite. The inverse of this positive definite matrix L_{ki} will be used later to discuss and determine the type of extremum for the variational principle to be formulated.

We therefore obtain the expression relating the constraints $\{F_k\}$ to the Lagrange multipliers $\{\lambda_k\}$ through the symmetric positive definite matrix L_{ki}

$$F_k\left(\boldsymbol{\lambda}\right) = \sum_{i} L_{ki}\left(\boldsymbol{\lambda}\right) \lambda_i. \tag{18}$$

Denoting the inverse of the positive definite matrix L_{ki} by R_{ki}, which is a positive definite matrix as well, and multiplying both sides of Eq. (18) by R_{ki} gives

$$\lambda_k\left(\boldsymbol{F}\right) = \sum_{i} R_{ki}\left(\boldsymbol{\lambda}\right) F_i. \tag{19}$$

In passing we note from Eq. (19) that Lagrange multipliers in general can be regarded as representing the reactions of a system against given constraints.

Eq. (18) allows us to write the Lagrangian function associated with the Gaussian form of Gyarmati's principle (see Verhas [9]) as in the expression below

$$\mathcal{L} = -\frac{1}{2} \sum_{k,i} R_{ki} \left(F_k - \sum_{\alpha} L_{k\alpha}\left(\boldsymbol{\lambda}\right) \lambda_\alpha\right) \left(F_i - \sum_{\alpha} L_{i\alpha}\left(\boldsymbol{\lambda}\right) \lambda_\alpha\right). \tag{20}$$

The summand including the factor of $-1/2$on the right-hand side of Eq. (20) is multiplied out to yield the universal form of Lagrangian function, i.e.,

$$\mathcal{L} = \sum_{k} \lambda_k F_k - \frac{1}{2} \sum_{k,i} L_{ki}\left(\boldsymbol{\lambda}\right) \lambda_k \lambda_i - \frac{1}{2} \sum_{k,i} R_{ki}\left(\boldsymbol{\lambda}\right) F_k F_i. \tag{21}$$

Defining the mean dissipation function $D\left(\boldsymbol{F}\right)$ by the ensemble average of a statistically fluctuating dissipation rate of the form $\frac{1}{2}\sum_{k=1}^{m} \lambda_k f_k$ and using Eq. (19) yields the relation

$$D\left(\boldsymbol{F}\right) = \frac{1}{2} \sum_{k,i} R_{ki}\left(\boldsymbol{\lambda}\right) F_k F_i. \tag{22}$$

Similarly, we can also obtain the following expression of mean dissipation function from Eq. (18):

$$D\left(\boldsymbol{\lambda}\right) = \frac{1}{2} \sum_{k,i} L_{ki}\left(\boldsymbol{\lambda}\right) \lambda_k \lambda_i. \tag{23}$$

Using Eqs. (22) and (23) for the second and third terms of Eq. (21) respectively, we can rewrite the universal form of Lagrangian function $\mathcal{L}$ as

$$\mathcal{L} = \sum_{k} \lambda_k F_k - D\left(\boldsymbol{\lambda}\right) - D\left(\boldsymbol{F}\right). \tag{24}$$

It should be pointed out here that $D\left(\boldsymbol{\lambda}\right)$ is not a quadratic function of $\boldsymbol{\lambda}$, whereas $D\left(\boldsymbol{F}\right)$ depends on $\boldsymbol{\lambda}$ **t**hrough $R_{ki}\left(\boldsymbol{\lambda}\right)$.

Now, taking the gradient of $D(\boldsymbol{F})$ with respect to F_k yields

$$\frac{\partial D(\boldsymbol{F})}{\partial F_k} = \sum_i R_{ki}(\boldsymbol{\lambda}) F_i = \lambda_k \tag{25}$$

so that the orthogonality condition in $\boldsymbol{F}$-space is satisfied for the mean dissipation function $D(\boldsymbol{F})$. On the other hand, the orthogonality condition in $\boldsymbol{\lambda}$-space for $D(\boldsymbol{\lambda})$does not hold, as shown below.

$$\frac{\partial D(\boldsymbol{\lambda})}{\partial \lambda_k} = \sum_i L_{ki}(\boldsymbol{\lambda}) \lambda_i + \frac{1}{2}\sum_{j,i} \frac{\partial L_{ji}(\boldsymbol{\lambda})}{\partial \lambda_k} \lambda_j \lambda_i \neq F_k. \tag{26}$$

In spite of Eq. (26), the universal form of Gyarmati's principle is still valid, since the presence of $D(\boldsymbol{\lambda})$ in Eq. (24) does not affect the outcome in evaluating the gradient of the Lagrangian function $\mathcal{L}$ with respect to F_k (see Verhas [9]), namely,

$$\frac{\partial \mathcal{L}}{\partial F_k} = \frac{\partial}{\partial F_k}\left(\sum_k \lambda_k F_k - D(\boldsymbol{F})\right) = 0. \tag{27}$$

This is the $\boldsymbol{F}$-space representation of Gyarmati's variational principle generalized to nonlinear cases (see Verhas [9]).

In referring to Eq. (20), since R_{ki} is a positive definite matrix, the Lagrangian function $\mathcal{L}$ is always negative unless Eq. (18) is satisfied. Therefore, $\mathcal{L}$ serves to define an action functional which will always yield a maximum at its stationarizing elements in $\boldsymbol{F}$-space. Now, if we take each f_k to represent for example a flux, its average F_k can be regarded as the corresponding thermodynamic flux, λ_k as its conjugate thermodynamic force, and the first term on the right-hand side of Eq. (24) represents the entropy production in bilinear form. The Lagrangian function so obtained therefore enters into an extremum principle of dissipated power or equivalently an extremum principle of entropy production as the integrated form of Eq. (24) with respect to space and time. We mention here that this extension of Gyarmati's principle to nonlinear irreversible processes is quite general in the sense that the only assumption we have made in deriving it is the C^2-smoothness requirement of the constraint vector $\{F_k\}$, which is safely said to be not a strong requirement from a physical standpoint.

4. Edelen representation of thermodynamic forces

It was pointed out by Ostoja-Starzewski and Zubelewicz [5] that there are physical situations where it becomes more advantageous to represent thermodynamic forces $\boldsymbol{\lambda}$ as the sum of the gradient of a force potential $\phi(\boldsymbol{F})$ and vector-valued function $\boldsymbol{U}(\boldsymbol{F})$ that is orthogonal to the conjugate thermodynamic fluxes $\boldsymbol{F}$, namely, $\boldsymbol{\lambda}(\boldsymbol{F}) = \nabla_{\boldsymbol{F}}\phi(\boldsymbol{F}) + \boldsymbol{U}(\boldsymbol{F})$ with $\boldsymbol{F}\cdot\boldsymbol{U}(\boldsymbol{F}) = \boldsymbol{0}$. Note in the above expressions that we have not made any explicit reference to the thermostatic state variables for brevity. It was also mentioned in the same paper that it is not possible to decompose $\boldsymbol{\lambda}$ as above by retracing the result of Dewar's work [7] based on the maximum entropy formalism. However, it is shown in this section that our approach adopted in the last section makes it possible to write $\boldsymbol{\lambda}$ as the sum of their dissipative and non-dissipative parts.

Starting with Eq. (15) in Section 3, we decompose the second term $\sum_j b_{kji}\lambda_j$ into a sum of a symmetric matrix and an anti-symmetric matrix and write it as

$$F_k(\boldsymbol{\lambda}) = -\sum_i B_{ki}\lambda_i + \sum_{j,i}\left(b_{kji}\lambda_j\right)^s\lambda_i + \sum_{j,i}\left(b_{kji}\lambda_j\right)^{as}\lambda_i. \tag{28}$$

We combine the first and second terms of Eq. (28) to write

$$\sum_i L^s_{ki}\lambda_i \equiv \sum_i\left(-B_{ki} + \sum_j\left(b_{kji}\lambda_j\right)^s\right)\lambda_i. \tag{29}$$

It follows from the arguments below Eq. (17) in Section 3 that L^s_{ki} is a symmetric positive definite matrix. For notational convenience, we rewrite the last term of Eq. (28) as

$$\sum_i L^{as}_{ki}\lambda_i \equiv \sum_{j,i}\left(b_{kji}\lambda_j\right)^{as}\lambda_i. \tag{30}$$

Eq. (28) can now be written as

$$F_k(\boldsymbol{\lambda}) = \sum_i L^s_{ki}\lambda_i + \sum_i L^{as}_{ki}\lambda_i. \tag{31}$$

Since L^{as}_{ki} is an anti-symmetric matrix, it is implied that the quadratic form associated with it is zero so that

$$\sum_k \lambda_k F_k(\boldsymbol{\lambda}) = \sum_{k,i} L^s_{ki}\lambda_k\lambda_i. \tag{32}$$

Eq. (31) allows us to define new constraints $\left\{F_k^E\right\}$ by

$$F_k^E\left(\boldsymbol{\lambda}\right) \equiv \sum_i L_{ki}^s \lambda_i = F_k\left(\boldsymbol{\lambda}\right) - \sum_i L_{ki}^{as} \lambda_i. \tag{33}$$

Then, it follows from Eqs. (32) and (33) that

$$\sum_k \lambda_k F_k\left(\boldsymbol{\lambda}\right) = \sum_k \lambda_k F_k^E\left(\boldsymbol{\lambda}\right). \tag{34}$$

Eq. (34) states that the change of variables defined by Eq. (33) leaves the form of the mean dissipation function unaltered. With the remark following Eq. (29), we can use all relevant arguments of Section 3 for the new constraints $\left\{F_k^E\right\}$ defined by Eq. (33) to obtain

$$\frac{\partial D\left(\boldsymbol{F}^E\right)}{\partial F_k^E} = \sum_i R_{ki}^s\left(\boldsymbol{\lambda}\right) F_i^E, \tag{35}$$

where R_{ki}^s is the inverse of L_{ki}^s. Substitution of Eq. (33) into F_i^E on the right-hand side of Eq. (35) gives

$$\frac{\partial D\left(\boldsymbol{F}^E\right)}{\partial F_k^E} = \sum_i R_{ki}^s F_i - \sum_{j,i} R_{kj}^s L_{ji}^{as} \lambda_i. \tag{36}$$

Since it follows from Eq. (34) that $\partial D\left(\boldsymbol{F}^E\right)/\partial F_k^E = \partial D\left(\boldsymbol{F}\right)/\partial F_k$, Eq. (36) can be put in the form

$$\lambda_k = \frac{\partial D\left(\boldsymbol{F}\right)}{\partial F_k} + U_k, \tag{37}$$

where U_k denotes the second term on the right-hand side of Eq. (36). Here, the inner product $\sum_k U_k F_k$ vanishes because

$$\sum_k U_k F_k = \sum_{k,j,i} R_{jk}^s F_k L_{ji}^{as} \lambda_i = \sum_{j,i} L_{ji}^{as} \lambda_j \lambda_i = 0. \tag{38}$$

Thus, the desired result, indicated at the beginning of this section, follows from Eqs. (37) and (38), namely, if stated in a force-flux format, each force λ_k can be represented as the sum of the gradient of the mean dissipation function $D\left(\boldsymbol{F}\right)$ and vector-valued function $\boldsymbol{U}$ that is orthogonal to the flux vector $\boldsymbol{F}$. Note that the mean dissipation function $D\left(\boldsymbol{F}\right)$ corresponds to the force potential of Edelen. To put it in a more physical perspective, the former quantity is the dissipative part of the thermodynamic force λ_k, while the latter the non-dissipative part of λ_k.

We conclude this section by observing from Eq. (37) that the equality of mixed second derivatives of the mean dissipation function $D\left(\boldsymbol{F}\right)$ of class C^2 gives the generalized symmetry relations

$$\frac{\partial\left(\lambda_k - U_k\right)}{\partial F_j} = \frac{\partial\left(\lambda_j - U_j\right)}{\partial F_k}, \tag{39}$$

as originally derived in the primitive thermodynamics of Edelen, namely, these symmetry relations are always satisfied by any system of thermodynamic forces diminished by its non-dissipative parts (see Theorem 4 of Edelen [1] or equation (2.19) of Edelen [2]), reducing to

$$\frac{\partial \lambda_k}{\partial F_j} = \frac{\partial \lambda_j}{\partial F_k}, \tag{40}$$

only when the non-dissipative part of the thermodynamic forces vanishes throughout $\boldsymbol{F}$-space. Needless to say, Eq. (37) reduces to Eq. (25) in the absence of non-dissipative forces.

5. Conclusion

Applying the method of Verhas to the statistical mechanical expression (7) involving the partition function, which relates a set of given constraints to the corresponding Lagrange multipliers in the maximum entropy formalism of Jaynes, we have generalized Gyarmati's principle to nonlinear cases. Examining the problem of decomposing thermodynamic forces into the sum of the gradient of a scalar-valued force potential and vector-valued function that yields no entropy production from a maximum entropy principle point of view, we have re-derived the force representation for the general solution of the Clausius–Duhem inequality due to Edelen by making use of the procedure developed in Section 3. Now that the Edelen representation of thermodynamic forces has been shown to be derivable from within the maximum entropy formalism, we hope that the results of Sections 3 and 4 will be further deepened and explored so as to shed light on the potentially important issue of resolving restrictions on the choices of non-dissipative forces/fluxes in irreversible processes, as briefly discussed in Section 6 of Okada [6], since the answers must come from outside of the scope of macroscopic phenomenological, non-equilibrium thermodynamics, most likely from research work in experimental and statistical mechanical interpretations of them in mesoscopic or quantum transport phenomena.

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