

Optimization of Processes by Equipartition

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Abstract

We examine the problem of energy-efficient production in an industrial process. By energy-efficient we mean minimum entropy production. We use the possibility to redistribute the production in different times or parts of the system for a given total production, and show that a distribution, that equipartitions the derivative of the local entropy production rate with respect to the local production, minimizes the entropy production. Equipartition in time implies stationary state production. Equipartition in space implies production for a given position independent force. The same constant derivative of the local entropy production rate is found if one optimizes the production for a given total entropy production.

Close of equilibrium the equipartition condition is found to reduce to the isoforce principle. Further from equilibrium, this reduction is extended to a whole class of nonlinear flux-force relations. We show that, when one increases the total production, the entropy production per unit produced starts to increase linearly, as a function of this total production.

It is shown which process conditions give an optimum path with an equipartition of the entropy production rate. How this relates to the isoforce principle is discussed. In general constraints on process conditions restrict the freedom to optimize, and therefore make it impossible to realise the most favorable conditions. The importance of the Onsager relations for the systematic description of the optimization is discussed.

1. Introduction

The most efficient use of energy is made if the entropy production has a minimum. Prigogine [9] pointed out many years ago, that stationary stages, when given freedom to self organize, have a minimum entropy production rate, if one is not too far from

equilibrium. Prigogine's observation implies that the transport of mass and heat in a reactor will self organize, as much as this is possible, in order to minimize the entropy production. For time dependent processes one should minimize the entropy production rate integrated over time.

In an industrial process, chemicals and/or energy are converted into other chemicals and/or energy. There is normally a certain freedom to vary the production process both globally and locally. In this manner one seeks to optimize the process. The possibility to modify the process is crucial for optimization procedures. If no changes are possible, there is nothing to optimize. Constraints for the optimization may be given: like the production(s) one wants to achieve; the time span one has available to accomplish the production; or limitations on the space that is available, [2] and [3]. Specifying the total production, for instance, implies that a possible increase in the production at one location and/or time, is compensated by an equal decrease at another location and/or time. This then affects the nature of the achievable optimum.

Sauar *et al.* [12] showed that the optimization of the entropy production with given productions, leads to equipartition of driving forces in the process. The result was called the principle of equipartition of forces, or shorter the isoforce principle. According to this result, the optimum operating line of a distillation column, [13], or a chemical reactor [13] is an isoforce operating line.

In finite-time thermodynamics Andresen and coworkers, (see for instance [1]), use the time as the (only) constraint in the optimization of an objective function, that need not be the entropy production, but can be almost any function of interest (e.g. the power, the energy-efficiency, the yield of a reaction). When finite-time thermodynamics is used to optimize specifically the energy-efficiency, the optimal path was found to have a constant entropy production [15]. Sauar *et al.* (see Ref. [11]) compared the paths that were obtained from finite-time thermodynamics and from the isoforce operating lines, in tray distillation columns, to the numerically found minimum entropy production of the column. Even though finite-time thermodynamics and the isoforce principle predict different optimum paths (i.e. of constant entropy production and of constant force, respectively), the results of both methods give very nearly the path that is found by numerical optimization. One reason for this will be pointed out in the concluding section.

For a given duty (that is an amount of heat or mass exchanged), Tondeur and Kvaalen, [4] and [16], conclude that the best operating line of a process has a uniformly distributed entropy production rate. They assumed in their derivation that the phenomenological constants in the flux equations were constant. This implies also that the driving forces are equipartitioned. The same assumption of constant coefficients is used by Bejan and Tondeur in their review, [3], and they conclude "that of optimal performance of a finite-size system with purpose is always characterized by equipartition of driving forces". When the coefficients are not constant a controversy seems to appear: is the optimum operating line characterized by a constant entropy production or by constant forces? In this case these two principles are no longer equivalent.

A simple example of two time independent parallel resistors, R_1 and R_2 , may illustrate the two principles. The forces are the voltages, V_1 and V_2 . If one uses the isoforce principle one has $V_1 = V_2 = V$. The resulting constant electric currents are $I_1 = V/R_1$ and $I_2 = V/R_2$. The given total current is $I = I_1 + I_2 = V(1/R_1 + 1/R_2)$. Solving this equation for V one obtains for the entropy production rate $\sigma_V = I_1 V_1 + I_2 V_2 = IV = I^2/(1/R_1 + 1/R_2)$. If one uses the equipartition of the entropy production rate one has $\sigma_\sigma/2 = I_1 V_1 = I_2 V_2 = I_1^2 R_1 = I_2^2 R_2$. This results in $I_1 = \sqrt{\sigma_\sigma/2R_1}$ and $I_2 = \sqrt{\sigma_\sigma/2R_2}$. The total current is $I = \sqrt{\sigma_\sigma/2}(1/\sqrt{R_1} + 1/\sqrt{R_2})$. For the entropy production rate this gives $\sigma_\sigma = 2I^2/(1/\sqrt{R_1} + 1/\sqrt{R_2})^2$. Using that $(1/R_1 + 1/R_2) \geq (1/\sqrt{R_1} + 1/\sqrt{R_2})^2/2$ it follows that $\sigma_V \leq \sigma_\sigma$. One only finds the equal sign when $R_1 = R_2$. This simple example illustrates the use of both principles. In this case the isoforce principle gives a lower entropy production rate. The two principles become equivalent when the resistances are equal, as pointed out already by Sauar *et al.* [12]. It should be noted that due to the time independent nature of the resistors, the optimum operation is stationary. This is clearly not the case if the resistors would be time dependent.

For time independent conditions, like constant resistors, stationary state operation will usually give the best efficiency. The general optimization problem considers the entropy production rate integrated over both space and time. This makes it possible to consider, for instance, contributions due to start-up or to assess the possible advantages of oscillatory operation. In the mathematical analysis the roles of time and position are similar, so that the general problem does not pose any serious additional difficulties.

One may also ask whether these principles are only applicable for fully linear flux-force relations, which are in general valid only close to equilibrium. Chemical reactions are certainly not linear in this sense. The application to batch or plug flow reactors is therefore clearly not straightforward, [17]. Bejan and Tondeur [3] and Sauar and coworkers [11], [14], [8] have pointed out, that the isoforce principle applies to certain nonlinear flux force relations, as well as certain reactor conditions. This possibility, which enlarges the application range for irreversible thermodynamics to engineering problems greatly, deserves to be pursued further within a general context.

The aim of this paper is to give a better mathematical foundation for the isoforce principle, than the one that has been presented in various contexts over the last years. It is our hope thereby to also resolve the apparent controversy, between equipartition of forces versus equipartition of entropy production rate, described above. A good understanding of the freedom to change the process, used in the optimization, is found to be crucial. As for the object function, we mainly deal with the entropy production of the total system, Σ . This means that our analysis is relevant for optimizations of the energy-efficiency, η . According to the second law of thermodynamics this efficiency is, for a work-producing process,

$$\eta = \frac{W_{\text{real}}}{W_{\text{max}}} = \frac{W_{\text{max}} - T_o \Sigma}{W_{\text{max}}} \quad (1)$$

where T_o is the temperature of the surroundings, W_{\max} is the maximum theoretical work that the process can deliver, i.e. at reversible conditions, and W_{real} is the real work output. We shall also indicate how object functions that are related to the entropy production can be introduced by Legendre transformations and discuss their role. Only parallel processes will be considered.

Functions, characterizing the objective of our optimization, are given first in the following section. The general optimization criterion for a process, is then specified (Sect. 3–4). With linear relations between the forces and the productions, the general criterion reduces to the isoforce principle (Sect. 5). However, a path of constant entropy production is found when certain constraints are introduced on the transport coefficients (Sect. 6). In Section 8 we construct a general class of nonlinear relations between fluxes and forces for which the isoforce principle is valid. The importance of the Onsager relations for the systematic description of the optimization is then discussed in Section 9, before the paper is concluded in Section 10.

2. The Object Functions

Object functions in a process are the product streams out of, or into, the system. The product can be a chemical compound or energy in some form. We shall use the word production for the total output of product from a process, and allow the production to be negative to indicate an input. It is of interest to analyze the efficiency of a process with specified productions. These productions, or object functions, are denoted $\mathbf{I} = (I_1, I_2, \dots, I_n)$. They are integrals over time, t , and position, $\mathbf{r} = (x, y, z)$, of the local production per unit volume and time, $\mathbf{J}(\mathbf{r}, t)$, in the process:

$$\mathbf{I} = \int_V d\mathbf{r} \int_{t_i}^{t_f} dt \mathbf{J}(\mathbf{r}, t) \quad (2)$$

The first integral is over the volume V of the process. The second integral is taken from the start to the end of the production, i.e. from t_i to t_f , respectively. The local productions are related to the fluxes of heat, mass, charge, and chemical reactions, as given in irreversible thermodynamics [5], [7]. As is used in the above equation the local productions are all parallel, i.e. they add up to give the total productions. The production from a vectorial flux is obtained by integration over the corresponding transfer area. The production from a scalar flux is obtained by integration over its production volume.

We assume next that a set of different local productions exists, which give the same total production. This makes it possible to choose a distribution of local productions, out of the possible set of such distributions, which gives the desired optimization. All the different productions, I_j for $j = 1, \dots, n$, must be independent of one another. This ensures the freedom to vary them independent of one another.

The object function needed to optimize the energy-efficiency, is the total entropy production. This is the integral over the local entropy production per unit of volume

and time (short: local entropy production rate):

$$\Sigma = \int_V d\mathbf{r} \int_{t_i}^{t_f} dt \sigma(\mathbf{r}, t) \quad (3)$$

The local entropy production rate is a function of the local productions. The function we really want to know is the minimum entropy production for given total productions.

An important optimization problem can now be stated: Find the minimum entropy production, $\Sigma_{\min}(\mathbf{I})$, for given total productions, \mathbf{I} . One of the aims of this paper is to discuss how to find $\Sigma_{\min}(\mathbf{I})$ for given productions, and see how the productions should be distributed.

3. The Optimization Problem

The Euler-Lagrange method, can now be used to determine the distribution of local productions, that give minimum entropy production (or best second law efficiency) for given total productions. In a world with changing energy prices, and limits on emissions (for instance CO₂), it is reasonable to study this question, decoupled from investment costs and other economic arguments. These can be brought in later as additional constraints.

$$\frac{\delta \Sigma(\mathbf{I})}{\delta \mathbf{J}(\mathbf{r}, t)} + \lambda \cdot \frac{\delta \mathbf{I}}{\delta \mathbf{J}(\mathbf{r}, t)} = 0 \quad (4)$$

Where $\lambda = (\lambda_1, \dots, \lambda_n)$ are the Lagrange multipliers. The derivatives in this equation are functional derivatives. The period indicates the n-dimensional scalar product of the two vectors. The derivation results in

$$\frac{\partial \sigma(\mathbf{J}(\mathbf{r}, t))}{\partial \mathbf{J}(\mathbf{r}, t)} = -\lambda \quad (5)$$

using that all the productions are independent. This equation says that minimum entropy production is obtained if the local values of the conjugate variables

$$\lambda(\mathbf{r}, t) \equiv -\frac{\partial \sigma(\mathbf{J}(\mathbf{r}, t))}{\partial \mathbf{J}(\mathbf{r}, t)} \quad (6)$$

are constant throughout the process equipment and constant as a function of the time. They are everywhere equal to the values obtained from the minimum entropy production and the total productions.

Equation (5) says, in other words, that there is no efficiency gain possible by redistribution of the production between sites and or times, when the derivative $\partial \sigma(\mathbf{J}(\mathbf{r}, t)) / \partial \mathbf{J}(\mathbf{r}, t)$ is constant. This argument resembles the cost-benefit analysis of economic theory, and was used in Ref. [10] when the isoforce principle was first derived for a simple system.

In the application of the Euler-Lagrange method we vary over all possible distributions $\mathbf{J}(\mathbf{r}, t)$. Not necessarily all of these distributions can be realized in practice. In particular, it is very likely that the optimum distribution itself, $\lambda(\mathbf{r}, t) = \lambda$, cannot be realized (for instance if there are temperature limitations on the catalyst in the reactor that is used). As such the variations as well as the solution are sometimes, as one says, virtual. A situation with virtual variations is not uncommon, as one knows from classical mechanics where only the extremal path is realizable. Even if the optimum distribution cannot be realized, it is important to know the target of the optimization. The target is a constant value of all the n components of $\lambda(\mathbf{r}, t)$. An important practical question that arises is how sensitive is the optimum for variations or the operating conditions around the optimum. One should assess the relative importance of the constant nature of all these n derivatives, for each particular process separately. From the experience we have regarding this matter ([10], [12]), we conclude that in many systems the optimum is not narrow. See also Section 9 regarding this sensitivity.

Further restrictions in the variation, like the use of adiabatic flow conditions, may lead to modifications of equation (5). Solutions that give the best second law efficiency under those more restrictive conditions, will be discussed in section 6.

4. Maximum Production for a Given Entropy Production

The mathematical formulation of the optimization problem above is such, that the object function and the constraint can be interchanged, without altering the solution to the problem [12]. It gives an answer also to the following question: What is the maximum production I_k that can be obtained in a process with a given entropy production? This question is relevant when there is a restriction on the energy available to the production. The Euler-Lagrange method gives, if one wants to optimize the production I_k for a given Σ :

$$\frac{\delta}{\delta J_j(\mathbf{r}, t)} (\Sigma + \lambda_k I_k) = 0 \quad (7)$$

This then results in

$$\lambda_j(\mathbf{r}, t) = \lambda_k \delta_{kj} \quad (8)$$

where δ_{kj} is the Kronecker delta. Again the solution is that we should have constant conjugate variables throughout the process and as a function of time. Variables conjugate to productions of no interest, I_j for $j \neq k$ in this case, are zero.

5. Trade-Off Analysis

The interchange of object function and constraint that takes place in the above analysis, introduces an important possibility of making trade-off's between resource input and productions. By specifying the energy one can afford to waste, the maximum production is found, or equivalently: By specifying the production, the

minimum energy to be wasted is found. The family of isoforce operating lines, that are generated by this procedure, constitute information that is required to make a sound trade-off between production and energy costs. Such considerations may add to chemical reactor design, that normally uses the maximum rate of the reaction, and no energy constraint, as the design criterion [6].

Minimum entropy production per unit of production, I_k , may also be of interest as an objective function. The corresponding Euler-Lagrange relation is

$$\frac{\delta}{\delta J_j(\mathbf{r}, t)} = (\Sigma/I_k) = 0 \quad (9)$$

This results in

$$\lambda_j(\mathbf{r}, t) = -\frac{\Sigma}{I_k} \delta_{kj} \quad (10)$$

Again conjugate variables that are constant throughout the process and as a function of time, give the optimum. Also now the conjugate variables corresponding to productions of no interest, I_k for $j \neq k$ in this case, are zero. The difference is that the conjugate variable for the production of interest is explicitly given in terms of the entropy production and the total production.

We have seen in Sections 3–5 that for a variety of relevant optimization problems, one finds that the optimum solution is obtained for distributions that have constant conjugate variables. The value of the conjugate variables depend on the particular optimization problem.

6. The Isoforce Principle for Linear Flux Force Relations

In order to know the force, for which one shall construct the isoforce operating line, one has to know the entropy production rate of the system (the process). The local entropy production rate in irreversible thermodynamics is derived from Gibbs equations, conservation laws for mass and charge, and the first law of thermodynamics [5], [7]. The general expression found for the local entropy production rate is

$$\sigma(\mathbf{r}, t) = \mathbf{X}(\mathbf{r}, t) \cdot \mathbf{J}(\mathbf{r}, t) \quad (11)$$

where $X(\mathbf{r}, t) = (X_1(\mathbf{r}, t), \dots, X_n(\mathbf{r}, t))$ are the thermodynamic forces and $X_n(\mathbf{r}, t)$ is conjugate to $J_n(\mathbf{r}, t)$. Sufficiently close to equilibrium one may always use a linear relation between the forces and the fluxes, even for chemical reactions:

$$X(\mathbf{r}, t) = \mathcal{R}(\mathbf{r}, t) \cdot \mathbf{J}(\mathbf{r}, t) \quad (12)$$

Here $\mathcal{R}(\mathbf{r}, t)$ is the $n \times n$ resistance matrix, which, following Onsager, is symmetric. Substituting the linear relations into the expression for the entropy production, we find that

$$\sigma(\mathbf{r}, t) = \mathbf{J}(\mathbf{r}, t) \cdot \mathcal{R}(\mathbf{r}, t) \cdot \mathbf{J}(\mathbf{r}, t) \quad (13)$$

The optimization criteria from the previous sections now give, using the symmetry of the resistance matrix,

$$\lambda = \lambda(\mathbf{r}, t) \equiv -\frac{\partial \sigma(\mathbf{r}, t)}{\partial \mathbf{J}(\mathbf{r}, t)} = -2\mathcal{R}(\mathbf{r}, t) \cdot \mathbf{J}(\mathbf{r}, t) = -2\mathbf{X}(\mathbf{r}, t) \quad (14)$$

The force distribution therefore satisfies

$$\mathbf{X}(\mathbf{r}, t) = -\frac{\lambda}{2} \quad (15)$$

This shows specifically how the isoforce principle applies to linear flux-force relations. The principle is discussed for nonlinear force-flux relations in Section 8.

It is remarkable that the resistance matrix does not appear in the result, 14, both for stationary and nonstationary processes. Whether the resistances are dependent on space and/or time or not, the isoforce principle is valid. We remember that Tondeur and coworkers [16], [3], used the restriction of constant coefficients in their proof for equipartition of entropy production or equipartition of forces. Only the Onsager symmetry of the resistance matrix enters in the analysis [12]. We show in Section 9 that, if the Onsager relations are not true, minimum entropy production can not be defined in a systematic context.

It is relatively easy to give solutions for the Lagrange multiplier, the optimum force, and the corresponding productions in the linear case, so we proceed to do so. In order to find the unknown λ in terms of the known productions, we define first the conductivity matrix, $\mathcal{L}(\mathbf{r}, t)$, through:

$$\mathcal{R}(\mathbf{r}, t) \cdot \mathcal{L}(\mathbf{r}, t) = \mathcal{L}(\mathbf{r}, t) \cdot \mathcal{R}(\mathbf{r}, t) = \mathbf{1} \quad (16)$$

where $\mathbf{1}$ is the unit matrix. We then have, from the isoforce principle,

$$\mathbf{J}(\mathbf{r}, t) = \mathcal{L}(\mathbf{r}, t) \cdot \mathbf{X}(\mathbf{r}, t) = -\frac{1}{2} \mathcal{L}(\mathbf{r}, t) \cdot \lambda \quad (17)$$

An expression for λ is obtained by integration:

$$\mathbf{I} = -\frac{1}{2} \left[\int_V d\mathbf{r} \int_{t_i}^{t_f} dt \mathcal{L}(\mathbf{r}, t) \right] \cdot \lambda \quad (18)$$

We introduce the integrated conductivities by

$$\mathcal{L} \equiv \int_V d\mathbf{r} \int_{t_i}^{t_f} dt \mathcal{L}(\mathbf{r}, t) \quad (19)$$

and their inverse matrix \mathbf{R} through

$$\mathbf{R} \cdot \mathcal{L} = \mathcal{L} \cdot \mathbf{R} = \mathbf{1} \quad (20)$$

The constant thermodynamic forces that give minimum entropy production for the given productions I , are then equal to:

$$\mathbf{X}(\mathbf{r}, t) = -\frac{\lambda}{2} = R \cdot \mathbf{I} \quad (21)$$

The resulting minimum entropy production is

$$\Sigma_{\min} = \int_V d\mathbf{r} \int_{t_i}^{t_f} dt \mathbf{X}(\mathbf{r}, t) \cdot \mathcal{L}(\mathbf{r}, t) \cdot \mathbf{X}(\mathbf{r}, t) = \mathbf{I} \cdot \mathcal{R} \cdot \mathbf{I} \quad (22)$$

The specified productions together with the inverse of the integrated conductivity matrix determine the minimum entropy production.

From the definition we see that the order of magnitude of the integrated conductivities, L , will be proportional to $(t_f - t_i)$ and to the volume (or transfer area). This is similarly the case for the productions. The resistivities, R , found from the inverse of the integrated conductivity matrix, consequently have an order of magnitude inversely proportional to $(t_f - t_i)$ and to the volume (or transfer area). As a result we find that the constant thermodynamic optimal force, $R \cdot \mathbf{I}$, does not depend on the size of the system or on the duration of the process. The magnitude of the minimum entropy production for given productions is proportional to the size of the system and the duration of the process, and therefore to the amount produced. The expression above shows in other words that, if one scales up in volume or in time, with the objective to scale up the production, that the entropy production increases accordingly. If one alternatively scales the system up in volume and in time, without increasing the total productions, \mathbf{I} , the minimum entropy production decreases proportionally. Also the constant thermodynamic force then decreases proportionally bringing the operating line of the system closer to equilibrium.

Suppose now that only one production I_k is of interest. We want to optimize I_k for a given entropy production Σ . Then there is only one conjugate variable unequal to zero. The entropy production is:

$$\Sigma = \frac{1}{4} \lambda_k^2 \mathcal{L}_{kk} \quad (23)$$

and the resulting thermodynamic forces, which give the optimum production I_k for the entropy production Σ , are therefore

$$X_j(\mathbf{r}, t) = -\frac{\lambda_j}{2} = \delta_{jk} \sqrt{\Sigma / \mathcal{L}_{kk}} \quad (24)$$

The productions are

$$J_j(\mathbf{r}, t) = \mathcal{L}_{jk}(\mathbf{r}, t) \sqrt{\Sigma / \mathcal{L}_{kk}} \quad (25)$$

The optimum production is found by taking $j = k$ and integrating. This gives

$$I_k = \sqrt{\Sigma \mathcal{L}_{kk}} \quad (26)$$

The specified entropy production together with the integrated diagonal matrix element, the conductivity \mathcal{L}_{kk} , determine the optimum production of the corresponding component (or energy), I_k . The order of magnitude of the various quantities in terms of system size and process duration is the same as above. If one scales up, in volume or in time, while one keeps the total entropy production the same, the optimum production increases proportionally to the square root of \mathcal{L}_{kk} . The constant thermodynamic force then decreases inversely proportional to the square root of \mathcal{L}_{kk} .

In order to get the minimum entropy production per unit produced one finds, in a similar manner, the force distribution:

$$X_j(\mathbf{r}, t) = -\frac{1}{2}\lambda_j = \frac{\Sigma_{\min}}{2I_k}\delta_{jk} \quad (27)$$

The corresponding production becomes

$$I_k = \sqrt{\frac{1}{2}\Sigma_{\min}\mathcal{L}_{kk}} \quad (28)$$

The optimization procedure does not give separate values of I_k and Σ_{\min} in this case. We have

$$\frac{\Sigma_{\min}}{I_k} = \frac{2I_k}{\mathcal{L}_{kk}} \quad (29)$$

The result is rather provoking. It says that the entropy production per unit produced, in the most optimal distribution, increases proportionally with the production. In the limit of $I_k \rightarrow 0$ the process becomes reversible, and the entropy production is zero. Equation (29) therefore says that the further one comes away from equilibrium, the higher is the price one must pay in terms of entropy production. This result explains why the trade-off analysis that was described in the previous section is important: A maximum production rate, that is frequently used as a design criterion in a chemical reactor, is according to equation (29) associated with a relatively much higher entropy production than any other lower rate. If one scales up, in volume or in time, the minimum entropy production per unit produced, remains constant. The constant thermodynamic force is also independent of the system size.

The explicit expressions given above can all be used, when the heat exchangers, chemical or electrochemical reactions involved are sufficiently close to equilibrium. In all three cases the order of magnitude of the various quantities in terms of system size and process duration is the same. The change of system scale, in volume or in time, leads to interesting conclusions for the optimization targets discussed above.

7. More Constraints: The Path of Constant Entropy Production

We saw above that the Euler-Lagrange principle gave minimum entropy production with constant conjugate variables, $\lambda(\mathbf{r}, t) = \lambda$. For linear relations between fluxes and

forces, this gave the isoforce principle, $\mathbf{X}(\mathbf{r}, t) = -\lambda/2$. In the derivation it was crucial to allow all (possibly also virtual) variations of the distribution in the production, $\mathbf{J}(\mathbf{r}, t)$, to obtain the isoforce principle.

In practice the possibility to choose all forces everywhere constant, is limited. One must choose the most important one of them, or a combination of them, constant. The relative importance of the various forces should be weighted. There is no general way to do this. It depends on the process. One could argue, however, that in many processes the most important forces correspond to the largest productions. This suggests to take the productions as weighting factors, and we then obtain:

$$\mathbf{X}(\mathbf{r}, t) \cdot \mathbf{J}(\mathbf{r}, t) = \sigma(\mathbf{r}, t) = \sigma \quad \text{is constant} \quad (30)$$

The above is not a mathematical derivation, but rather a motivation as a reasonable choice, for an optimal path that has constant entropy production. We show below that a path of constant entropy production can be derived also mathematically for a special case. The derivation, which was first given by one of us for the optimization of fuel cells [18], illustrates the importance of restrictions in the spacial and temporal variations of the productions.

Consider a stationary one dimensional process with only one production of interest, like the production of a chemical or an electric current as for a fuel cell. The materials are flowing down a tube between $x = 0$ and $x = 1$. The local entropy production rate is

$$\sigma(x) = X(x)J(x) \quad (31)$$

The linear force-flux relation is

$$X(x) = R(x; c(x))J(x) \quad (32)$$

The resistance to the reaction depends on x both directly and via the local conversion $c(x)$. The materials have a constant velocity and the total production is given in terms of the local production (that is the reaction rate per unit length) by

$$c(x) = \int_0^x J(x') dx' \quad (33)$$

We have minimum entropy production for given total production from the Euler-Lagrange equation. For this case this gives:

$$X(x) = -\frac{\lambda}{2} - \frac{1}{2} \int_x^1 \frac{\partial R(x'; c(x'))}{\partial c(x')} J^2(x') dx' \quad (34)$$

Due to the dependence of the resistivity in the point x , on the local conversion, i.e. the integral over the current between 0 and x , the optimum distribution is no longer an isoforce line. The partial derivative of the resistance with respect to the local

conversion is generally non-zero. If R depends only directly on x , however, the above condition reduces to the isoforce condition.

In the case that R depends only on x via the local conversion, $R(x; c(x)) = R(c(x))$, we can show that the above condition gives a path of constant entropy production rate. For this purpose we differentiate equation (34) with respect to x and obtain:

$$\begin{aligned} \frac{dX(x)}{dx} &= \frac{dR(c(x))}{dx} J(x) + R(c(x)) \frac{dJ(x)}{dx} \\ &= \frac{1}{2} \frac{\partial R(c(x))}{\partial c(x)} J^2(x) = \frac{1}{2} \frac{\partial R(c(x))}{\partial x} J(x) \end{aligned}$$

where we have used that $dc(x)/dx = J(x)$ in the last identity. Multiplying this equation with $J(x)$ gives

$$\frac{d}{dx} R(c(x)) J^2(x) = \frac{d\sigma(x)}{dx} = 0 \quad (35)$$

The entropy production rate is constant.

The above example shows how important the constraints are in combination with the object function, to the results of the optimization. The isoforce principle is based on a possibility to freely redistribute the productions (and thus the forces). The Euler-Lagrange principle uses virtual variations in the distribution of the productions. No real freedom is needed.

As soon as there are restrictions on this redistribution, as done by putting $R(x; c(x)) = R(c(x))$, the absolute optimum cannot be reached, and one must settle for a higher entropy production. It is higher by definition, as one has a smaller set of variables to vary. The restriction that is introduced in this case is complete, in the sense that the resistivity is uniquely determined by the production up to that point. If some freedom is reintroduced through explicit x dependence of the resistivity, the resulting entropy production will lie between that given by the isoforce line and a path of constant entropy production rate. If we would, for instance, have the freedom to choose $R(x)$ equal to the $R(c(x))$ corresponding to the path of constant entropy production rate, we could then proceed to vary $J(x)$ and therefore $c(x)$, keeping $R(x)$ fixed, and obtain the isoforce line as the one with the lowest entropy production. The path of constant entropy production is therefore not the absolute minimum, but the best achievable one given the constraint $R(x; c(x)) = R(c(x))$.

In their comparison of optimization methods, Sauar *et al.* (see Ref. [11]) found that finit-time thermodynamics and the isoforce principle gave results for distillation columns that both were very close to the numerically found minimum entropy production. At first glance this may seem to be a peculiar result, given that one method predicts a path of constant entropy production rate and the other method an isoforce path. From the above analysis we can find an explanation. The distillation column that was chosen, had a constraint on the trays of the column: The liquid and vapor leaving the trays were always considered to be in equilibrium. This is a

restriction, beyond that required to use the isoforce principle. The constraint is of the kind, described by $R(c)$ above. It does not permit the explicit variation of R with time and/or space. The extra constraint gives an optimal path with constant local entropy production rate. Without this constraint, the isoforce principle would probably predict a path with lower entropy production. The only significant transport coefficient used in the isoforce optimization, varied largely only near the ends of the column. The differences between the results of the two methods were correspondingly only significant near the ends of the column, and around the feed-tray.

As we discussed above, one may alternatively use weighting factors, to motivate that a constant entropy production will give a practical optimization criterion.

8. The Isoforce Principle for Nonlinear Force-Flux Relations

In order to investigate the validity of the isoforce principle for nonlinear force-flux relations, it is most convenient to write them in the following form

$$\mathbf{J}(\mathbf{r}, t) = \mathcal{L}(\mathbf{r}, t; \mathbf{X}(\mathbf{r}, t)) \cdot \mathbf{X}(\mathbf{r}, t) \quad (36)$$

The conductance matrix, which now depends on the thermodynamic forces, is symmetric. The local entropy production at time t is given by

$$\sigma(\mathbf{r}, t) = \mathbf{X}(\mathbf{r}, t) \cdot \mathcal{L}(\mathbf{r}, t; \mathbf{X}(\mathbf{r}, t)) \cdot \mathbf{X}(\mathbf{r}, t) \quad (37)$$

The Euler-Lagrange principle, giving the minimum total entropy production for given total productions, now gives

$$\frac{\partial[\mathbf{X}(\mathbf{r}, t) \cdot \mathcal{L}(\mathbf{r}, t; \mathbf{X}(\mathbf{r}, t)) \cdot \mathbf{X}(\mathbf{r}, t) + \lambda \cdot \mathcal{L}(\mathbf{r}, t; \mathbf{X}(\mathbf{r}, t)) \cdot \mathbf{X}(\mathbf{r}, t)]}{\partial \mathbf{X}(\mathbf{r}, t)} = 0 \quad (38)$$

In view of the fact that $\mathbf{X}(\mathbf{r}, t)$ is a unique function of $\mathbf{J}(\mathbf{r}, t)$ in each point \mathbf{r}, t and vice versa, one may use variations with respect to $\mathbf{X}(\mathbf{r}, t)$. Upon differentiation and application of the resistivity matrix one obtains

$$X_i(\mathbf{r}, t) = -\frac{\lambda_i}{2} - R_{ij}(\mathbf{r}, t; \mathbf{X}(\mathbf{r}, t)) \left[\frac{\partial}{\partial X_j(\mathbf{r}, t)} L_{kl}(\mathbf{r}, t; \mathbf{X}(\mathbf{r}, t)) \right] X_l(\mathbf{r}, t) X_k(\mathbf{r}, t) \quad (39)$$

Here the differentiation works only on the conductivity matrix. This may be written in a more compact vector notation as

$$\mathbf{X}(\mathbf{r}, t) = -\frac{\lambda}{2} - \mathcal{R}(\mathbf{r}, t; \mathbf{X}(\mathbf{r}, t)) \cdot \left[\frac{\partial}{\partial \mathbf{X}(\mathbf{r}, t)} \mathcal{L}(\mathbf{r}, t; \mathbf{X}(\mathbf{r}, t)) \right] : \mathbf{X}(\mathbf{r}, t) \mathbf{X}(\mathbf{r}, t) \quad (40)$$

where: indicates a double contraction, the definition of which becomes clear by comparing the above two equations.

In order to derive the isoforce condition, we now assume a multiplicative dependence of the resistivity matrix, on \mathbf{r}, t on the one hand and on $\mathbf{X}(\mathbf{r}, t)$ on the other hand, of the following form:

$$\mathcal{R}(\mathbf{r}, t; \mathbf{X}(\mathbf{r}, t)) = A(\mathbf{r}, t) \mathcal{R}_1(\mathbf{X}(\mathbf{r}, t)) \quad (41)$$

The conductivity matrix, which is defined by

$$\mathcal{R}_1(\mathbf{X}(\mathbf{r}, t)) \cdot \mathcal{L}_1(\mathbf{X}(\mathbf{r}, t)) = \mathcal{L}_1(\mathbf{X}(\mathbf{r}, t)) \cdot \mathcal{R}_1(\mathbf{X}(\mathbf{r}, t)) = \mathbf{1} \quad (42)$$

is as a consequence, also multiplicative

$$\mathcal{L}(\mathbf{r}, t; \mathbf{X}(\mathbf{r}, t)) = A^{-1}(\mathbf{r}, t) \mathcal{L}_1(\mathbf{X}(\mathbf{r}, t)) \quad (43)$$

Substitution in the above condition for the force distribution gives

$$\mathbf{X}(\mathbf{r}, t) = -\frac{\lambda}{2} - \mathcal{R}_1(\mathbf{X}(\mathbf{r}, t)) \cdot \left[\frac{\partial}{\partial \mathbf{X}(\mathbf{r}, t)} \mathcal{L}_1(\mathbf{X}(\mathbf{r}, t)) \right] : \mathbf{X}(\mathbf{r}, t) \mathbf{X}(\mathbf{r}, t) \quad (44)$$

The dependence on \mathbf{r}, t in this expression for $\mathbf{X}(\mathbf{r}, t)$ is no longer explicit. The only dependence is via $\mathbf{X}(\mathbf{r}, t)$. This implies that the resulting thermodynamic force distribution is independent of \mathbf{r}, t . We may therefore conclude that

$$\mathbf{X}(\mathbf{r}, t) \text{ is constant} \quad (45)$$

We have thus found that for all processes where the resistance matrix can be written in the multiplicative form, given in equation (41) above, the isoforce principle is valid. Saunar showed that this is in good approximation possible even for non-linear chemical reactions like the ammonium synthesis or the disproportionation of N_2O_4 , [11].

9. The Use of Legendre Transforms in Optimization

The role of the minimum total entropy production in irreversible thermodynamic is analogous to the role of the entropy in equilibrium thermodynamics, [7]. If one varies the productions, one changes the total entropy production in the following way:

$$\begin{aligned} d\Sigma(\mathbf{I}) &= \frac{\delta\Sigma(\mathbf{I})}{\delta\mathbf{J}(\mathbf{r}, t)} \cdot d\mathbf{J}(\mathbf{r}, t) = \int_V d\mathbf{r} \int_{t_i}^{t_f} dt \frac{\partial\sigma(\mathbf{J}(\mathbf{r}, t))}{\partial\mathbf{J}(\mathbf{r}, t)} \cdot d\mathbf{J}(\mathbf{r}, t) \\ &= - \int_V d\mathbf{r} \int_{t_i}^{t_f} dt \lambda(\mathbf{r}, t) \cdot d\mathbf{J}(\mathbf{r}, t) \end{aligned} \quad (46)$$

where the prefix d indicates a small change of the corresponding quantity. The minimum total entropy production is obtained when the conjugate variables are

constant, $\lambda(\mathbf{r}, t) = \lambda$. Taking the constant conjugate variables outside the integral, it then follows for the minimum total entropy production that

$$d\Sigma(\mathbf{I}) = \frac{\partial \Sigma(\mathbf{I})}{\partial \mathbf{I}} \cdot d\mathbf{I} = -\lambda \cdot d\mathbf{I} \quad (47)$$

The constant conjugate variables $\lambda = (\lambda_1, \dots, \lambda_n)$ are the Lagrange multipliers in the minimization. The minimum total entropy production is a unique function of the productions. It does not depend on the “history” of these productions. Its change in the equation above, in terms of the changes of the productions, is a total differential.

Legendre transforms can be used in irreversible thermodynamics in a similar fashion as in equilibrium thermodynamics. With n independent variables, there are $(2^n - 1)$ possibilities for such transforms. We shall only use:

$$\Lambda(\lambda) \equiv \Sigma(\mathbf{I}) + \lambda \cdot \mathbf{I} \quad (48)$$

and

$$\Lambda_k(I_1, \dots, I_{k-1}, \lambda_k, I_{k+1}, \dots, I_n) \equiv \Sigma(\mathbf{I}) + \lambda_k I_k \quad (49)$$

In the usual manner one finds that these transforms satisfy

$$d\Lambda(\lambda) = \mathbf{I} \cdot d\lambda \quad (50)$$

and

$$d\Lambda_k(I_1, \dots, I_{k-1}, \lambda_k, I_{k+1}, \dots, I_n) = I_k d\lambda_k - \sum_{j \neq k} \lambda_j dI_j \quad (51)$$

Minimizing the Legendre transform Λ , is equivalent to finding the minimum entropy production for given productions. The optimum production for a given entropy production is similarly given by the minimum of Λ_k .

Using equation (47), one may write down the following Maxwell relations

$$\frac{\partial \lambda_j}{\partial I_k} = \frac{\partial \lambda_k}{\partial I_j} \quad (52)$$

As irreversible thermodynamics is based on the validity of local equilibrium, one may also use this equation locally, which gives

$$\frac{\partial \lambda_j(\mathbf{r}, t)}{\partial J_k(\mathbf{r}, t)} = \frac{\partial \lambda_k(\mathbf{r}, t)}{\partial J_j(\mathbf{r}, t)} \quad (53)$$

When one substitutes the conjugate variables in the linear case, see Section 6, this equation gives

$$\mathcal{R}_{jk}(\mathbf{r}, t) = \mathcal{R}_{kj}(\mathbf{r}, t) \quad (54)$$

These are the Onsager relations, which are fundamental for the consistent formulation of irreversible thermodynamics [5], [7]. Their validity is a consequence of microscopic time reversal invariance. As we have just seen, that are also required for the validity of the isoforce principle. In this section, we find them as a consequence of our assumption that the minimum total entropy production, is a unique function of the given total productions. Therefore, if the Onsager relations were not true, such a minimum total entropy production can not be defined in a systematic context. In the general case, that also includes nonlinear force-flux relations, the Maxwell relations assure that the minimum total entropy production is a unique function of the total productions. There is no dependence on the thermodynamic path. The Maxwell (Onsager) relations must be obeyed to arrive at the conclusion that isoforce operation gives the optimal case.

One may also use the Lagrange transforms to analyze the sensitivity of the optimum for changes of the operating conditions away from the optimum. If one considers, for instance, the case that one wants to optimize the entropy production for given total productions one should use $\Lambda(\lambda)$. This function has a minimum in the optimum. For small changes of $\lambda(\mathbf{r}, t)$ around the constant optimal value λ_{opt} , i.e.

$$\Delta\lambda(\mathbf{r}, t) \equiv \lambda(\mathbf{r}, t) - \lambda_{opt} \quad (55)$$

one therefore has

$$\Delta\Lambda = \int_V d\mathbf{r} \int_V d\mathbf{r}' \int_{t_i}^{t_f} dt \int_{t_i}^{t_f} dt' \Delta\lambda(\mathbf{r}, t) \cdot \frac{\delta^2\Lambda}{\delta\lambda(\mathbf{r}, t)\delta\lambda(\mathbf{r}', t')} \cdot \Delta\lambda(\mathbf{r}', t') \quad (56)$$

It is clear that the magnitude of the second derivatives determines the sensitivity of the optimum. If they are small the optimum is broad, and if they are large the optimum is going to be narrow. For a given system one should construct this matrix for an in-depth analysis. Here we only indicate how this problem should be analyzed. If one wants to optimize the production I_k , one should use the Lagrange transform Λ_k .

10. Discussion and Conclusion

We have given a general mathematical basis for the optimization of processes by applying the Euler-Lagrange variational method and irreversible thermodynamics. We start with the simple assumption that for given total productions a unique minimum total entropy production exists. The minimum does not depend on the thermodynamic “history” of the production unit. It is shown that this assumption is not correct if the Onsager symmetry relations are not true. It is good to realize that the validity of this very fundamental relation, which follows from microscopic time reversal invariance, is crucial also for the description of a very practical problem, like optimization.

A general optimization criterion was formulated: The derivative of the local entropy production rate at a given time with respect to the local productions at the same time must be constant in order to give the minimum total entropy production. This criterion was given by Kjelstrup Ratkje *et al.* [10], using the analogy with the cost-benefit analysis of economic theory, in their first optimization of a distillation column.

For a general class of systems, with both linear and nonlinear relations between thermodynamic forces and productions, we have shown that this condition leads to an isoforce operating path. This is the isoforce principle, as presented by Sauar *et al.* [12]. The isoforce principle states that the thermodynamic driving forces should be constant in space and time to give a minimum total entropy production in a process for a specified total production. The new information that is gained from the isoforce principle relates to the distribution of the thermodynamic driving forces in space and time.

The fundamental assumption in the derivation of the isoforce principle is that it is possible to redistribute productions in the process. The isoforce principle therefore characterizes the most ideal situation. An effectuation of the isoforce principle makes it necessary to keep all independent forces constant. In real systems, practical and other restrictions may make the optimum goal unattainable. One must accommodate. With confined paths, one can also have a path of constant entropy production as the optimal one. This path, is however more dissipative than the optimum path, a path with less restrictions. In general one may therefore conclude that constraints will have a decisive role in the validity of a criterion, that describes the achievable optimum. The absolute optimum is the one that follows in analogy with the cost-benefit analysis in economic theory, and which in many cases, discussed in this paper, reduces to the isoforce principle.

In the practical application of the optimization criterion to a system unit, one should first construct the path for the optimization desired. The next step is to see how the boundary conditions of the unit may be changed to approach the optimum path. With boundary conditions we mean, for instance, the temperature of cooling water, feed temperature, location of feeds, etc.. This then optimizes one process unit. An important question that comes up is whether the required changes are going to be excessive or easy to accomplish. Our experience in some practical cases, like distillation and chemical reactors, is that considerable improvements are reasonably easy to accomplish by, for instance, adding a heat exchanger.

In system optimizations, one must deal with several processes combined. The number of constraints in a final set-up may then be so many that it is difficult, if not impossible, to apply the isoforce principle to all parts of the system at the same time. The value of the isoforce principle will be larger in the initial design phase. From knowledge of how the system units produce entropy, one will be able to choose a good combination in the outset.

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