Optimal finite-time endoreversible processes

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We treat the general problem of transferring a system from a given initial state to a given final state in a given finite time such that the produced entropy or the loss of availability is minimized. We give exact equations for the optimal process for the general case of a system with several state variables. For linear processes, e.g., in the limit of slow processes or if the Onsager coefficients do not depend on the fluxes, we find a constant entropy production rate or constant loss rate of availability. An alternative kinetic process length is introduced. The entropy production rate is the square of the speed based on this length and clock time. This length adequately treats variations of the system time scale matrix along the path. For the nonlinear case, the entropy production rate or loss rate of availability is generally not constant for an optimal process.

I. INTRODUCTION

The problem of transferring a system from a given initial state to a given final state while producing a minimum of entropy or a minimum loss of availability leads to reversible processes. These processes are all equivalent to each other and have zero value of both of the entropy or loss of availability, but need infinitely much process time.

In many applications it is natural to introduce a constraint for the available process time. This approach is known as finite-time thermodynamics and discussed, e.g., in [1,2]. In this context, endoreversible [3] processes are generally considered, where the system internally is reversible and the production of entropy is caused by the transport to the system. The restriction on endoreversible processes excludes, e.g., distributed systems, nonequilibrium systems [4], and systems where different species are not in chemical equilibrium among each other.

However, in chemically interacting systems as discussed by Mironova *et al.* [5] some species may be regarded as driving the concentration and reaction rates of the others. If the concentration of sufficiently many of these species may be externally controlled, then such systems may be in principle treated in the framework outlined in this work. For instance, the discussion of near-equilibrium processes, called slow processes in this work, can easily be generalized to the case where the kinetic coefficients depend on the concentrations of the noncontrollable species. These systems thus may be treated as endoreversible systems, since the controllable species may always be chosen such that the other species are in equilibrium. The boundary condition of given average chemical rates [5] in effect specifies the final concentra-

tions. This conforms with the boundary condition of a given final state as used in the present work.

It is widely stated that for the optimal process the entropy production rate, or the loss rate of availability, is constant [1,2]. However, this result is obtained under different simplifying assumptions, such as the following.

(A1) The kinetic coefficients relating driving forces and fluxes, the Onsager coefficients, are constant [1] or do not depend on the fluxes, but only on the system state.

(A2) The process is slow, i.e., the available process time is large compared to the time scales inherent to the system so that the differences in the intensive variables between the external source and the system are small. This is the regime of linearized thermodynamics of irreversible processes. This assumption implies a situation essentially equivalent to assumption (A1) because the intensive variables of the external source are close to the system's internal variables, and thus the dependency of the kinetic coefficients on the state of the external source can be ignored.

(A3) The difference between the initial and the final state is small. This implies assumption (A2) since all kinetic coefficients, the heat capacity, etc., are effectively assumed to be constant during the process. This assumption is not considered at all in the present paper.

We treat the general problem and require none of these assumptions. From our results we show that any one of these assumptions is sufficient for the entropy production rate or loss rate of availability to be constant along an optimal process trajectory. Processes satisfying one of these assumptions are called linear processes in the sequel. If none of these assumptions is fulfilled, the corresponding rate is generally not constant along the optimal process.

II. GENERAL PROBLEM

We consider a system with extensive parameters X which are, e.g., the internal energy U, the volume V, and the particle numbers N_α each referring to a different

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species α. The system is described by an equation of state $S = S(X)$ in the entropy representation. The intensive parameters are the conjugate of the extensive variables X_i,

$$Y_i = \frac{\partial S(X)}{\partial X_i}, \tag{1}$$

such as the inverse temperature $1/T$, the pressure variable p/T, and the chemical variables $-\mu_\alpha/T$ [6], where μ_α is the chemical potential for species α. It is assumed that the intensive variables are constant all over the system. The system is controlled by a source which is defined by intensive parameters Y_i^e. It is assumed that the intensive variables of the source can be controlled at will.

The potential differences $Z_i = Y_i - Y_i^e$ cause fluxes of the associated extensive variables X_i. The entropy production rate due to the transfer of heat, volume, and mass is

$$\frac{d\sigma}{dt} = Z_i \frac{dX_i}{dt}. \tag{2}$$

We use Einstein's convention of summing over all indices appearing twice in a product. The functional relation between the fluxes $\dot{X}_i = dX_i/dt$ and the driving forces Z_i is written as

$$Z_i = Z_i(X, \dot{X}). \tag{3}$$

It is the essence of this contribution that we make no further assumption about the functions $Z_i(X, \dot{X})$ other than it is differentiable once. The objective is now to find the optimal process such that the entropy production σ in a given interval $[t^i, t^f]$,

$$\sigma = \int_{t^i}^{t^f} \frac{d\sigma}{dt} dt, \tag{4}$$

assumes a minimum, with the initial and final states fixed, $X(t^i) = X^i$ and $X(t^f) = X^f$. We refer to such a function $X(t)$ as trajectory. In contrast, a path is the ordered set of system states without referring explicitly to time.

All conclusions remain valid if the objective is, instead of minimization of produced entropy, the minimization of dissipated availability [2]. Then one starts with an equation of state $U = U(X)$, with S instead of U as one of the extensive variables X, and takes $Y_i = \partial U/\partial X_i$, e.g., T from S, $-p$ from V, and μ_α from N_α. However, the following derivation is written in terms of minimum entropy production.

In order to find the optimal process trajectory $X(t)$ we could use Pontrjagin's general maximum principle [7]. However, the problem is greatly simplified by the fact that $\dot{X}$ appears in the expression for $\dot{\sigma}$ and at the same time determines the evolution of the system. We consider a variation $X \to X + \delta X$, $\dot{X} \to \dot{X} + \delta \dot{X}$. The variation of the entropy production σ is

$$\delta\sigma = \int_{t^i}^{t^f} (\delta Z_i \dot{X}_i + Z_i \delta \dot{X}_i)\, dt \tag{5}$$

$$= \int_{t^i}^{t^f} \left[\dot{X}_i \left(\frac{\partial Z_i}{\partial X_j} \delta X_j + \frac{\partial Z_i}{\partial \dot{X}_j} \delta \dot{X}_j \right) + Z_i \delta \dot{X}_i \right] dt \tag{6}$$

$$= \int_{t^i}^{t^f} \delta X_j \left[\dot{X}_i \frac{\partial Z_i}{\partial X_j} - \frac{d}{dt} \left(\dot{X}_i \frac{\partial Z_i}{\partial \dot{X}_j} + Z_j \right) \right] dt. \tag{7}$$

The last term is obtained by transforming the terms containing $\delta \dot{X}_i$ with partial integration, using the fact that the value of δX_i must be zero at t^i and t^f. In order to have zero variation of the entropy, the term in square brackets must be zero for each time t,

$$0 = \dot{X}_i \frac{\partial Z_i}{\partial X_j} - \frac{d}{dt} \left(\dot{X}_i \frac{\partial Z_i}{\partial \dot{X}_j} + Z_j \right). \tag{8}$$

These second order differential equations, in conjunction with the fixed values of the initial and the final state, determine the optimal trajectory. These equations can be written as

$$0 = -\dot{X}_i \frac{\partial Z_i}{\partial X_j} + \ddot{X}_i \frac{\partial Z_i}{\partial \dot{X}_j} + \dot{X}_i \frac{d}{dt} \left(\frac{\partial Z_i}{\partial \dot{X}_j} \right) + \frac{\partial Z_j}{\partial X_i} \dot{X}_i + \frac{\partial Z_j}{\partial \dot{X}_i} \ddot{X}_i \tag{9}$$

$$= -\dot{X}_i \left(\frac{\partial Z_i}{\partial X_j} - \frac{\partial Z_j}{\partial X_i} \right) + \ddot{X}_i \left(\frac{\partial Z_i}{\partial \dot{X}_j} + \frac{\partial Z_j}{\partial \dot{X}_i} \right) + \dot{X}_i \frac{d}{dt} \left(\frac{\partial Z_i}{\partial \dot{X}_j} \right). \tag{10}$$

In order to analyze the entropy production rate, we multiply with $\dot{X}_j$. For the case of several state variables, this reduces the full information of the set of differential equations to a single equation. The first antisymmetric term cancels and leaves a total differential:

$$0 = \dot{X}_j \ddot{X}_i \left(\frac{\partial Z_i}{\partial \dot{X}_j} + \frac{\partial Z_j}{\partial \dot{X}_i} \right) + \dot{X}_j \dot{X}_i \frac{d}{dt} \left(\frac{\partial Z_i}{\partial \dot{X}_j} \right) = \frac{d}{dt} \left(\dot{X}_i \frac{\partial Z_i}{\partial \dot{X}_j} \dot{X}_j \right). \tag{11}$$

Thus for the optimal process a necessary condition is

$$\dot{X}_i \frac{\partial Z_i}{\partial \dot{X}_j} \dot{X}_j = \text{const}. \tag{12}$$

If the function Z is expressed by a resistance matrix R_{ij},

$$Z_i(X, \dot{X}) = R_{ij}(X, \dot{X}) \dot{X}_j, \tag{13}$$

then Eq. (12) reads

$$\frac{d\sigma}{dt} + \dot{X}_i \frac{\partial R_{ij}}{\partial \dot{X}_k} \dot{X}_k \dot{X}_j = \text{const}. \tag{14}$$

This is the generalization of the known result [1,2], derived with one of the assumptions (A1)–(A3), that the

rate of entropy production rate or loss of availability is constant along the optimal trajectory. The theory outlined here is exact for small as well as for large fluxes, and with no assumption on the form of $Z(X, \dot{X})$ except that it is differentiable once.

A. Constant entropy production rate

For the case of $\dot{X}_k \partial R_{ij}/\partial \dot{X}_k \ll R_{ij}$, the second term in Eq. (14) is negligible, and the entropy production rate is constant for the optimal process. This occurs for linear processes, that is, if the fluxes are small or if R_{ij} does not depend on $\dot{X}$, but is a function of X only. The case of small fluxes, that is, the case of a slow process, may also be treated as if $R_{ij}(X, \dot{X})$ is a function of X only since the other argument, $\dot{X}$, is approximately zero, $R_{ij} = R_{ij}(X, 0)$. In this case the R_{ij} are the inverse of the matrix of Onsager coefficients L_{ij}.

Then constant entropy production rate follows from the Cauchy-Schwarz inequality [2]:

$$\sigma = \int_{t^i}^{t^f} \dot{X}_i R_{ij} \dot{X}_j \, dt \geq \frac{\mathcal{K}_S^2}{t^f - t^i}. \tag{15}$$

Here the kinetic process length $\mathcal{K}_S$ is defined as

$$\mathcal{K}_S = \int_{t^i}^{t^f} \left| \dot{X}_i R_{ij} \dot{X}_j \right|^{\frac{1}{2}} \, dt. \tag{16}$$

It is based on the metric

$$(d\mathcal{K}_S)^2 = R_{ij} \, dX_i \, dX_j. \tag{17}$$

The entropy production rate is equal to the square of the speed measured by this metric,

$$\frac{d\sigma}{dt} = \left(\frac{d\mathcal{K}_S}{dt} \right)^2. \tag{18}$$

The value of $\mathcal{K}_S$ does not depend on the parametrization t, but it depends on the path of integration. With the minimum kinetic process length, taken over all possible paths from the initial to the final state, the right-hand side of Eq. (15) is a lower bound on σ; it is taken if the integrand is constant, i.e., if the entropy production rate is constant. The global optimization problem can be split into (a) finding the path with the shortest length $\mathcal{K}_S$ and (b) optimizing the trajectory along this path, i.e., traveling this path with constant speed based on the metric $\mathcal{K}_S$. Assume that an optimal solution is known. The optimal path for taking the same system between the same initial and final points, but with different total available time, is the same. The trajectory can simply be deduced by scaling the time with a constant factor. For the general nonlinear case, however, a different total available time might lead to a different path which has to be found with Eq. (8).

The thermodynamic length $\mathcal{L}$ defined in [2] does not contain the kinetic functions R. Therefore the thermodynamic length in general bears no relationship to the entropy production or loss of availability if a certain trajectory is traversed. For calculating the loss of availability from $\mathcal{L}$ the authors have to introduce an average system time scale, which then becomes trajectory dependent. The kinetic process lengths $\mathcal{K}_S$ and $\mathcal{K}_U$ as defined in Eq. (16) incorporate the kinetic functions R. The functions R may be arbitrary functions of the system state X consistent with thermodynamics. Formally the same expression for an analog kinetic process length $\mathcal{K}_U$ is obtained if the objective is minimum loss of availability.

B. Single state variable

In the case of a single free state variable Eq. (12) reads

$$\frac{d\sigma}{dt} = Z\dot{X} \propto \frac{Z}{\dot{X}} \left(\frac{\partial Z}{\partial \dot{X}} \right)^{-1} = \left(\frac{\partial \ln(Z)}{\partial \ln(\dot{X})} \right)^{-1}$$

$$= \left(1 + \frac{\partial \ln(R)}{\partial \ln(\dot{X})} \right)^{-1}. \tag{19}$$

Instead of writing the driving force Z as a function of the flux $\dot{X}$, $Z(X, \dot{X})$, we can describe the flux as a function of Z, $\dot{X}(X, Z) = L(X, Z)Z$. Then Eq. (19) is

$$\frac{d\sigma}{dt} = Z\dot{X} \propto \frac{Z}{\dot{X}} \frac{\partial \dot{X}}{\partial Z} = \frac{\partial \ln(\dot{X})}{\partial \ln(Z)} = 1 + \frac{\partial \ln(L)}{\partial \ln(Z)}. \tag{20}$$

In the case of a single state variable, there is only a single path $[X^i, X^f]$ connecting the initial with the final state. Thus for linear processes, the kinetic process length can be directly computed with Eq. (16), and the trajectory can be calculated from $\dot{\sigma} = \text{const}$.

III. HEAT CONDUCTION

In the following we analyze the special case of plain heat conduction, where the temperature is the only state variable considered. We substitute $Y = 1/T$, $Z = Y - 1/T^e$, and $\dot{X} = \lambda(T, T^e)(T^e - T)$ in Eq. (20):

$$\frac{d\sigma}{dt} \propto \frac{T^e}{T} \left[1 + (T^e - T) \frac{\partial \ln \lambda}{\partial T^e} \right]. \tag{21}$$

The inverse temperature $1/T$ plays the role of the intensive variable. Therefore L_{11} refers to the inverse temperatures, $\dot{X} = L_{11}(1/T - 1/T^e)$, and the thermal conductance λ, with $\dot{X} = \lambda(T^e - T)$, is given by

$$L_{11} = TT^e \lambda. \tag{22}$$

Hence even if λ does not depend on T^e, L_{11} is a function of T and T^e, i.e., of X and $\dot{X}$, and the entropy production rate for the optimal process is generally not constant.

A. The slow case

In the case of a slow process, where the driving forces $T^e - T$ are small, the optimal entropy production rate per time t is constant, for any form of the specific heat $C_V(T) = dU/dT$ and of $\lambda(T, T^e)$. The optimal process

is characterized by

$$\frac{|T^e - T|}{T^e} \propto \frac{1}{\sqrt{\lambda(T,T)}}, \qquad (23)$$

and the minimum entropy production is

$$\sigma = \frac{\mathcal{K}_S^2}{t^f - t^i}, \quad \text{where} \quad \mathcal{K}_S = \int_{T^i}^{T^f} \frac{C_V(T)}{\sqrt{\lambda(T,T)}} \frac{dT}{T}. \qquad (24)$$

It is remarkable that the specific heat does not appear in Eq. (21). From this it can be seen that $d\sigma/d\xi$, where $d\xi = \lambda/C_V \, dt$ is the normalized process time [8], is generally not constant for variable time scale C_V/λ. The thermodynamic length, on the other hand, is

$$\mathcal{L}_S = \int_{T^i}^{T^f} \frac{\sqrt{C_V(T)} \, dT}{T}. \qquad (25)$$

For constant time scale, $\mathcal{L}_S$ and $\mathcal{K}_S$ are proportional to each other, $\mathcal{K}_S = \sqrt{C_V/\lambda} \, \mathcal{L}_S$.

B. The case $\partial\lambda/\partial T^e = 0$

We discuss the case that the heat conduction does not depend on the external temperature, $\partial_{T^e}\lambda = 0$, i.e., λ is a function of T only, $\lambda(T)$. This is the most general case considered in [8].

From Eq. (21) we obtain

$$\text{const} = \frac{d\sigma}{dt}\frac{T}{T_e} = \lambda(T)\left(1 - \frac{T}{T^e}\right)^2. \qquad (26)$$

Thus for an optimal process the temperature ratio T^e/T should be a function of λ, and Eq. (23) applies. In the special case of constant heat conductance λ the entropy production rate is constant [1] although none of the assumptions (A1)–(A3) are satisfied.

C. Blackbody radiative transfer

As an example for a process where the conductance strongly depends on the source temperature T^e, we discuss radiative heat transfer between two black surfaces,

$$\dot{X} = \alpha[(T^e)^4 - T^4]. \qquad (27)$$

We assume that α is constant. From Eq. (12) follows, with a dimensionless constant b,

$$\dot{X}^2 \frac{\partial Z}{\partial X} = \left\{ \alpha[(T^e)^4 - T^4] \right\}^2 \frac{1}{4\alpha(T^e)^5} = \text{const} = \frac{\alpha}{4} b^2 T_0^3, \qquad (28)$$
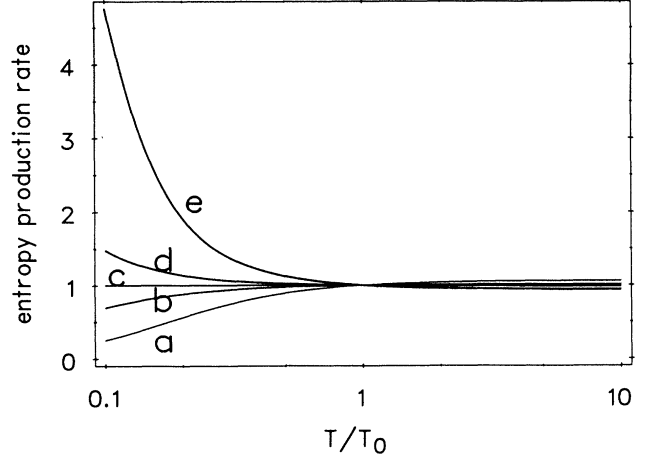

FIG. 1. Entropy production rate for an optimized process with heat transfer via blackbody radiation as a function of system temperature, for different values of the speed parameter b equal to -0.1 (a), -0.02 (b), 0 (c), 0.02 (d), and 0.1 (e). Each sector of each curve belongs to a certain process. For each curve the entropy rate is normalized to 1 for $T = T_0$, the temperature is normalized to a reference temperature T_0.

whereby T_0 is an arbitrary reference temperature. Thus for the optimal process holds

$$(T^e)^4 - T^4 = bT_0^{\frac{3}{2}}(T^e)^{\frac{5}{2}}. \qquad (29)$$

The constant speed parameter b is a decreasing function of the available process time; $b > 0$ for heating and $b < 0$ for cooling. In the limit of slow processes it is given by

$$\frac{\alpha}{4} b^2 T_0^3 = \frac{\mathcal{K}_S^2}{(t^f - t^i)^2}, \qquad (30)$$

where $\mathcal{K}_S$ is calculated from Eq. (24) with the limit value of the radiative heat conductance for small temperature differences, $\lambda = 4\alpha T^3$. Figure 1 shows the entropy production rate for the optimized process as a function of the system temperature T, for different values of b equal to -0.1, -0.02, 0, 0.02, and 0.1. For each curve the entropy rate is normalized to 1 for $T = T_0$. Note that, in accordance with the results in [9], for large b the entropy production rate is not constant, especially at low temperatures. In this case the heat conductance is low but strongly increases with T^e, thus justifying an increased entropy production rate.

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