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Generalized exergy for finite-time heat transfer processes

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Abstract— **The problem of the maximal work that can be extracted from a system consisting of one infinite heat reservoir and one subsystem with a generalized heat transfer law [$q \propto (\Delta(T^n))^m$], which includes the generalized convective heat transfer law [$q \propto (\Delta T)^m$] and the generalized radiative heat transfer law [$q \propto \Delta(T^n)$], is investigated in this paper. Finite-time exergy is derived for the fixed process duration by applying optimal control theory. Effects of heat transfer laws on the finite-time exergy and the corresponding optimal thermodynamic process are analyzed. The optimal thermodynamic process for the finite-time exergy with the heat transfer laws that the power exponents m and n satisfy the inequality $n(m+1)/(mn-1) < 0$ is that the temperature of the subsystem switches between two optimal values during the heat transfer process, while that with other heat transfer laws is that the temperature of the subsystem is a constant， and the temperature difference between the reservoir and the subsystem is also a constant during the heat transfer process. Numerical examples for the cases with some special heat transfer laws are given, and the results are also compared with each other. The finite-time exergy tends to the classical thermodynamic exergy and the average power tends to zero when the duration tends to infinite large. Some modifications to the results of recent literatures are also performed. The finite-time exergy is a more realistic, stronger limit compared to the classical thermodynamic exergy.**

Keywords: finite time thermodynamics; finite-time exergy; heat transfer law; optimal control

I. INTRODUCTION

The exergy analysis method has two advantages over the energy analysis method for design and performance analysis of energy-related systems. First, it provides a more accurate measurement of the actual inefficiencies in the system and the true location of these inefficiencies. It accomplishes this for any system, whether simple or complex. Second, the exergy analysis method provides a true measurement of the system efficiency for complex combined cycles or open systems, while the energy analysis method gives an erroneous efficiency value [1-2]. The conventional exergy is the classical thermodynamic exergy and the solution methodology of classical thermodynamics problems assumes reversible thermodynamic processes, i.e., processes in which the system preserves internal equilibrium, the total entropy of the system and the environment does not increase, the differences between the values of intensive variables (temperatures, pressures, chemical potentials et al) of the system and those of the environment is infinitely small, and the process duration is infinitely long. The classical reversible bounds are too high for real processes and require further refinement.

Since the mid 1970s, finite time thermodynamics has made great progress in the fields of physics and engineering [9-12]. Ondrechen *et al* [13] investigated the problem of maximizing work output from a finite thermal capacity heat reservoir by infinite sequential Carnot cycles. Yan [14] derived the efficiency of a sequence of Carnot cycles with a finite thermal capacity heat reservoir at maximum power output. Andresen *et al* [15] first put forward the concept of finite-time exergy. With the help of conventional exergy analysis approach, Mironova *et al* [16] introduced the criterion of thermodynamic ideality to evaluate performances of various thermodynamic systems. Sieniutycz and von Sparkovsky [17] obtained the optimal reservoir temperature profiles of multistage endoreversible continuous CA heat engine [3] systems operating between a finite thermal capacity high-temperature reservoir and an infinite thermal capacity low-temperature reservoir for maximum work output (also called finite time exergy in Ref. [17]), in which the heat transfer between the working fluid and the reservoirs obeys Newton's heat transfer law [$q \propto \Delta(T)$]. Sieniutycz [18] further obtained those of multistage endoreversible discrete heat engine systems for maximum work output. Tsirlin [6, 10], Berry *et al* [7] and Mironova *et al* [9] investigated the problem of the maximal work that can be extracted from a system consisting of one infinite heat reservoir and one subsystem with the generalized radiative heat transfer law [$q \propto \Delta(T^n)$], and showed that the optimal thermodynamic process for the finite-time exergy with the heat transfer laws that the power exponent n satisfies the condition $0 < n < 1$ is that the temperature of the subsystem switches between two optimal values during the heat transfer process, while that with other heat transfer laws is that the temperature of the subsystem is a constant, and the temperature difference between the reservoir and the subsystem is also a constant during the heat transfer process. Tsirlin and Kazakov [19] investigated the maximum work problems of several subsystems with an infinite heat reservoir and one subsystem with an infinite mass reservoir. Sieniutycz [20, 21] obtained a finite-rate generalization of the maximum-work potential called the rate-dependent exergy with the method of variational calculus [20], and further investigated effects of heat transfer laws on the finite-rate exergy [21]. One of aims of finite time thermodynamics is to pursue generalized rules and results. This paper will extend the previous work [6, 7, 9, 10] by using a generalized heat transfer law [$q \propto (\Delta T^n)^m$] [22-27], which includes the generalized convective heat transfer law [28, 29] and the generalized radiative heat transfer law [30, 31], in the heat transfer processes between the infinite heat reservoir and the subsystem to derive the finite-time exergy for the given initial state of the subsystem and the fixed process duration by applying optimal control theory.

II. MODEL

The model to be considered in this paper is illustrated in Fig. 1, which consists of one infinite heat reservoir and one subsystem. There are no mechanical interaction and mass transfer between the subsystem and the reservoir, and only heat transfer between them. The infinite heat reservoir could also be considered as the universal environment with constant temperature, and its temperature, entropy, pressure, volume, and internal energy are denoted as T_1, S_1, p_1, V_1, and E_1, respectively. While the corresponding parameters of the subsystem are denoted as T_2, S_2, p_2, V_2, and E_2, respectively. The heat transfer between the reservoir and the subsystem obeys a generalized heat transfer law [$q(T_1,T_2)=k(T_1^n-T_2^n)^m$] [22-27], including generalized convective heat transfer law [$q\propto(\Delta T)^m$] [28, 29] and generalized radiative heat transfer law [$q\propto\Delta(T^n)$] [30, 31], where k is the heat transfer coefficient. Different values of power exponents m and n denote different heat transfer laws [22-32]. Both the reservoir and the subsystem have fixed composition and are assumed to be in internal equilibrium, so the states of them could be described by two independent thermodynamic variables. Once these two independent variables are chosen, the other variables are determined by the independent variables via the equation of state. For example, when the independent variables of internal energy E and volume V are chosen to describe the state of the system, then one has the following relationships:

$$S=S(E,V),\quad 1/T=\partial S/\partial E,\quad p/T=\partial S/\partial V \tag{1}$$

The independent variables of entropy S and volume V are chosen, then

$$E=E(S,V),\quad T=\partial E/\partial S,\quad p=-\partial E/\partial V \tag{2}$$

The reservoir has an infinite thermal capacity, so its temperature T_1 and pressure p_1 are constants, i.e.

$$1/T_1=\partial S_1/\partial E_1,\quad p_1/T_1=\partial S_1/\partial V_1 \tag{3}$$

The right hand sides of Eq. (3) are constants, then combining Eq. (1) with Eq. (3) yields

$$S_1=E_1/T_1+p_1V_1/T_1, \tag{4}$$

If the working fluid of the subsystem is an ideal gas, its constant volume heat capacity C_{V2} and mole number N_2 are constants. From Eq. (1), one can obtain

$$S_2=C_{V2}\ln E_2+N_2R\ln V_2, T=E_2/C_{V2}p_2=N_2RT_2/V_2 \tag{5}$$

where R is the universal gas constant. Now suppose that the duration of the process τ is a finite value. Then the maximal work output A^* of the system is smaller than the classical exergy A_{rev} that is attained in a reversible process, i.e. a process in which the parameters of the system are infinitesimally separated from those of the environment and the duration of the process is effectively infinite. It is natural to call $A^*(\tau)$ the finite-time exergy or finite-time availability herein.

In terms of the first law of thermodynamics, for the reservoir and the subsystem, one has

$$\begin{aligned}&\dot{E}_1=-q(T_1,T_2),\quad \dot{S}_1=\sigma_1=-q(T_1,T_2)/T_1,\\&\dot{E}_2=q(T_1,T_2)-P,\dot{S}_2=\sigma_2=q(T_1,T_2)/T_2\end{aligned} \tag{6}$$

where σ_1 and σ_2 are the entropy change rates of the reservoir and the subsystem, respectively. $\dot{E}_1=dE_1/dt$, the dot notation signifies the time derivative. From the second law of thermodynamics, the total entropy generation in the heat transfer process ΔS is given by

$$\Delta S=\int_0^\tau q(T_1,T_2)(1/T_2-1/T_1)dt=\Delta S_1+\Delta S_2 \tag{7}$$

where $\Delta S_1=\int_0^\tau[-q(T_1,T_2)/T_1]dt$ and $\Delta S_2=\int_0^\tau[q(T_1,T_2)/T_2]dt$ are the entropy changes of the reservoir and the subsystem, respectively. The power of the subsystem is given by

$$P=q-\dot{E}_2=-(\dot{E}_1+\dot{E}_2)=-T_1\dot{S}_1-\dot{E}_2=-\dot{E}_2+T_1\dot{S}_2-T_1\dot{S} \tag{8}$$

The work done by the subsystem is $A=\int_0^\tau P(t)dt$. From Eq. (8), one obtains

$$A=-\Delta E_2+T_1\Delta S_2-T_1\Delta S=A_{rev}-T_1\Delta S=A_{rev}-\tau T_1\bar{\sigma} \tag{9}$$

where A_{rev} is the work which can be done in a reversible process., i.e. the classical thermodynamic exergy, and $\bar{\sigma}=\Delta S/\tau$ is the average entropy production rate for the whole process. The over bar here denotes the averaging of the corresponding function over the interval $(0,\tau)$.

III. FINITE-TIME EXERGY

If the initial and final states of the subsystem are fixed, the work output A is a monotonically decreasing function of the entropy generation ΔS. For the fixed duration of the process τ, this maximum work problem is equivalent to minimizing the average entropy generation rate $\bar{\sigma}$.

If the objective is to find the minimal $\bar{\sigma}$, the optimization problem becomes

$$\begin{aligned}&\bar{\sigma}^*=\min_{T_2}(\bar{\sigma}_1+\bar{\sigma}_2)\\&\overline{q(T_1,T_2)}=-T_1\bar{\sigma}_1=(A+\Delta E_2^{rev})/\tau\\&(\sigma_1,\sigma_2)\in\Sigma,\quad \Delta E_2^{rev}=E_2(T_1)-E_2(T_2(0))\end{aligned} \tag{10}$$

This is the problem of averaged nonlinear programming with the variables σ_1 and σ_2, which belong to the set Σ. The latter is defined by the conditions imposed on the temperatures T_1 and T_2, and by the heat transfer law $q(T_1,T_2)$. For the generalized heat transfer law $q(T_1,T_2)=k(T_1^n-T_2^n)^m$, from Eq. (6), the set Σ is defined by

$$\sigma_2(\sigma_1)=-T_1\sigma_1/[T_1^n-(-T_1\sigma_1/k)^{1/m}]^{1/n} \tag{11}$$

The domain of σ_1 is defined by the condition that the temperature of the subsystem T_2 is non-negative, and from Eq. (6), one obtains

$$\sigma_1>\sigma_1^{\min}=-T_1^{mn-1}k \tag{12}$$

The value of $\sigma_1^{\max}$ is determined by the maximum admissible temperature ($T_2^{\max}$) of the working fluid. Differentiating Eq. (11) with respect to σ_1 yields the first derivative $d\sigma_2/d\sigma_1$ and the second derivative $d^2\sigma_2/d\sigma_1^2$

$$\frac{d\sigma_2}{d\sigma_1}=\frac{-kT_1[(1-mn)(-T_1\sigma_1/k)^{1/m}+mnT_1^n]}{mnk[T_1^n-(-T_1\sigma_1/k)^{1/m}]^{(n+1)/n}} \tag{13}$$

$$\begin{aligned}\frac{d^2\sigma_2}{d\sigma_1^2}=&\frac{kT_1^2(-T_1\sigma_1/k)^{(1-m)/m}[T_1^n-(-T_1\sigma_1/k)^{1/m}]^{1/n}}{\{mnk[T_1^n-(-T_1\sigma_1/k)^{1/m}]^{(n+1)/n}\}^2}\\&\cdot[n(1+m)T_1^n+(1-mn)(-T_1\sigma_1/k)^{1/m}]\end{aligned} \tag{14}$$

Let σ_1^* and σ_1^{**} be the roots of the equations $d\sigma_2/d\sigma_1=0$ and $d^2\sigma_2/d\sigma_1^2=0$ (except zero point), respectively. From Eqs. (13) and (14), one obtains σ_1^* and σ_1^{**}, as follows

$$\begin{aligned}&\sigma_1^*=-k[mn/(mn-1)]^mT_1^{mn-1},\\&\sigma_1^{**}=-k[n(m+1)/(mn-1)]^mT_1^{mn-1}=[(m+1)/m]^m\sigma_1^*\end{aligned} \tag{15}$$

For different heat transfer laws, the set Σ defined by Eq. (11) has different curve characteristics as shown in Fig. 2. As a result, the corresponding optimal thermodynamic processes for the finite-time exergy are different significantly and include two categories [15]:

(1) The function $\sigma_2(\sigma_1)$ is a strictly convex function on σ_1, i.e. the regular case as shown in Fig. 2(a), then there is only one basic solution, and the corresponding optimal thermodynamic process is that the temperature of the subsystem is a constant and the temperature difference between the reservoir and the subsystem is also a constant during the heat transfer process;

(2) The function $\sigma_2(\sigma_1)$ is not a strictly convex function on σ_1, i.e. the singular case as shown in Fig. 2(b), then there are two basic values, and the corresponding optimal thermodynamic process is that the temperature of the subsystem switches between these two values during the heat transfer process. One of these two basic values of T_2 must be the maximal admissible temperature of the subsystem $T_2^{\max}$. The other, T_2^*, is to be found jointly with the Lagrange multipliers from the stationarity condition on T_2 of the Lagrange function

$$L=\sigma_2(T_1,T_2)+\lambda(\sigma_1(T_1,T_2)-\bar{\sigma}_1) \tag{16}$$

(i.e. $\partial L/\partial T_2^*=0$) and from the equality of the values of this function at points $T_2^{\max}$ and T_2^* [i.e. $L(T_1,T_2^*)=L(T_1,T_2^{\max})$]. For the heat transfer laws that the power exponents m and n satisfy the inequality $n(m+1)/(mn-1)<0$, the second derivative $d^2\sigma_2/d\sigma_1^2$ changes sign at the point $\sigma_1=\sigma_1^{**}$, i.e. the concave and convex characteristic of the function $\sigma_2(\sigma_1)$ changes at the point $\sigma_1=\sigma_1^{**}$. In this case, it is evident that the function $\sigma_2(\sigma_1)$ belongs to the singular case as shown in Fig. 2(b) and attains its minimum at the point $\sigma_1 = \sigma_1^* = [m/(m+1)]^m \sigma_1^{**}$. While for other heat transfer laws, the function $\sigma_2(\sigma_1)$ belongs to the regular case as shown in Fig. 2(a) and the corresponding optimal thermodynamic process is that the temperature of the subsystem is a constant and the temperature difference between the reservoir and the subsystem is also a constant during the heat transfer process. Besides, the entropy generation rate during the heat transfer process is also a constant.

Combining Eq. (10) with Eq. (11) yields the minimal entropy generation rate

$$\sigma^* = (A + \Delta E_2^{rev})\{T_1 - \{T_1^n - [(A + \Delta E_2^{rev})/(k\tau)]^{1/m}\}^{1/n}\} \\ /\{T_1 \tau \{T_1^n - [(A + \Delta E_2^{rev})/(k\tau)]^{1/m}\}^{1/n}\} \quad (17)$$

Substituting Eq. (17) into Eq. (9) yields

$$A = A_{rev} - (A + \Delta E_2^{rev})\{T_1/\{T_1^n - [(A + \Delta E_2^{rev})/(k\tau)]^{1/m}\}^{1/n} - 1\} \quad (18)$$

The finite-time exergy could be obtained by solving Eq. (18). Eq. (18) can be solved analytically for only a few heat transfer laws, for instance, Newton's heat transfer law $(m=1, n=1)$ and the linear phenomenological heat transfer law $(m=1, n=-1)$. For other heat transfer laws, it can only be solved numerically. From Eq. (18), one can see that $A^* \to A_{rev} = -\Delta E_2^{rev} + T_1 \Delta S_2^{rev}$ when $\tau \to \infty$.

IV. NUMERICAL EXAMPLES AND DISCUSSION

The temperature of the heat reservoir is $T_1 = 1000K$, the subsystem is 1 mol ideal gas. The universal gas constant is $R = 8.314J/(mol\bullet K)$, the mole constant volume heat capacity is $C_{V2} = 3R/2$, the initial volume is $V_2(0) = 22.4liter$, the initial temperature is $T_2(0) = 300K$, the amount of heat transfer is $Q = 1\times 10^4 J$, and the initial internal energy is $E_2(0) = 3741.5J$. $k = 13.5W/K$ is set for Newton's heat transfer law, $k = -4.0\times 10^6 W\cdot K$ is set for the linear phenomenological heat transfer law, $k = 1.0\times 10^{-8} W/K^4$ is set for the radiative heat transfer law, $k = 2.48W/K^{5/4}$ is set for the Dulong-Petit heat transfer law， and $k = 8\times 10^{-8} W/K^5$ is set for a complex heat transfer law $q \propto (\Delta(T^4))^{1.25}$. For the heat transfer law $q \propto (\Delta(T^4))^{1.25}$, one obtains $m = 1.25$ and $n = 4$, which don't satisfy the inequality $n(m+1)/(mn-1) < 0$. In this case, the optimal configuration of the heat transfer branch for the finite-time exergy is that the temperature of the subsystem is a constant，and the temperature difference between the reservoir and the subsystem is also a constant during the heat transfer process.

Fig. 3 shows the optimal subsystem temperature T_2^* versus process duration τ for the heat transfer branch. Fig. 4 shows the finite-time exergy A^* versus process duration τ. From Fig. 3, the optimal subsystem temperature T_2^* is an increasing function of process duration τ. The subsystem temperature is equal to the reservoir temperature when the process duration is infinite, i.e. the heat transfer between the reservoir and the subsystem is reversible with no temperature difference. Also from Fig. 3, the profiles of the optimal subsystem temperature T_2^* are different for the cases with different heat transfer laws. For a fixed process duration τ, the subsystem temperature T_2^* for the case with the linear phenomenological heat transfer law is the lowest, while that for the case with radiative heat transfer law is the highest; the subsystem temperature T_2^* for the case with the heat transfer law $q \propto (\Delta(T^4))^{1.25}$ is lower than that for the case with radiative heat transfer law, and the subsystem temperature T_2^* for the case with the Dulong-Petit heat transfer law is higher than that for the case with the linear phenomenological heat transfer law; the subsystem temperature T_2^* for the case with Newton's heat transfer law lies between those for the cases with the Dulong-Petit heat transfer law and the heat transfer law $q \propto (\Delta(T^4))^{1.25}$. As a result of different profiles of the optimal subsystem temperature T_2^* for the cases with different heat transfer laws, the profiles of the finite-time exergy are also different for the cases with different heat transfer laws, as shown in Fig. 4. Therefore, heat transfer laws have significantly effects on the finite-time exergy and the corresponding optimal thermodynamic process. From Fig. 4, the finite-time exergy A^* is also an increasing function of process duration τ. The finite time exergy tends to the classical reversible exergy when the process duration tends to infinite. For a fixed process duration τ, the maximum average power is $P(\tau) = A^*(\tau)/\tau$, which is equal to the tangent of the slope of the line segment connecting the origin with the point $A^*(\tau)$ in Fig. 4. Fig. 5 shows the maximum average power P versus process duration τ. From Fig. 5, the maximum average power P attains its maximum value at some point along the axis of process duration τ, and the average power $P(\tau) \to 0$ when $\tau \to \infty$, i.e. the power for the reversible process is zero. It is evident that the finite-time exergy is a more realistic, stronger limit compared to the classical thermodynamic exergy.

V. CONCLUSION

On the basis of Refs. [6, 7, 8, 10], the problem of the maximal work that can be extracted from a system consisting of one infinite heat reservoir and one subsystem with a generalized heat transfer law [$q \propto (\Delta(T^n))^m$] is investigated in this paper. Finite time exergy is derived for the fixed duration of the process by applying optimal control theory. Effects of heat transfer laws on the finite-time exergy and the corresponding optimal thermodynamic process are also analyzed. The optimal thermodynamic process for the finite-time exergy with the heat transfer laws that the power exponents m and n satisfy the inequality $n(m+1)/(mn-1) < 0$ is that the temperature of the subsystem switches between two optimal heat transfer process, while that for the finite-time exergy with other heat transfer laws is that the temperature of the subsystem is a constant and the temperature difference between the reservoir and the subsystem is also a constant during the heat transfer process. The results for some special heat transfer laws are further obtained on the basis of those obtained with the generalized heat transfer law, and some modifications to the results in Ref. [15] is also performed. When the working fluid of the subsystem is an ideal gas, the finite-time exergy is also obtained. The results also show that the finite-time exergy tends to the classical thermodynamic exergy when the duration of the process tends to infinite large. The finite-time exergy in this paper is derived under the constraint of the process duration is finite and the assumption that both the reservoir and the subsystem are in internal equilibrium. If the internal irreversibility of the subsystem is further considered, the corresponding maximum work output is lower than the obtained finite-time exergy in this paper. The finite-time exergy is a more realistic, stronger limit compared to the classical thermodynamic exergy.

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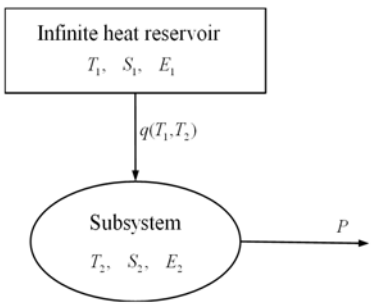

Figure 1 Model of one infinite heat reservoir and one subsystem

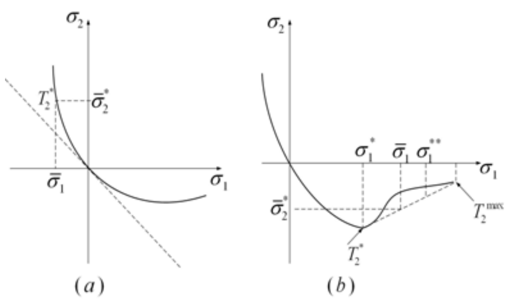

Figure 2 The set Σ for σ_1 and σ_2 with different heat transfer laws. (a) the regular case; (b) the singular case

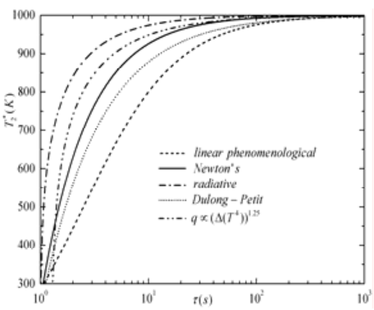

Figure 3 The optimal subsystem temperature T_2^* versus process duration τ

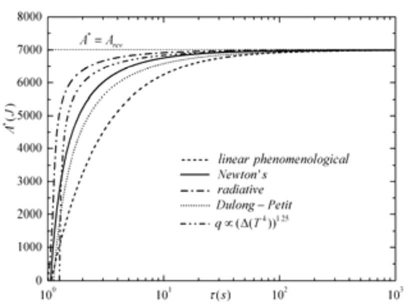

Figure 4 The finite-time exergy A^* versus process duration τ

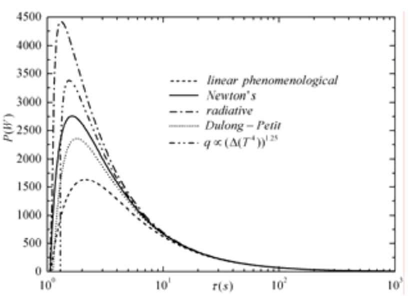

Figure 5 The maximum average power P versus process duration τ