Irreversible entropy production in low- and high-dissipation heat engines and the problem of the Curzon-Ahlborn efficiency

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Heat engines performing finite time Carnot cycles are described by positive irreversible entropy functions added to the ideal reversible entropy part. The model applies for macroscopic and microscopic (quantum mechanical) engines. The mathematical and physical conditions for the solution of the power maximization problem are discussed. For entropy models which have no reversible limit, the usual "linear response regime" is not mathematically feasible; i.e., the efficiency at maximum power cannot be expanded in powers of the Carnot efficiency. Instead, a physically less intuitive expansion in powers of the ratio of heat-reservoir temperatures holds under conditions that will be inferred. Exact solutions for generalized entropy models are presented, and results are compared. For entropy generation in endoreversible models, it is proved for all heat transfer laws with general temperature-dependent heat resistances, that minimum entropy production is achieved when the temperature of the working substance remains constant in the isothermal processes. For isothermal transition time t, entropy production then is of the form $a/[t\,f(t) \pm c]$ and not just equal to a/t for the low-dissipation limit. The cold side endoreversible entropy as a function of transition times inevitably experiences singularities. For Newtonian heat transfer with temperature-independent heat conductances, the Curzon-Ahlborn efficiency is exactly confirmed, which—only in this unique case—shows "universality" in the sense of independence from dissipation ratios of the hot and cold sides with coinciding lower and upper efficiency bounds for opposite dissipation ratios. Extended exact solutions for inclusion of adiabatic transition times are presented.

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I. INTRODUCTION

Macroscopic heat engines operating between two heat baths (reservoirs) with low and high temperatures T_c and T_h unavoidably experience losses by irreversible positive entropy generation. Thus, the efficiency η of such engines, defined as the ratio of mechanical or electrical work output W and absorbed heat Q_h from the hot reservoir, is always below the Carnot efficiency $\eta_C = 1 - T_c/T_h$ of an ideal heat engine without irreversible entropy generation. The Carnot efficiency is based on the classical work of Carnot [1] for an engine working in recurrent cycles with four steps (e.g., a cylinder with working fluid compressed or expanded by a movable piston). In order to suppress losses, isothermal expansion and compression of the fluid at temperature T_h and T_c, respectively, has to be performed infinitely slowly to keep the system in thermal equilibrium with the heat baths. In the two adiabatic branches of the cycle, the fluid is expanded and compressed very rapidly to change the temperature of the working fluid between T_h and T_c. Denoting the time for isothermal expansion and compression by t_h and t_c and ignoring the time for adiabatic cycle branches, the engine's output power is $P = W/(t_h + t_c)$, which tends to zero for $t_h, t_c \to \infty$.

"Finite time thermodynamics" [2–13] with $t_h, t_c < \infty$ and $P > 0$ requires model assumptions for the irreversible entropy production due to thermal nonequilibrium conditions, friction of moving parts, and/or heat leakage current introduced by the engine's setup between hot and cold reservoirs.

In microscopic and quantum mechanical systems [5,6,14–22], deviations from principally positive entropy production rates sometimes are considered possible on short timescales [21], since energy transfers in those systems are random and thermal fluctuations induce transient decreases of entropy, allowing for possible violations of the Carnot limit for some cycles in the time sequence. Thus the system in Ref. [21], i.e., a single optically trapped Brownian particle as working substance [5,6], seems to be able to work at the Carnot limit. On the other hand, several studies [17–20] rule out the possibility of Carnot efficiency at nonzero power, at least if the engine-bath interactions are not designed purposefully [17].

In the following, the usual convention is used that heat absorbed by the engine is counted positive. Thus, Q_h absorbed from the hot reservoir during one cycle is positive and heat Q_c released to the cold reservoir is negative. By the first law of thermodynamics (energy conservation), the work obtained in one cycle and the efficiency η is

$$W = Q_h + Q_c = Q_h - |Q_c|, \quad \eta = W/Q_h = 1 + Q_c/Q_h. \tag{1}$$

Generally, the entropy S absorbed by a system is given by the sum over the increments of absorbed heat dQ divided by system temperature $T(t)$ at time t of absorption:

$$S = \int \frac{dQ}{T(t)} = \int \frac{q(t)}{T(t)} dt \quad \text{with heat flow} \quad q(t) = \frac{dQ(t)}{dt}. \tag{2}$$

In the case of an ideal Carnot engine, the entropy absorbed by the working fluid in the isothermal process, when in contact with the hot reservoir, is $\Delta S = Q_h/T_h$, and the hot reservoir releases the same amount $-\Delta S$, so that the full system including reservoirs does not change entropy. The entropy released from the working fluid to the cold reservoir during the isothermal compression stroke is Q_c/T_c. After disconnection from the cold reservoir and having finished one full cycle, the engine is in thermal equilibrium at its initial state without change of entropy. During the adiabatic processes no heat or entropy is exchanged. Since the system is always in thermal equilibrium, it can be shown that $\Delta S = Q_h/T_h = -Q_c/T_c$ [23]. Thus from Eq. (1), $\eta_C = 1 - T_c/T_h$ is derived.

By reverse operation of the ideal Carnot engine, the opposite entropy with same magnitude $|\Delta S|$ is rejected from the working fluid during compression at temperature T_h and the reversible entropy $+\Delta S$ is absorbed during expansion at T_c. The engine then works in the refrigerator or heat-pump mode with coefficient of performance defined by $\phi = Q_d/(-W)$. Since again $Q_h/T_h = -Q_c/T_c$, $\phi_c = T_c/(T_h - T_c)$ is inferred.

In the presence of irreversible entropy production, the heat Q_h absorbed per cycle by the heat engine is reduced, e.g., because of expansion with finite time t_h and limited heat conductivity between working fluid and heat bath, or since friction of the piston causes the working fluid to be heated, thus reducing the heat flow from the reservoir. Such effects, also in combination, can be represented by an additional general irreversible entropy term $S_h(t_h)$ to the reversible entropy part ΔS for the hot side process, resulting in

$$Q_h = T_h[\Delta S - S_h(t_h)]. \tag{3}$$

Similarly for the cold side process with finite time t_c, heat rejection Q_c to the cold reservoir is increased in magnitude by the same effects with reversed sign. Thus with cold side irreversible entropy production $S_c(t_c)$, Q_c per cycle is

$$Q_c = T_c[-\Delta S - S_c(t_c)]. \tag{4}$$

The restriction $S_c(t_c), S_h(t_h) \geqslant 0$ applies, due to the second law of thermodynamics, but for the time being no further conditions are assumed. The $S_c(t_c)$, $S_h(t_h)$ may depend in addition to t_h, t_c on T_h, T_c, ΔS and further system parameters. In particular, the $S_c(t_c)$, $S_h(t_h)$ may include the effect of a heat leakage current [12,13] caused, e.g., by the engine's housing between hot and cold reservoirs, which typically is a steady state process, not linked to the cyclic operation. This is of importance in steady state heat engines. Especially for thermoelectric and thermionic converters [24–26] such a description is necessary [27].

Equations (3) and (4) are a straightforward extension of the models in Ref. [5–7], where

$$S_h(t_h) = \Sigma_h/t_h, \quad S_c(t_c) = \Sigma_c/t_c, \tag{5}$$

with positive constants Σ_h, Σ_c. That model is widely used and known as the "low-dissipation" approximation, although $S_c(t_c)$, $S_h(t_h)$ thus defined are unlimited in size for short times t_h, t_c. The low-dissipation assumption is plausible for sufficiently large t_h, t_c, provided that the limit toward the ideal Carnot engine $S_c(t_c), S_h(t_h) \to 0$ for $t_h, t_c \to \infty$ exists. In that case, the low-dissipation entropy generations can be obtained after series expansion in the variable $1/t : \Sigma_i a_i(1/t)^i$, by discarding all terms with $i > 1$.

For practical applications the low-dissipation assumption often is too rough an approximation, e.g., for the endoreversible model of the Carnot engine with ideal gas (see the Appendix). The endoreversible model is obtained by attributing the irreversibilities $S_c(t_c)$, $S_h(t_h)$ exclusively to finite heat conductances connecting the engine's working medium to the heat baths, while the core engine is assumed to be in an ideal Carnot modus. The heat conductances can be chosen according to different heat transfer laws for the heat flows $q_h(t)$, $q_c(t)$ at the hot and cold side with temperatures $T_{fh}(t)$, $T_{fc}(t)$ of the working fluid, when in contact with the T_h, T_c reservoirs:

$$q_j(t) = \kappa_j(T_{fj}(t), T_j) \quad [T_j - T_{fj}(t)], \quad j = h, c. \tag{6}$$

The κ_j are constants for the most common heat transfer, Newton's law. In several publications [4,8,10], the heat flows q_j are set proportional to the "thermodynamic force" $1/T_{fj}(t) - 1/T_j$ with constant κ_{tj} in the context of linear irreversible thermodynamics. The κ_{tj} are related to the κ_j by

$$\kappa_j(T_{fj}(t), T_j) = \kappa_{tj}/[T_{fj}(t)T_j]. \tag{7}$$

Originally, linear irreversible thermodynamics was applied for the full temperature drop T_h, T_c, without introducing the $T_{fj}(t)$, under the condition $T_h - T_c \ll T_h, T_c$ [28–31]. In the present paper no such approximation will be made.

In Ref. [4] the heat transfers $q_j(t) = \kappa_{nj}[T_{fj}^n(t) - T_j^n]$ have been investigated which correspond for $n = 1$ to the Newtonian case and for $n = -1$ to the thermodynamic force heat flow according to Eq. (7). Heat transfer by thermal radiation is included in the case of $n = 4$. These heat transfers are covered for all positive and negative integers n by Eq. (6) with $\kappa_j(T_{fj}, T_j) = \sum_{i=1}^{\mathrm{n}} T_{fj}^{n-i} T_j^{i-1}$ for positive n and by $\kappa_j(T_{fj}, T_j) = \sum_{i=1}^{\mathrm{n}} T_{fj}^{-i} T_j^{i-1-\mathrm{n}}$ for negative n with $\mathrm{n} = |n|$, so that $\kappa_j(T_{fj}, T_j)$ is always positive.

During the adiabatic branches of the Carnot cycle, the engine is completely isolated from the heat reservoirs. Therefore, in the case of the endoreversible models, the adiabatic branches are reversible without any irreversible entropy production. Usually the time t_a spent in the adiabatic processes is very short compared to isothermal process times, and t_a is nearly always ignored in the literature. Endoreversible models with inclusion of adiabatic t_a will be treated in detail in Sec. III, and it will turn out, even for the most general heat transfer law in Eq. (6), that the irreversibilities $S_j(t_j)$ are of the form $\Delta S^2/[\mathrm{t_j} f(t_j) \pm \Delta S]$ and are not just equal to Σ_j/t_j.

II. GENERAL ENTROPY PRODUCTION

In this section low and high irreversible entropy generation will be treated on the same footing. In the case of entropy production according to Eqs. (3) and (4), the heat engine is in the same state after one full cycle and its entropy content is not changed. However, the entropy of the full system including heat reservoirs has changed by $-Q_h/T_h - Q_c/T_c = S_h(t_h) + S_c(t_c) > 0$. In the refrigerator mode, the heat engine operates in the reverse direction, absorbing heat Q_c and releasing heat $|Q_h|$ which is also described by Eqs. (3) and (4) with the opposite sign of reversible entropy production ΔS, but the same sign for the $S_j(t_j)$. Then again the entropy production of the full system is given by $S_h(t_h) + S_c(t_c) > 0$. In this work only the power generator mode will be treated and $\Delta S < 0$ is always assumed.

The irreversibilities reduce the power output:

$$P(t_h, t_c) = \frac{Q_h + Q_c}{t_h + t_c} = \frac{(T_\mathrm{h} - T_c)\Delta S - T_\mathrm{h}S_h(t_h) - T_cS_c(t_c)}{t_h + t_c}. \tag{8}$$

The corresponding efficiency according to Eqs. (1), (3), and (4) is

$$\eta(t_h, t_c) = 1 - \frac{T_c}{T_h}\frac{\Delta S + S_c(t_c)}{\Delta S - S_h(t_h)} < \eta_C. \tag{9}$$

η can also be directly expressed by the full irreversible entropy production $S_\mathrm{irr} = -Q_h/T_h - Q_c/T_c = S_h(t_h) + S_c(t_c)$ without use of the reversible ΔS. Dividing S_irr by Q_h and utilizing Eq. (1) yields

$$\eta = \eta_C - T_cS_\mathrm{irr}/Q_h.$$

For $S_h(t_h) \to \Delta S$ a singularity arises in Eq. (9) with $\eta \to \pm\infty$, because $Q_h \to 0$ and no work output is possible. Physically $S_h(t_h) \geqslant \Delta S$ is not excluded. $P(t_h, t_c)$ can be maximized with respect to the cycle times t_h, t_c by solving the following equations for t_h, t_c with solutions $\tau_h, \tau_c \geqslant 0$. By use of Eqs. (8) and (9),

$$\begin{aligned} &\partial P/\partial t_h = 0 = \partial P/\partial t_c \to P_\mathrm{max} = P(\tau_h, \tau_c), \\ &\eta_{P\,\mathrm{max}} = \eta(\tau_h, \tau_c). \end{aligned} \tag{10}$$

The weak dissipation Carnot limit with $t_h, t_c \to \infty$ may not exist for general and more realistic $S_c(t_c), S_h(t_h)$, since—at least for macroscopic engines—friction is always present and can increase with lower piston speed, depending on the kind and roughness of surfaces. Physically it is not mandatory that the $S_j(t_j)$ are monotonous decreasing functions with t_j.

The low-dissipation assumption (5) has the advantage of allowing for rather simple analytical calculations, whereas other forms for $S_j(t_j)$ lead to involved computations with hardly or not at all manageable analytical expressions. The optimized τ_h, τ_c for model (5) can be calculated exactly analytically [7]. Introducing the ratios $r = T_c/T_h, \sigma = \Sigma_c/\Sigma_h$, the τ_h, τ_c, and $\eta_{P\mathrm{max}}$ can be written as

$$\begin{aligned} \tau_h &= \frac{2\Sigma_h}{(1-r)\Delta S}(1+\sqrt{r\sigma}), \\ \tau_c &= \frac{2\Sigma_c}{(1/r-1)\Delta S}[1+\sqrt{1/(r\sigma)}], \\ \eta_{P\,\mathrm{max}} &= \frac{(1-r)(1+\sqrt{r\sigma})}{(1+\sqrt{r\sigma})^2 + r(1-\sigma)}. \end{aligned} \tag{11}$$

It turned out [7] that $\eta_{P\mathrm{max}} = \eta(\tau_h, \tau_c)$ is equal to the Curzon-Ahlborn (CA) efficiency η_CA [2,32,33] in the case of symmetric dissipation $\Sigma_h = \Sigma_c$; i.e., $\sigma = 1$:

$$\eta_\mathrm{CA} = 1 - \sqrt{T_c/T_h} = 1 - \sqrt{1-\eta_C},$$
$$\eta_- = \frac{\eta_C}{2}, \quad \eta_+ = \frac{\eta_C}{2-\eta_C}.$$

Here η_-, η_+ are the lower and upper efficiency bounds for asymmetric dissipation $\sigma = \Sigma_c/\Sigma_h \to \infty$ and $\to 0$, respectively. $\eta_{P\mathrm{max}}$ in Eq. (11) can be expanded in powers of $\eta_C = 1 - r$:

$$\eta_{P\,\mathrm{max}} = \frac{\eta_C}{2} + \frac{{\eta_C}^2}{4}\frac{1}{1+\sqrt{\sigma}} + \frac{\eta_C^3}{8}\frac{1}{1+\sqrt{\sigma}} + O(\eta_C^4).$$

A. General conditions for maximum power

The general system conditions for the determination of P_max, $\eta_{P\mathrm{max}}$, and τ_h, τ_c from given entropies $S_j(t_j)$ will be formulated. The following physical and mathematical consequences are valid:

1. $S_j(t_j) \geqslant 0$, $t_j \geqslant 0$, for $j = h, c$.

2. If $W(t_h, t_c) > 0$ for t_h, $t_c \to 0$, then $P_\mathrm{max} \to \infty$. Equation (10) for τ_h, τ_c, and P_max determination can only be applied for $W(0, 0) \leqslant 0$. For the endoreversible model, t_c is restricted to $t_c > \Delta S/\kappa_c > 0$, since otherwise $S_c(t_c) < 0$ (cf. Sec. III).

3. For $S_h(t_h) \to \Delta S$, according to Eq. (9) $\eta \to \pm\infty$, because of $Q_h \to 0$ and the work and power output is negative. Thus $S_h(t_h) \geqslant \Delta S$, although physically admissible, is no possible solution for power maximization and has to be excluded. For the endoreversible model, $S_h(t_h = 0) = \Delta S$ is the maximum with $W(t_h = 0, t_c) < 0$ (cf. Sec. III). Thus $\tau_h = 0$ is not possible.

4. From Eqs. (8) and (10) it can be inferred that

$$\begin{aligned} &P_\mathrm{max} + T_j\frac{dS_j}{dt_j}(\tau_j) = 0, \\ &j = h, c \ \text{ and thus } \ \frac{dS_j}{dt_j}(\tau_j) < 0 \end{aligned} \tag{12}$$

for $P_\mathrm{max} < 0$. This means that, at least within a neighborhood of τ_h, τ_c, the $S_j(t_j)$ are decreasing functions. If $S_j(t_j)$ are continuously increasing functions, P_max is achieved for the smallest t_j compatible with $S_j(t_j) \geqslant 0$. Equation (12) can be used to calculate P_max for τ_h, $\tau_c < \infty$, if one of the τ_h or τ_c is known.

5. If $S_c(t_c)$, $S_h(t_h)$ are increasing or decreasing *linear* functions, a physical local maximum of $P(t_h, t_c)$ in the sense of Eq. (10) does not exist, and Eq. (12) is not valid. P_max then is given by the largest or lowest t_j in the physical time domain compatible with $S_j(t_j) \geqslant 0$.

6. If a physical local maximum of $P(t_h, t_c)$ with solutions τ_h, τ_c exists, Eq. (12) is valid and yields, by use of the derivatives $S_j'(t_j) = dS_j/dt$, $S_c'(\tau_c) = S_h'(\tau_h)T_h/T_c$, resulting in $\tau_c(\tau_h) = S_c'^{-1}[S'_h(\tau_h)T_h/T_c]$ with $S_c'^{-1}$ denoting the inverse function of $S_c'(t_c)$. $S_c'^{-1}$ exists at least in a surrounding of τ_c. Similarly, $\tau_h(\tau_c) = S_h'^{-1}[S'_c(\tau_c)T_c/T_h]$.

7. In the linear response regime, i.e., for $T_c \approx T_h$, the first few terms of the series expansion in η_C of $\eta_{P\mathrm{max}}$ or other efficiencies are often compared for different models to discuss "universality" [34]. For $\eta_{P\mathrm{max}} = \eta(\tau_h, \tau_c)$ in Eq. (9), the expansion in η_C can only exist when the τ_h, τ_c depend on T_c, T_h through their ratio $r = T_c/T_h$ under the proviso that $S_j(t_j)$ has no further T_j dependence. This can be confirmed generally by maximizing in Eq. (10) P/T_h instead of P, with unaltered result for the τ_h, τ_c, $\eta_{P\mathrm{max}}$, which thus only depend on r. P_max itself is proportional to T_h and a factor containing r. In the case that $S_c(\tau_c)$, $S_h(\tau_h) > 0$, due to Eq. (9), $\eta_{P\mathrm{max}} < 0$ for $\eta_C = 0$.

Furthermore, the series expansion of $\eta_{P\max}$ in powers of η_C (i.e., in r around $r = 1$) does not generally exist.

In the case of additional T_j dependence of the $S_j(t_j)$, expansion of $\eta_{P\max}$ in powers of η_C or r usually is not directly possible. Then one of the T_j, e.g., T_h, has to be chosen as a fixed parameter and T_c is expressed as rT_h.

Examples for additional entropy T_j dependence have been presented for microscopic and quantum mechanical engines. Nearly always the low-dissipation entropy production $\sim 1/t_j$ is deduced, Refs. [6,14,21,22]. In Ref. [22] a perturbation theory for quantum master equations led to a systematic expansion of entropies in powers of $(1/t_j)$. After discarding all higher powers of $(1/t_j)$, again the low-dissipation approximation was used for thermodynamic descriptions with different efficiencies. A microscopic engine for a colloidal Brownian particle described by a Fokker-Planck equation (drift-diffusion approximation) was treated in Ref. [6]. This again led to the entropy model (5), $S_j(t_j) = \Sigma_j(T_j)/t_j$, which assumes different forms with different efficiencies by the functions $\Sigma_j(T_j)$ associated with the mobility $\mu(T)$ of the Brownian particle: $T_c\Sigma_c(T_c)/[T_h\Sigma_h(T_h)] = \mu(T_h)/\mu(T_c)$. The $\eta_{\rm CA}$ efficiency following Eq. (11) is only obtained in the case of $\mu(T) \sim 1/T$.

B. Power maximization with different entropy models

Calculation results pertaining to maximized power will be presented utilizing generalized irreversibilities $S_j(t_j)$, $j = h, c$. The objective is to give a nearly complete list of those $S_j(t_j)$ functions, for which an analytical solution to the power maximization problem according to Eq. (10) is possible.

By adding a constant and linear term to the low-dissipation model of Eq. (5), the following expressions are obtained:

$$S_j(t_j) = c_{-1}^{(j)}/t_j + c_0^{(j)} + c_1^{(j)} t_j, \quad j = h, c. \tag{13}$$

This model can be used to investigate the consequences of nonmonotonous entropy production also in the case of absence of a reversible limit for $t_j \to \infty$. How this can occur was explained following Eq. (10). Because of $S_j(t_j) \geqslant 0$ for $t_j > 0$, $c_{-1}^{(j)} \geqslant 0$, $c_1^{(j)} \geqslant 0$. The constants $c_0^{(j)}$ are limited from below by the minimum condition $S_j(t) \geqslant 0$ at $t = \sqrt{c_{-1}/c_1}$:

$$c_0^{(j)} \geqslant -2\sqrt{c_1^{(j)} c_{-1}^{(j)}}, \quad j = h, c.$$

The solution of Eq. (10) for this model leads to

$$\frac{1}{\tau_h} = \frac{-b \mp \sqrt{d}\sqrt{r\sigma}}{2\big(c_{-1}^{(h)} - c_{-1}^{(c)} r\big)}, \quad \frac{1}{\tau_c} = \frac{b \pm \sqrt{d}/\sqrt{r\sigma}}{2\big(c_{-1}^{(h)} - c_{-1}^{(c)} r\big)}, \tag{14}$$

with $r = T_c/T_h$, $\sigma = c_{-1}^{(c)}/c_{-1}^{(h)}$, and

$$b = c_0^{(h)} + c_0^{(c)} r - \Delta S(1 - r),$$
$$d = b^2 - 4c_{-1}^{(h)}\big(c_1^{(h)} - c_{-1}^{(h)} r\big)(1 - r\sigma).$$

For a physical solution in Eq. (14), both τ_h and $\tau_c \geqslant 0$, which is equivalent to $1/\tau_h + 1/\tau_c \geqslant 0$ and $(1/\tau_h)(1/\tau_c) \geqslant 0$. In addition, $d \geqslant 0$ is required. Because of $1/\tau_h + 1/\tau_c \geqslant 0$, only the upper sign in Eq. (14) in front of $\sqrt{d}$ can give a valid solution. Because of $(1/\tau_h)(1/\tau_c) \geqslant 0$, b must be positioned between $-\sqrt{d}\sqrt{r\sigma}$ and $-\sqrt{d}/\sqrt{r\sigma}$. Thus necessarily $b \leqslant 0$ and $b = 0$ only together with $d = 0$. These requirements imply strong restrictions for the parameter space of the entropy model (13). In particular, a solution for $\eta_{P\max}(\eta_C)$ at $\eta_C = 0$, i.e., at $r = 1$, only exists if $c_0^{(h)} + c_0^{(c)} \leqslant 0$ and if $d \geqslant 0$. Although systems with $c_0^{(h)} + c_0^{(c)} > 0$ are physically possible, a mathematical description by a series expansion of $\eta_{P\max}(\eta_C)$ around $\eta_C = 0$ in that case is not possible, and the solution (14) of Eq. (10) is not valid. This also holds for $c_1^{(h)}, c_1^{(c)} = 0$; i.e., the $S_j(t_j)$ are monotonously decreasing with $S_j = c_0^{(j)} > 0$ for $t_j \to \infty$. It suffices that the reversible regime cannot be approached, to prevent the usual "linear response regime" to be mathematically feasible. Thus, this traditional concept is in question and other avenues have to be considered.

An expansion of $\eta_{P\max}(\eta_C)$ around $\eta_C = 1$, i.e., around $r = 0$, is always possible, at least for a neighborhood of $r = 0$, because for all systems with a nonsingular denominator, Eq. (9) yields $\eta_{P\max}(r = 0) = 1$. For $r = 0$, b can assume any value in the interval $(-\infty, 0)$ and is only restricted by the requirement $b = c_0^{(h)} - \Delta S < 0$ by the above statement No. 3. If $d = b^2 - 4c_1^{(h)} c_{-1}^{(h)} \geqslant 0$ is fulfilled for sufficiently small $c_1^{(h)} c_{-1}^{(h)}$, the solution (14) for $r = 0$ is $\tau_h(r = 0) = -2c_{-1}^{(h)}/b$, $\tau_c(r = 0) = 2c_{-1}^{(h)}/(b + \sqrt{d/\sigma}/\sqrt{r}) \Rightarrow \tau_c \to 0$ for $r \to 0$. A singularity $1/\sqrt{r}$ in Eq. (9) will be removed by the prefactor r and $\eta_{P\max}(r = 0) = 1$ is obtained. Also in the case of $r = 0$, less severe restrictions for the parameter space of the model (13) have to be observed.

With Eqs. (12)–(14) for $j = h$, $P_{\max}$ is easily inferred:

$$P_{\max} = T_h\left[\frac{\big(b + a_r\sqrt{d}\big)^2}{4c_{-1}^{(h)}\big(1 - a_r^2\big)^2} - c_1^{(h)}\right],$$

where $a_r = \sqrt{\sigma r}$, $r = T_c/T_h$, $\sigma = c_{-1}^{(c)}/c_{-1}^{(h)}$. The efficiency $\eta_{P\max} = \eta(\tau_h, \tau_c)$ from Eq. (9) is more complicated:

$$\eta_{P\max} = 1 - r\frac{N}{D},$$

$$N = 2\big(1 - a_r^2\big)\big[\big(\Delta S + c_0^{(c)}\big) + 2\big(1 - a_r^2\big)a_r c_1^{(c)} c_{-1}^{(h)}/(a_r b + d)\big] + (a_r b + d)a_r/r,$$

$$D = 2\big(1 - a_r^2\big)\big[\big(\Delta S - c_0^{(h)}\big) + 2\big(1 - a_r^2\big)c_1^{(h)} c_{-1}^{(h)}/(b + a_r d)\big] + b + a_r d.$$

Other irreversibilities, which are of special importance for the endoreversible models (Sec. III), are represented by

$$S_j(t_j) = c_{-1}^{(j)}/(t_j - t_{j0}), \quad j = h, c. \tag{15}$$

These models allow for exact solutions also in the case that the adiabatic transition times t_a are explicitly taken into account for power maximization. Then in Eq. (8) the denominator for P has to be replaced by $t_h + t_c + t_a$. Analytical solutions for the problem (10) are only possible without the inclusion of additional terms $c_0^{(j)} + c_1^{(j)} t_j$. Despite its simplicity, the solution for model (15) is involved, but can be achieved with the help of a symbolic calculator [35]. The following solutions are obtained:

$$\tau_c - t_{c0} = \frac{c_{-1}^{(c)} r + a\big(-1 - b_m/c_{-1}^{(h)}\big)}{\Delta S(1-r)}, \quad \tau_h - t_{h0} = \frac{c_{-1}^{(h)} - a + b_m}{\Delta S(1-r)},$$
$$\tau_c - t_{c0} = \frac{c_{-1}^{(c)} r + a\big(-1 + b_m/c_{-1}^{(h)}\big)}{\Delta S(1-r)}, \quad \tau_h - t_{h0} = \frac{c_{-1}^{(h)} - a - b_m}{\Delta S(1-r)},$$
$$\tau_c - t_{c0} = \frac{c_{-1}^{(c)} r + a\big(+1 + b_p/c_{-1}^{(h)}\big)}{\Delta S(1-r)}, \quad \tau_h - t_{h0} = \frac{c_{-1}^{(h)} + a + b_p}{\Delta S(1-r)},$$
$$\tau_c - t_{c0} = \frac{c_{-1}^{(c)} r + a(+1 - b_p/c_{-1}^{(h)})}{\Delta\,(1-r)}, \quad \tau_h - t_{h0} = \frac{c_{-1}^{(h)} + a - b_p}{\Delta S(1-r)},$$
$$\tau_c - t_{c0} = \frac{c_{-1}^{(c)} r}{\Delta S\,(1-r)}, \quad \tau_h - t_{h0} = \infty,$$
$$\tau_c - t_{c0} = \infty, \quad \tau_h - t_{h0} = \frac{c_{-1}^{(h)}}{\Delta S(1-r)}, \tag{16}$$

with $r = T_c/T_h$, and the positive constants $a = \sqrt{c_{-1}^{(c)} c_{-1}^{(h)} r}$,

$$b_m = \sqrt{c_{-1}^{(h)}\Big[\Big(\sqrt{c_{-1}^{(h)}} - \sqrt{c_{-1}^{(c)} r}\Big)^2 + \Delta S(1-r)(t_a + t_{c0} + t_{h0})\Big]},$$
$$b_p = \sqrt{c_{-1}^{(h)}\Big[\Big(\sqrt{c_{-1}^{(h)}} + \sqrt{c_{-1}^{(c)} r}\Big)^2 + \Delta S(1-r)(t_a + t_{c0} + t_{h0})\Big]}.$$

with b_m, b_p including the adiabatic time t_a. The solutions in Eq. (16) correspond to local extrema of $P(t_h,\, t_c)$. The last two solutions lead to infinite cycle times $\tau_h + \tau_c \to \infty$ with $P(\tau_h,\, \tau_c) = 0$. For a valid physical solution, it is required that $(\tau_j - \tau_{j0}) \geqslant 0$. Since for the endoreversible model $t_{h0} < 0$ (cf. Sec. III), the additional requirement $\tau_h \geqslant 0$ has to be posed. Only the solution in the third line of Eq. (16),

$$\tau_c - t_{c0} = \frac{c_{-1}^{(c)} r + a\big(+1 + b_p/c_{-1}^{(h)}\big)}{\Delta S(1-r)},$$
$$\tau_h - t_{h0} = \frac{c_{-1}^{(h)} + a + b_p}{\Delta S(1-r)},$$

satisfies $(\tau_j - \tau_{j0}) \geqslant 0$ for all physical parameters $c_{-1}^{(h)}$, $c_{-1}^{(c)}$, r, ΔS. Furthermore, only for this solution in the case of $t_{j0} \to 0$ or $t_{h0} \to -t_{c0}$, and $t_a = 0$, is the low-dissipation limit in Eq. (11) obtained. This is verified by inserting the constants a, b_p, b_m for that limit in Eq. (16), together, i.e.,

$$a = c_{-1}^{(h)}\sqrt{\sigma r}, \quad b_m = c_{-1}^{(h)}|1 - \sqrt{\sigma r}|, \quad b_p = c_{-1}^{(h)}(1 + \sqrt{\sigma r}).$$

Here again $\sigma = c_{-1}^{(c)}/c_{-1}^{(h)}$. Generally, $\eta_{P\max}$ is expressed by Eq. (9) and the above solution for τ_h, τ_c $P_{\max}$ is obtained by utilizing Eq. (12) with τ_h which stays valid also in the case of $t_a > 0$. The resulting expressions can be simplified by extracting the factor $c_{-1}^{(h)}$ out of $a = c_{-1}^{(h)} a_r$ and $b_p = c_{-1}^{(h)} b_r$ yielding $a_r = \sqrt{\sigma r}$ and $b_r = \sqrt{(1+\sqrt{\sigma r})^2 + \Delta S(1-r)(t_a + t_{c0} + t_{h0})/c_{-1}^{(h)}}$. Then,

$$\eta_{P\max} = (1-r)\frac{b_r}{(a_r + b_r + r)},$$
$$P_{\max} = T_h \frac{\Delta S^2(1-r)^2}{(a_r + b_r + 1)^2 c_{-1}^{(h)}}. \tag{17}$$

It should be noted that in principle the radicand of b_r can become negative for $t_a + t_{h0} + t_{c0} < 0$ and the solutions (16) may lose their meaning. For the low-dissipation limit with $t_{h0} + t_{c0} = 0$, $t_a = 0$, $P_{\max}$ reduces to

$$P_{\max} = T_h \frac{\Delta S^2(1-r)^2}{4c_{-1}^{(h)}(1+\sqrt{\sigma r})^2}.$$

The model (15) makes use of five independent system parameters: ΔS, $c_{-1}^{(c)}$, $c_{-1}^{(h)}$, t_{h0}, t_{c0}. For the less general endoreversible model with constant heat conductances κ_j, to be treated in Sec. III, these parameters reduce to three: ΔS, κ_c, κ_h [cf. Eq. (23)], with considerable simplifications for $\eta_{P\max}$, $P_{\max}$, and b_r, so that in this case limits for dissipation ratios σ lead to lower and upper efficiency bounds $\eta_- = \eta_+ = \eta_{\rm CA}$ which coincide with the Curzon-Ahlborn efficiency. Equation (17) should not be used in general for deriving efficiency bounds for limits of σ, since the t_{h0}, t_{c0} parameters may also depend on dissipation values.

The first two terms of the series expansion of Eq. (11) in powers of η_C can be compared with that of Eq. (17):

$$\eta_{P\max} = \frac{\eta_C}{2} + \frac{\eta_C^2}{4}\left[\frac{1}{1+\sqrt{\sigma}} + \frac{\Delta S(t_a + t_{c0} + t_{h0})}{2c_{-1}^{(h)}(1+\sqrt{\sigma})^2}\right] + O\big(\eta_C^3\big).$$

One further entropy model which allows for analytical solutions is of the form

$$S_j(t_j) = c_2^{(j)}(t_j - t_{j0})^2 + c_0^{(j)}, \quad j = h, c,$$

with $c_2^{(j)}$, $c_0^{(j)} \geqslant 0$ and $t_{j0} < 0$. This model is of some theoretical interest, since it is always limited in the decreasing part of the $S_j(t_j)$, where the solutions τ_h, τ_c are located. However, further investigations will not be pursued in this paper. Other models with analytical solutions can hardly be identified, except the simple monoterms $S_j(t_j) = c_{-2}^{(j)}/t_j{}^2$.

A different method for the solution of Eq. (10) is the maximization of work $W(t_h, t_c)$ with the constraint that the total cycle time $t_h + t_c = \tau$ is a fixed value. Afterward $W(\tau)/\tau$ is maximized with respect to τ. This is equivalent to maximizing $P(t_h,\, t_c)$. With Lagrange parameter λ for the constraint, the work to be varied is $W_\lambda = W(t_h, t_c) + \lambda(t_h + t_c - \tau)$:

$$\frac{\partial W_\lambda}{\partial t_j} = \lambda - T_j S_j(t_j) = 0, \quad j = h, c.$$

This is solved for $t_j(\lambda)$ and then, λ has to be determined from the constraint equation to express t_j as functions of τ. In the case of the model (15):

$$t_j(\lambda) = \sqrt{c_{-1}^{(j)} T_j/\lambda} + t_{j0}, \quad \sqrt{\lambda} = \frac{\sqrt{c_{-1}^{(c)} T_c} + \sqrt{c_{-1}^{(h)} T_h}}{\tau - t_{c0} - t_{h0}},$$
$$t_h(\tau) = \frac{\tau - t_{c0} + a_r t_{h0}}{1 + a_r}, \quad t_c(\tau) = \frac{a_r \tau + t_{c0} - a_r t_{h0}}{1 + a_r},$$

with parameter a_r from Eq. (17). This is inserted into $W(t_h,\, t_c)$ which can be expressed with the help of parameter b_r and $t_{c0} + t_{h0} = [b_r^2 - (1 + a_r{}^2)]c_{-1}^{(h)}/[\Delta S(1-r)]$. Differentiating $d[W(\tau)/\tau]/d\tau = 0$ leads to a quadratic equation for τ with one physical solution:

$$\tau = c_{-1}^{(h)} b_r \frac{(1 + a_r + b_r)}{\Delta S(1-r)}.$$

Simplifying $\eta[t_h(\tau), t_c(\tau)]$ yields exactly Eq. (17) for $\eta_{P\max}$. Similarly, $W[t_h(\tau), t_c(\tau)]/\tau$ yields $P_{\max}$. These results are more easily obtained compared to method (10), if the parameters a_r, b_r are introduced from the beginning, in order to simplify expressions. Thus some prior knowledge from the initial solution procedure is used.

Further methods for power maximization can be envisaged. For example, in the case that the $S_j(t_j)$ are invertible and $t_j(S_j)$ can be expressed as analytical functions, it may be possible to maximize $P(S_h, S_c)$ with respect to the independent variables S_h, S_c. For model (15), this is more cumbersome than the original method, but the results seem to be the same. Another method can use η and S_h in $P(S_h, \eta)$ as independent variables. This has the advantage that the obtained solution pairs (S_h, η) directly give the corresponding efficiencies η for the local extrema of $P(S_h, \eta)$. For model (15) the same solution, Eq. (17), is obtained successfully, but this method poses no real advantage. However, for the maximization in an endoreversible system with heat transfer due to thermodynamic force, Eq. (7), this proves to be a powerful method (Sec. III B).

III. ENDOREVERSIBLE MODELS

Performance and entropy production of heat engines generally not only depend on the times t_h, t_c, where the system is in contact with the hot and cold reservoirs, but also on the detailed "protocol" (time dependence of engine parameters) of the changing containment of the working substance during t_h, t_c. The standard example is a working fluid enclosed in a cylinder with a moving piston and the volume of the working fluid as control parameter. For microscopic stochastic heat engines, a prominent (nonendoreversible) example is a colloidal Brownian particle as working substance enclosed in a time-dependent harmonic potential [5,6,21]. For endoreversible models, it is assumed that irreversible entropy production arises without friction merely by heat conductances according to Eq. (6) between working medium and heat baths. Many studies on the endoreversible model exist and often comparisons with the low-dissipation model (5) are carried out [10,12,13]. Both models reveal similar, but by no means equivalent behavior with respect to irreversible entropy production and system performance. In particular, in the short time region strong deviations occur.

Principally, the temperature of the working medium $T_{fj}(t)$ at the hot and cold sides ($j = h,\ c$) varies during the "isothermal" processes, because of the variation of $V(t)$ (fluid volume or external potential) of the enclosing containment. $V(t)$ can be a multiparameter set $V = \{V_i\}$ related as control parameters to $T_{fj}(t)$. For nonconstant $T_{fj}(t)$, the isothermal processes can be considered as quasi-isothermal. In the case of an ideal gas as working fluid, the relation between $T_{fj}(t)$ and prescribed volume evolution $V(t)$ of the gas can be expressed analytically as detailed in the Appendix. Generally the question arises as to the optimum cycle path $V(t)$ or $T_{fj}(t)$, respectively, for maximum system performance. The objective is to minimize the irreversible entropies $S_j(t_j)$, for given t_j of the isothermal processes, with the constraint that the initial and final positions of the control parameters, different for the hot and cold sides, are independent engine parameters and will not change with the transition times t_j. The detailed protocol $V_j(t)$ or $T_{fj}(t)$ has to be optimized in the interval $(0, t_j)$. In a second step, power generation or other system performances can be maximized with respect to the times t_j, as set forth in Sec. II.

This problem was successfully treated in Ref. [8] for heat flows q_j set proportional to the thermodynamic force $1/T_{fj}(t) - 1/T_j$, Eq. (7). The problem will be tackled here for the most general heat transfer law according to Eq. (6). The endoreversible entropy production for the full system (including reservoirs) during isothermal process time t_j is given according to Eq. (2) by the heat increments $dQ_j = q_j(t)dt$ absorbed or released by the working medium at temperature $T_{fj}(t)$ plus the same heat increment $-dQ_j$ of the reservoir released or absorbed at temperature T_j. Thus,

$$S = \int_0^{t_j} q_j(t)\left(\frac{1}{T_{fj}(t)} - \frac{1}{T_j}\right)dt = \int_0^{t_j} \kappa_j(T_{fj}(t), T_j)\frac{[T_j - T_{fj}(t)]^2}{T_{fj}(t)T_j}dt, \tag{18}$$

where in the last integral Eq. (6) has been used. Since no friction or other entropy sources are assumed, Eq. (18) constitutes the complete irreversible entropy production for the isothermal process in the endoreversible limit. Equation (18) leads to zero as lowest possible entropy production in the case of $T_{fj}(t) \to T_j$. Due to Eq. (6), the absorbed or rejected heat $Q_j = \int_0^{t_j} q_j(t)dt$ then also is zero and no work can be done. In Ref. [8] the problem was solved by imposing the constraint that Q_j is a constant fixed value. This leads to the correct solution. For the general case of Eq. (6), it is more appropriate to choose the engine parameter ΔS as to be constrained to a fixed value. ΔS is independent of the varying working conditions and only depends on the initial and final positions of the control parameters in the isothermal processes. For the ideal gas heat engine with V equal to the gas volume (cf. Appendix): $\Delta S = mR\log(V_{\max}/V_{\min})$. ΔS thus is a measure for engine volume and mass of the working fluid and is independent of the transition times t_h, t_c.

For the general case, ΔS can be expressed by Eqs. (3) and (4) and by utilizing Eq. (18) for the $S_j(t_j)$:

$$\pm\Delta S = \frac{Q_j}{T_j} + S_j(t_j) = \int_0^{t_j} \frac{q_j(t)}{T_{fj}(t)}dt, \quad j = h, c. \tag{19}$$

The plus sign in front of ΔS applies for $j = h$. Otherwise the minus sign has to be used.

The minimization of the entropy in Eq. (18) is now performed by introducing a variational parameter in $T_{fj}(t)$ and by differentiation of the integral after that parameter, after the addition of the constraint Eq. (19), multiplied by a Lagrange parameter λ. Then $T_{fj}(t)$ can be varied without restriction in the complete functional:

$$\delta \int_0^{t_j} \left[\frac{q_j(t)}{T_{fj}(t)} - \frac{q_j(t)}{T_j} + \lambda\left(\frac{q_j(t)}{T_{fj}(t)} \mp \frac{\Delta S}{t_j}\right)\right]dt = 0.$$

Here δ denotes differentiation after the variation parameter, which means differentiation of the integrand after T_{fj} with subsequent differentiation of T_{fj} itself. This leads to an overall factor δT_{fj} in the integrand, which is an arbitrary function in

t. Thus the varied integrand necessarily is zero:

$$0 = (1+\lambda)\delta\frac{q_j(t)}{T_{fj}(t)} - \frac{\delta q_j(t)}{T_j} = (1+\lambda)\frac{\delta q_j T_{fj} - q_j \delta T_{fj}}{T_{fj}(t)^2} - \frac{\delta q_j}{T_j}.$$

From Eq. (6), $\delta q_j = [\kappa'_j(T_j - T_{fj}) - \kappa_j]\delta T_{fj}$, where $\kappa'_j = \partial\kappa_j/\partial T_{fj}$ and therefore

$$\frac{\kappa'_j(T_{fj}, T_j)}{\kappa_j(T_{fj}, T_j)} = \frac{(1+\lambda)T_j^2/T_{fj}^2 - 1}{(T_j - T_{fj})[(1+\lambda)T_j/T_{fj} - 1]}. \tag{20}$$

This equation determines the unknown temperatures T_{fj} of the working medium. Together with the constraint (19), two equations are formed for evaluation of T_{fj} and λ. Since the parameters T_j and λ are independent of time, $T_{fj}(t)$ itself is a constant independent of t, when solving Eq. (20) for T_{fj}. This is the essential result of the minimization procedure for entropy (18) and it is valid for all heat transfer laws $\kappa_j(T_{fj}, T_j)$.

For constant T_{fj}, Eq. (19) reduces to $\Delta S = Q_h/T_{fh} = -Q_c/T_{fc}$ which is the condition for a reversible ideal heat engine working between the temperature levels T_{fj}. This is the original criterion for endoreversibility according to Ref. [2]. Furthermore, by use of Eq. (6) in Eq. (19),

$$\pm\Delta S = t_j\kappa_j(T_{fj}, T_j)\left(\frac{T_j}{T_{fj}} - 1\right), \quad j = h, c, \tag{21}$$

which serves as determining equation for the constant T_{fj} in the case of given heat transfer law $\kappa_j(T_{fj}, T_j)$. By replacing Q_j with $\pm\Delta S\, T_{fj}$, the first part of Eq. (19) leads to

$$S_j(t_j) = \pm\Delta S\left(1 - \frac{T_{fj}}{T_j}\right), \quad j = h, c.$$

By elimination of T_{fj}/T_j with the help of Eq. (21), the final result is obtained for the irreversible entropies, minimized with respect to the detailed protocols in $(0, t_j)$:

$$S_j(t_j) = \frac{\Delta S^2}{t_j\kappa_j(T_{fj}, T_j) \pm \Delta S}, \quad j = h, c. \tag{22}$$

For general $\kappa_j(T_{fj}, T_j)$, Eq. (21) determines T_{fj} which then in turn depends on the transition time t_j. Thus an effective heat conductance $\kappa_j^{(e)}(t_j) = \kappa_j[T_{fj}(t_j), T_j]$ has to be used in the denominator of Eq. (22). The consequences of different assumptions for $\kappa_j(T_{fj}, T_j)$ will now be investigated.

A. Newtonian heat transfer and CA efficiency

For constant κ_j (Newton's law), the entropies of Eq. (15) in Sec. II B are valid with coefficients given by Eq. (22):

$$c_{-1}^{(j)} = \Delta S^2/\kappa_j, \quad t_{h0} = -\Delta S/\kappa_h, \quad t_{c0} = +\Delta S/\kappa_c. \tag{23}$$

Thus, also for adiabatic time $t_a > 0$, all the conclusions expressed in Eq. (17) for power maximization are in force, including the low-dissipation limit of Eq. (11). Equation (11) also holds for $t_{j0} \neq 0$ provided that $t_{h0} = -t_{c0}$ and $t_a = 0$. This is fulfilled for symmetric dissipation $\kappa_h = \kappa_c$ which leads to $\sigma = c_{-1}^{(c)}/c_{-1}^{(h)} = 1$. Inserting the coefficients (23) in the expressions for $\eta_{P\max}$ and $P_{\max}$ in Eq. (17), b_r is simplified for $t_a = 0$ to $b_r = \sqrt{\sigma} + \sqrt{r} > 0$, although $t_{h0} + t_{c0} = \Delta S(1/\kappa_c - 1/\kappa_h)$ can assume any negative value. From Eq. (17) the Curzon-Ahlborn efficiency $\eta_{\rm CA}$ is obtained for all ratios $\sigma = \kappa_h/\kappa_c = \sigma = \kappa_h/\kappa_c = c_{-1}^{(c)}/c_{-1}^{(h)}$, since this ratio drops out in the evaluation:

$$\eta_{P\max} = \eta_{\rm CA} = 1 - \sqrt{r} = 1 - \sqrt{T_c/T_h},$$
$$P_{\max} = T_h\frac{\kappa_h(1-\sqrt{r})^2}{(1+\sqrt{\sigma})^2} = T_h\frac{(1-\sqrt{r})^2}{(\sqrt{1/\kappa_h} + \sqrt{1/\kappa_c})^2}. \tag{24}$$

This result is valid for irreversible entropies minimized with respect to the detailed protocol of the control parameters and it is not restricted to linear irreversible thermodynamics or the linear response regime. It states the universal nature of $\eta_{\rm CA}$ for temperature-independent heat transfer coefficients κ_j without need for lower and upper bounds for asymmetric heat dissipation which coincide with $\eta_{\rm CA}$. Thus it is strikingly different from all other models, in particular in comparison to the low-dissipation model in Eq. (11). Equation (24) becomes plausible by the expression for $P_{\max}$ which depends on κ_j symmetrically by some kind of harmonic average of κ_j. The low-dissipation $P_{\max}$ following Eq. (17) does not have that symmetry with respect to the $c_{-1}^{(j)}$, at least not for $r \neq 1$.

Some annotations are appropriate on the result (24). In the original work, Refs. [32,33], the efficiency $\eta_{\rm CA}$ was established not within finite time thermodynamics with transition times t_h, t_c, but for heat flows q_j averaged over full cycle time [thus different from those in Eq. (6)]. The problem of power maximization with corresponding efficiency was solved for the extremely asymmetric case with finite heat conductance only on the hot side. Then P maximization with respect to T_{fh} led to $T_{fh} = \sqrt{T_h T_c}$. Published in specialized journals and less conclusive, Refs. [32,33] apparently did not receive much attention. In Ref. [2], $\eta_{\rm CA}$ was inferred exactly analytically for arbitrary constant κ_j by introducing the endoreversibility definition $Q_h/T_{fh} = -Q_c/T_{fc}$ with ensuing $\eta_{\rm CA}$. The only approximation made was $T_{fj}(t) = $ const. and neglect of general adiabatic cycle times. Later on it was proved by variational techniques in Refs. [3,4] that for maximized work output, $T_{fj}(t) = $ const. is valid. In Ref. [3], the κ_j were restricted to the symmetric case $\kappa_h = \kappa_c$. Nevertheless, the universality of $\eta_{\rm CA}$ posed a problem in subsequent works in the literature. The answer given in the present work utilizes the more general exact analytical solution (16) for the entropies in Eq. (15), which include the Newtonian case of temperature-independent κ_j. The exact solution in the case of the endoreversible model [Eq. (23)] is completely independent of dissipation ratios of hot and cold sides and only for this unique case and in this sense, "universality" is obtained with coinciding lower and upper efficiency bounds for opposite dissipation ratios. This also explains why the originally strongly simplifying assumptions in Refs. [32,33] could be successful. Furthermore, since Newtonian heat transfer is a first (and often sufficient) approximation in many practical cases, $\eta_{\rm CA}$ thus can provide a good description.

As pointed out at the end of Sec. I, for all endoreversible models, irreversible entropy production does not occur during the adiabatic process time t_a. Thus the adiabatic processes can be included in power maximization by replacing in Eq. (8) the denominator $t_h + t_c$ by $t_h + t_c + t_a$. This was already done in the original CA paper [2] by introducing t_a as being proportional to $t_h + t_c$ by a factor $\gamma - 1$ according to varying engine speeds, so that $t_h + t_c + t_a = (t_h + t_c)\gamma$. Thus in the maximized power $P_{\max}$, Eq. (24), an additional factor γ appears in the denominator without altering the efficiency $\eta_{\rm CA}$. However, generally it is necessary to introduce t_a as an independent parameter. As will be shown below, this leads to more complicated expressions for $P_{\max}$ and $\eta_{P\max}$. It is not possible to tackle this problem with the formalism of Ref. [2], since in that theory only the transit-time ratios t_h/t_c can be calculated, but not the t_h, t_c individually, essentially because no use is made of the reversible entropy ΔS as system parameter of the ideal lossless heat engine. On the other hand, the more general formalism for the entropy model (15) with its solutions (17) lends itself well to this kind of problem.

Again using Eq. (23) for the model parameters in (15), the value for b_r with $t_a > 0$ is $b_r = \sqrt{(\sqrt{\sigma}+\sqrt{r})^2 + t_a\kappa_h(1-r)/\Delta S}$ and the efficiency and $P_{\max}$ can be inferred from (17):

$$\eta_{P_{\max}} = (1-r)\Bigg/\left[1+\sqrt{r}\Bigg/\sqrt{1+t_a\frac{\kappa_h(1-r)}{\Delta S(\sqrt{\sigma}+\sqrt{r})^2}}\right],$$

$$P_{\max} = \frac{\kappa_h T_h(1-r)^2}{\left[1+\sqrt{\sigma r}+(\sqrt{\sigma}+\sqrt{r})\sqrt{1+t_a\frac{\kappa_h(1-r)}{\Delta S(\sqrt{\sigma}+\sqrt{r})^2}}\right]^2}. \tag{25}$$

Obviously for $t_a \to 0$, $\eta_{\rm CA}$ of Eq. (24) is obtained and for $t_a \to \infty$ the Carnot efficiency $1-r$ arises, however, with $P_{\max} \to 0$. This is intuitively clear, because of vanishing irreversibilities for sufficiently large $t_j \ll t_a$. For $t_a \to 0$, also the CA power maximum in (24) is recovered. The lower efficiency bound for asymmetric dissipation with $\sigma \to \infty$ is $\eta_- = \eta_{\rm CA}$ with $P_{\max}$ from (24). The upper efficiency bound η_+ for $\sigma \to 0$ can be read off from (25) and in the case of $t_a > 0$ is larger than $\eta_{\rm CA}$.

The short time behavior of model (15) with coefficients (23) is quite different from that of model (5). The hot side entropy $S_h(t_h)$ is always finite with $S_h(t_h = 0) = \Delta S$ as its maximum, as shown by the solid line in Fig. 1. This is not so for the cold side $S_c(t_c)$. A singularity occurs at $t_{c0} = \Delta S/\kappa_c$ and t_c is restricted to $t_c > t_{c0} > 0$. The physical reason for this t_c limitation is given by Eq. (21), solved for $T_{fc} = T_c/[1 - \Delta S/(\kappa_c t_c)]$ leading to $T_{fc} \to \infty$ for $t_c \to \Delta S/\kappa_c$. In fact, for $T_{fc} \to \infty$ any amount of heat Q_c can be rejected from the fluid in an arbitrary short time, but not any amount of entropy Q_c/T_{fc} can be released. Thus, an infinite amount of work input is needed in the case of $T_{fc} \to \infty$ with infinite pressure. In Fig. 2, $S_c(t_c)$ approaches $t_{c0} = 10$ s asymptotically (solid line).

B. Heat transfer due to thermodynamic force

For the widely used heat transfer law of Eq. (7), Eq. (21) leads to a quadratic equation for T_{fj} with two solutions. Only that one with $T_{fj} > 0$ and with $T_{fj} \to T_j$ for $\kappa_{tj} \to \infty$ has to be chosen, i.e., valid for the limit to the ideal reversible engine:

$$T_{fj} = \frac{t_j\kappa_{tj}}{\pm 2\Delta S T_j}\left(-1+\sqrt{1\pm 4\Delta S T_j^2/(t_j\kappa_{tj})}\right), \quad j = h, c.$$

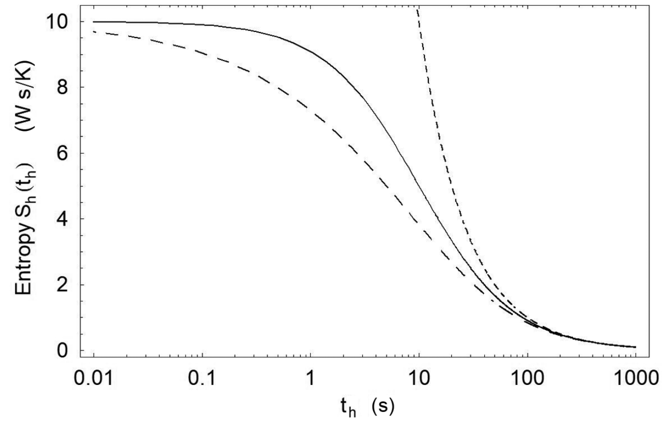

FIG. 1. Entropy functions $S_h(t_h)$ for low-dissipation model (5) (short dashed line), Newtonian model Eqs. (15) and (23) (middle solid line), thermodynamic force model Eq. (26) (lowest dashed line). Functions are adapted to the same leading term $c_{-1}^{(h)}/t_h$. $(\Delta S) = 10$ W s/K, $\kappa_h = 1$ W/K, $\kappa_{th} = \kappa_h T_h^2$, $c_{-1}^{(h)} = \Delta S^2/\kappa_h = \Delta S^2 T_h^2/\kappa_{th} = 100$ W s^2/K.

Here again, the lower sign has to be used for $j = c$ and the higher one for $j = h$. For $j = c$, the condition $t_c \geqslant 4\Delta S T_c^2/\kappa_{tc}$ has to be observed, in comparison to $t_c > \Delta S/\kappa_c$ above for Newton's law. T_{fj} inserted into Eq. (22) yields

$$S_j(t_j) = \frac{\pm 2\Delta S}{x}\left(1+\frac{x}{2}-\sqrt{1+x}\right), \quad x = \pm 4\Delta S T_j^2/(t_j\kappa_{tj}). \tag{26}$$

This result is identical to Eqs. (15) and (18) in Ref. [8] and written here in a different form in order to establish the power series expansion in x, i.e., in $1/t_j$ for large t_j. The term in brackets is of order $x^2/8 + O(x^3)$ and the full expression of order $O(x)$ with leading term $c_{-1}^{(j)}/t$ as first order low-dissipation limit. Here $c_{-1}^{(j)} = \Delta S^2 T_j^2/\kappa_{tj}$ is to be compared with Eq. (23). The limit of Eq. (26) for $t_j \to 0$ is $\pm\Delta S$. For $j = h$, this coincides with the previous (Newtonian) result ΔS. In the case of $j = c$, it is required that $t_c \geqslant 4\Delta S T_c^2/\kappa_{tc} = t_{tc0}$, i.e., $0 > x \geqslant -1$ and the maximum $S_c(t_{tc0}) = +\Delta S$ is

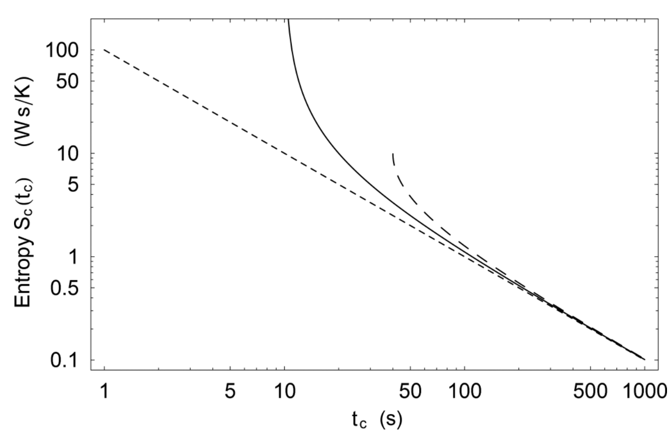

FIG. 2. Analog of Fig. 1 for entropy functions $S_c(t_c)$. Order now reversed: Model (5) lowest (short dashed line), thermodynamic force model Eq. (26) highest (dashed line), all with the same leading order term $c_{-1}^{(c)}/t_c$. $\kappa_c = 1$ W/K, $\kappa_{tc} = \kappa_c T_c^2$, $c_{-1}^{(c)} = \Delta S^2 T_c^2/\kappa_{tc}$.

obtained for the $x = -1$ limit corresponding to $t_c = t_{tc0}$. $S_c(t_c)$ is displayed as a dashed line in Fig. 2. For the transition time t_{tc0}, the maximum fluid temperature $T_{fc} = 2T_c$ is achieved.

It is more difficult to explain the physical meaning of the $S_c(t_{tc0})$ limit (finite maximum) and the restriction of $S_c(t_c)$ to the region $t_c > t_{tc0}$, than for the Newtonian heat transfer. In the Newtonian case, the rate of entropy released from the fluid on the cold side is $-q_c/T_{fc} = \kappa_c(1 - T_c/T_{fc})$ with maximum equal to κ_c for $T_{fc} \to \infty$. The maximum entropy rate corresponds to the shortest possible transition time t_{c0}, since according to Eqs. (19) and (21) $\Delta S = -t_c q_c/T_{fc}$ is a constant engine parameter. Thus for the shortest t_c, $\Delta S = \kappa_c t_{c0}$. For heat transfer according to Eq. (7), the entropy rate is $-q_c/T_{fc} = (\kappa_{tc}/T_c T_{fc})(1 - T_c/T_{fc})$ with limit equal to zero for $T_{fc} \to \infty$. A local maximum equal to $\kappa_{tc}/4T_c^2$ exists, for $T_{fc} \to 2T_c$, again for the shortest possible transition time $t_{t\ c0}$ with maximum fluid temperature $2T_c$, as noted above. Then $\Delta S = t_{tc0}\kappa_{tc}/4T_c^2$, which is equivalent to the previous definition of t_{tc0}. For transit times $t_c < t_{tc0}$, Eqs. (19) and (21) for ΔS cannot be fulfilled.

In order to solve the power maximization problem, the method described at the end of Sec. II is useful. $P(S_h, \eta)$ can be expressed by the independent variables η and S_h for the entropy model in Eq. (26). A procedure along similar lines was used in Ref. [4], also with heat transfer due to Eq. (7), by expressing $P(T_{fh}, \eta)$ as a function of fluid temperature T_{fh} as variable, which is associated with S_h.

Solving Eq. (26) for $t_j(S_j)$ and using Eq. (9) for η with independent variables S_h, S_c solved for S_c leads to

$$t_j(S_j) = (S_j \mp \Delta S)^2 T_j^2/(\kappa_{t\,j} S_j), \quad j = h, c,$$

$$S_c(S_h, \eta) = (1 - \eta)(\Delta S - S_h)T_h/T_c - \Delta S.$$

Both equations are inserted into Eq. (8) for $P(t_h, t_c)$ to obtain $P(S_h, \eta)$. Then the system $\partial P/\partial S_h = 0 = \partial P/\partial \eta$ can be solved for (S_h, η) by setting only the numerators of the derivatives equal to zero. The resulting solution is surprisingly simple with only two nontrivial solutions, one of which is excluded because of $S_h < 0$. The physical solution is

$$\eta_{P\max} = \frac{(1 - r)(1 + \sqrt{\sigma})}{2 + \sqrt{\sigma}(1 + r)},$$

$$P_{\max} = \frac{\kappa_{th}}{4T_c} \frac{(1 - r)^2}{(1 + r)\sqrt{\sigma} + 1 + r\sigma},$$

where $\sigma = \kappa_{th}/\kappa_{tc}$ and $r = T_c/T_h$. These results are equivalent to Eqs. (31) and (32) in Ref. [4] up to a sign error in $P_{\max}$. The boundaries for asymmetric dissipation are the same as for the low-dissipation equation (11), however, with opposite limits. $\eta_- = \eta_C/2$ is obtained for $\sigma \to 0$, and $\eta_+ = \eta_C/(2 - \eta_C)$ for $\sigma \to \infty$. In Eq. (11) those limits were obtained for $\sigma \to \infty$ and $\sigma \to 0$, respectively. In Ref. [4] it was shown by numerical calculation that for heat transfers $\kappa_{nj}[T_{fj}^n(t) - T_j^n]$ in endoreversible models for $n > 1$, $\eta_{P\max}(\sigma = \kappa_{nh}/\kappa_{nc})$ is a decreasing function of σ and for $n < 0$ an increasing function.

The various functions $S_j(t_j)$ are shown in Figs. 1 and 2 for the entropies of models (5), (23), and (26), with the functions for the thermodynamic force problem ($n = -1$) as dashed lines. To be comparable, all functions are adjusted to have the same leading power term $1/t_j$ with coefficient $c_{-1}^{(j)} = \Delta S^2/\kappa_j = 100\,\mathrm{W\,s^2/K}$. For the $S_h(t_h)$ functions in the semilogarithmic plot of Fig. 1, the highest curve is given by the low-dissipation graph (5), whereas the entropies for endoreversible cases $n = 1$ (Newtonian) and $n = -1$ (thermodynamic force) are below with maximum at $\Delta S = 10\,\mathrm{W\,s/K}$. In the double logarithmic plot of Fig. 2 for $S_c(t_c)$, the order is reversed with the low-dissipation model as the lowest curve and the Newtonian model approaching infinity for $t_c \to t_{c0} = \Delta S/\kappa_c = 10\,\mathrm{s}$. The higher $S_c(t_c)$ curve for the thermodynamic force case ($n = -1$) is restricted to $t_c \geqslant 4\Delta S T_c^2/\kappa_{tc} = 40\,\mathrm{s}$ with $\kappa_{tc} = \kappa_c T_c^2$ with maximum $S_c(t_{c0}) = \Delta S = 10\,\mathrm{W\,s/K}$. Thus, for short cycling times with short t_c, the lower Newtonian curve can be more suitable.

IV. CONCLUSION

The general theory of heat engines performing finite time Carnot cycles can be described by addition or subtraction of positive irreversible entropy functions to the ideal reversible entropy part ΔS. Those irreversibilities correspond to the isothermal process times t_j in the cycle. The model applies for macroscopic engines as well as for microscopic quantum mechanical engines.

The mathematical and physical conditions for the solution of the power maximization problem with associated efficiencies have been discussed for general entropy functions $S_j(t_j)$. It is shown following Eq. (14) that for irreversible entropy models, which have no reversible limit, the usual "linear response regime" is not mathematically feasible; i.e., the efficiency $\eta_{P\max}$ cannot be expanded in a power series of the Carnot efficiency η_C. Instead, a physically less intuitive expansion around $\eta_C = 1$ (i.e., in powers of $r = T_c/T_h$) is valid under the stated conditions.

The power maximization problem has been solved exactly analytically for different entropy models [Eqs. (13), (15), (23), and (26)], and results are compared with the standard low-dissipation limit, Eqs. (5) and (11). A special class of models are the endoreversible entropy models, where the irreversibilities are entirely caused by heat conductances connecting the engine's working medium with the external heat reservoirs. Then the entropy production not only depends on the engine's contact times with the heat reservoirs, but additionally on the detailed time dependence of engine parameters (detailed protocol) during the contact times. It is proved rigorously in Eqs. (18)–(20) that the detailed protocol that minimizes the irreversible entropy production is one, for which the temperature of the working substance remains constant in the isothermal processes. This result is valid for all heat transfer laws with arbitrary temperature dependence of the heat conductances in Eq. (6). A further major result is the general endoreversible entropy production of Eq. (22) in the form $S_j(t_j) = \Delta S^2/[t_j f(t_j) \pm \Delta S]$ for contact times t_j, which is unequal to Σ_j/t_j of the low-dissipation limit (5). For shorter times t_j both models are incompatible as shown in Figs. 1 and 2, because of the constant term $\pm\,\Delta S$ in the denominator. The endoreversible cold side entropy functions $S_c(t_c)$ inevitably experience singularities for $t_c > 0$ as shown in Fig. 2. The entropy model (15) with five independent model parameters comprises the endoreversible model for constant heat conductances with three independent parameters, Eq. (23). Only in that reduced unique case, the Curzon-Ahlborn efficiency η_{CA} is exactly confirmed. By its independence from hot and cold side dissipation ratios, "universality" is obtained with coinciding lower and upper efficiency bounds for opposite dissipation ratios. Since Newtonian heat transfer is a first (and often sufficient) approximation in many practical cases, η_{CA} thus can provide a good description under those circumstances. Exact results for an extended theory with inclusion of independent values for adiabatic transition times $t_a > 0$ are presented in Eq. (25). The derivations presented here are not restricted to linear irreversible thermodynamics or the linear response regime.

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APPENDIX: EXACT SOLUTION FOR THE ENDOREVERSIBLE IDEAL GAS HEAT ENGINE

In Sec. III, the relation between the engine's external control parameters $V(t)$ and the temperature of the working fluid $T_{fj}(t)$ was mentioned. In the case of an ideal gas with prescribed volume evolution $V(t)$ as control parameter, this relation can be given exactly analytically. For an ideal gas, its internal energy U is proportional to its temperature. By energy conservation the condition $dU = c_v dT_{fj} = dQ - dW$ holds for the time increments of absorbed heat dQ and work delivered by the fluid's expansion $dW = pdV$ with gas pressure $p(t) = mRT_{fj}(t)/V(t)$. Here R is the ideal gas constant and m the mole fraction of the enclosed gas. With the help of Eq. (6), the following differential equation,

$$c_v \frac{dT_{fj}}{dt} = \kappa_j[T_j - T_{fj}(t)] - mR\frac{\dot{V}(t)}{V(t)}T_{fj}(t), \quad j = h, c, \tag{A1}$$

yields the relation between $V(t)$ and $T_{fj}(t)$. For temperature-independent κ_j, Eq. (A1) is linear in T_{fj} and amenable to exact analytical solution:

$$T_{fj}(t) = \left[T_{fj}(0)V(0)^{mR/cv} + (\kappa_j T_j/c_v)\int_0^t g(t')\,dt'\right]\Big/ g(t),$$
$$g(t) = \exp(\kappa_j t/c_v)V(t)^{mR/cv}. \tag{A2}$$

With this, the $V(t)$ evolution for constant $T_{fj}(t)$ can be determined, which is necessary for minimized irreversible entropy generation, as was inferred following Eq. (20). Multiplying Eq. (A2) by $g(t)$ and differentiating both sides for constant T_{fj} yields $\dot{g}(t)/g(t) = (\kappa_j/c_v)T_j/T_{fj}$ and, finally,

$$V(t) = V(0)\exp\left[\frac{\kappa_j t}{mR}\left(\frac{T_j}{T_{fj}} - 1\right)\right]. \tag{A3}$$

Depending on the ratio T_j/T_{fj}, the volume has to be expanded or compressed exponentially to keep T_{fj} constant.

Equation (A1) gives the fluid temperature evolution $T_f(t)$ along the full cycle by setting $\kappa_j = 0$ in the adiabatic branches of the endoreversible model. Thus irreversible entropy production cannot occur in those parts, because heat flow $q_f(t)$ to the working fluid only exists during contact times t_j with the heat reservoirs. Division of (A1) by $T_f(t)$ and integration over time intervals (t_0, t_1) of interest with $q_f(t)$ from Eq. (6) leads to

$$c_v \log\frac{T_f(t_1)}{T_f(t_0)} = S_f(t)\big|_{t0}^{t1} - mR\log\frac{V(t_1)}{V(t_0)},$$
$$S_f(t)\big|_{t0}^{t1} = \int_{t0}^{t1}\frac{q_f(t)}{T_f(t)}dt. \tag{A4}$$

This equation and the following discussion also apply in the case of general temperature-dependent heat conductances $\kappa_j(T_j, T_f)$. For $t_1 = \tau$ equal to the full cycle time and $t_0 = 0$, the conditions for a closed cycle hold, $T_f(0) = T_f(\tau), V(0) = V(\tau)$, and then necessarily, the total entropy absorbed by the fluid is $S_f(\tau) - S_f(0) = 0$. Thus, the entropy absorbed during t_h is $\Delta S_h = S_f(t_h) - S_f(0)$ and is equal to $-\Delta S_c = -[S_f(t_c + t_{0c}) - S_f(t_{0c})]$, the entropy released from the fluid during t_c. Moreover, for $T_{fj}(t_j + t_{0j}) = T_{fj}(t_{0j})$, but $T_{fj}(t)$ not necessarily constant within $(t_{0j}, t_j + t_{0j})$, $\Delta S_h = -\Delta S_c = \Delta S = mR\log(V_{\max}^{(h)}/V_{\min}^{(h)})$ with ΔS the reversible entropy part of the ideal Carnot engine. Then also the maximum and minimum volume ratios at the hot and cold sides are equal and are the same for the reversible and endoreversible engine: $V_{\max}^{(h)}/V_{\min}^{(h)} = V_{\max}^{(c)}/V_{\min}^{(c)}$. Thus, Eqs. (3) and (4) for Q_j are exactly valid with the same ΔS for both irreversible entropy production $S_j(t_j)$, Eq. (18) [cf. Eq. (19)] turned on, and for $S_j(t_j)$ turned off. In general, for the less interesting case $T_{fj}(t_j + t_{0j}) \neq T_{fj}(t_{0j})$, the reversible ΔS in Eqs. (3) and (4) is only approximately valid and could be replaced by $\Delta S_h = -\Delta S_c$ as defined above:

$$\Delta S_j = mR\log\frac{V^{(j)}(t_j + t_{0j})}{V^{(j)}(t_{0j})} + c_v\log\frac{T_{fj}(t_j + t_{0j})}{T_{fj}(t_{0j})},$$
$$j = h, c. \tag{A5}$$

If the volume values $V^{(j)}(t_{0j})$, $V^{(j)}(t_j + t_{0j})$ are considered to be fixed by the engine's mechanics for all cases, the $T_{fj}(t_{0j})$, $T_{fj}(t_j + t_{0j})$ adapt themselves so that (A5) is valid with $\Delta S = \pm\Delta S_j$ independently for $j = h, c$. However, this ΔS in Eqs. (3) and (4) is not completely independent from the irreversibilities S_j, because of their common dependence on T_{fj}.

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