# Cyclic heat engines with nonisentropic adiabats and generalization to steady-state devices including thermoelectric converters

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For heat engines (including refrigerators) the separation of total entropy production in reversible parts $\Delta S$ and irreversible contributions has proved to be very useful. The $\Delta S$ are entropies for ideal lossless processes at the hot- and cold side and are important system parameters. For Carnot-like heat engines performing finite-time cycles, the concern was raised in a preceding paper that the $\Delta S$ are not always independent from irreversibilities, if initial and final working fluid temperatures $T_f(t)$ differ in the isothermal transitions. It turns out that the $\Delta S$ are unchanged and independent, if $T_f(t)$ evolution is optimized for entropy minimization and apparent inconsistencies are cleared up. If nonisentropic transitions in the adiabatic cycle branches are taken into account, the difference of cold- and hot-side entropy reversibilities is equal to the entropy production in the adiabats. Maximization of cooling power is studied for various irreversible entropy models. The concepts are extended to noncyclic steady-state engines. Power maximization and efficiency calculations are performed exactly analytically. This serves as prerequisite for the hitherto unsolved problem of an accurate definition of reversible and irreversible entropy parts in thermoelectric (TE) converters in the case of inhomogeneous three-dimensional material distributions. It is revealed that for nonconstant Seebeck coefficients, additional terms to the Joule heat arise that destroy positive generator performance in the limit of heat conductance $k \to 0$, in contrast to the traditional constant material properties model. Thus, the concept of improving TE materials by reducing $k$ is in question and an adapted figure of merit $Z$ is presented to deal with the situation.

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## I. INTRODUCTION

Heat engines operating in Carnot-like cycles between two heat reservoirs with low and high temperatures $T_c$ and $T_h$ can be described by irreversible entropy functions added to ideal reversible entropy parts. This concept can be extended to noncyclic steady-state engines (including refrigerators) and, in particular, to thermoelectric (TE) devices. This allows for a novel accurate definition of reversible and irreversible entropy parts in TE converters, also in the most general case of arbitrary inhomogeneous material distribution with arbitrary geometry in three dimensions, which is a hitherto unsolved problem.

The heat engines unavoidably experience losses by irreversible entropy generation, at least for macroscopic engines. Thus, the efficiency $\eta$ of such engines, defined as ratio of mechanical or electrical work output $W$ per cycle or per time unit and corresponding absorbed heat $Q_h$ from the hot reservoir, is below the Carnot efficiency $\eta_C = 1–T_c/T_h$ of an ideal heat engine with reversible entropy generation only. "Finite-time thermodynamics" [1–18] has been developed for engines performing cycles in finite time, ranging from macroscopic to microscopic systems. Usually the isothermal expansion and compression of the working fluid at temperatures $T_{fh}$ and $T_{fc}$, respectively, have to be performed infinitely slowly in order to avoid irreversible entropy generation. This is only possible if the system has a reversible limit for the cycle time $\to \infty$, which for macroscopic engines is an idealization. Denoting the time for isothermal expansion and compression of the fluid by $t_h$ and $t_c$, where the system is in contact with the hot and cold reservoirs, and the time for adiabatic cycle branches by $t_a$, the engine's output power $P = W/(t_h + t_c + t_a)$ tends to zero for $t_h + t_c \to \infty$. Finite-time thermodynamics with $t_h,\ t_c,\ t_a < \infty$, and $P > 0$ requires model assumptions for the irreversible entropy production $S_h(t_h)$, $S_c(t_c)$, and $S_a(t_a)$ [3,5–15], which are due to thermal nonequilibrium conditions during contact with reservoirs, friction of moving parts, and heat leakage currents introduced by the engine's setup between hot and cold reservoirs.

In a recent paper, Ref. [15], additional and more general expressions for the hot- and cold-side isothermal irreversible entropy generation $S_h(t_h)$ and $S_c(t_c)$ were introduced and the consequences investigated. Generally, the $S_h(t_h)$ and $S_c(t_c)$ functions do not only depend on the engine's isothermal transition times $t_h$ and $t_c$, but also on the detailed full time dependence of the engine's control parameters during that transition, e.g., containment potential or volume evolution $V(t)$ of the enclosed working fluid between initial and final states. As was pointed out in Refs. [4,7,8,15], the control parameter evolution functions, also called the detailed protocol, are chosen in such a way that for fixed transition times $t_h$ and $t_c$, the irreversible entropies are minimized. These minimized entropies $S_j(t_j)$, $j = h, c$, then are unequivocal functions of transition times $t_j$. In the context of endoreversible models, the irreversible entropy production $S_a(t_a)$ for adiabatic transitions is set to zero, because the engine is isolated from the environment during $t_a$. Models with $S_a(t_a) > 0$ have rarely been considered [9,10] and will be discussed in detail in Secs. II A and II B.

The heat $Q_h$ absorbed per cycle by the heat engine is reduced, e.g., because of volume expansion with finite time $t_h$ and limited heat conductivity between working fluid and heat bath, or since friction causes the working fluid to be heated, thus reducing the heat flow from the reservoir. With the ideal reversible entropy part denoted by $\Delta S$, the result for $Q_h$ is

$$Q_h = T_h[\Delta S - S_h(t_h)]. \tag{1}$$

Similarly for the cold-side process with finite time $t_c$, negative heat rejection $Q_c$ to the cold reservoir is increased in magnitude by the same effects with reversed sign. Thus, $Q_c$ per cycle is

$$Q_c = T_c[-\Delta S - S_c(t_c)]. \tag{2}$$

In Eqs. (1) and (2) and the following, the usual convention is used that heat absorbed by the engine is counted positive and otherwise negative. The restriction $S_c(t_c), S_h(t_h) \geqslant 0$ applies, due to the second law of thermodynamics. The $S_j(t_j)$ may depend in addition to the transition times $t_j$ on $T_h$, $T_c$, $\Delta S$, and further system parameters. In particular, the $S_j(t_j)$ may include the effect of a heat leakage current [13,14]. This effect is of importance especially for thermoelectric steady-state converters (Sec. IV).

A prominent and frequently used example for the $S_j(t_j)$ functions in Eqs. (1) and (2) is the low-dissipation model of Refs. [5,6,19], where

$$S_h(t_h) = \sigma_h/t_h, S_c(t_c) = \sigma_c/t_c, \tag{3}$$

with positive constants $\sigma_h$ and $\sigma_c$. Another class of entropy-models—the endoreversible models—attributes irreversible entropy production solely to heat conductances between working medium and heat baths, where different models for heat transfer have been used [1,3,7,8,12–15]. The model with linear (Newtonian) heat transfer is the well-known Curzon-Ahlborn (CA) theory, resulting in the CA efficiency [1,20,21], in the case of output power $P$ maximized with respect to $t_h$ and $t_c$:

$$\eta_{P\max} = \eta_{CA} = 1 - \sqrt{T_c/T_h} = 1 - \sqrt{1-\eta_C}. \tag{4}$$

However, this model is not *linear* in the sense of standard irreversible thermodynamics [22–26], where the heat transfer to the engine's working fluid is proportional to the thermodynamic force $1/T_{fj}(t)$–$1/T_j$, $j = h, c,$ with $T_{fj}(t)$ denoting the time-dependent temperature of the working fluid along the hot and cold side of the cycle. The $T_{fj}(t)$ itself always depends nonlinearly on cycle times and other system parameters like $T_h$ and $T_c$. The heat flow rates from $T_h$ and $T_c$ reservoirs to the working medium will be denoted by $q_h(t)$ and $q_c(t)$. In Ref. [15] a unified theory was presented for the most general heat-transfer law in endoreversible models:

$$q_j(t) = \kappa_j(T_{fj}(t), T_j)[T_j - T_{fj}(t)], j = h, c. \tag{5}$$

The heat conductances $\kappa_j$ are constants for the CA model.

The detailed protocol of the engine's control parameters determines the time dependence of $T_{fj}(t)$ in the intervals $(0, t_j)$. It was proved for the general heat-transfer law of Eq. (5) that endoreversible entropy production is minimized by constant $T_{fj}(t)$ and the explicit form of the corresponding $S_j(t_j)$ functions was deduced [15]:

$$S_j(t_j) = \frac{\Delta S^2}{t_j\,\kappa_j(T_{fj}, T_j) \pm \Delta S}, \quad j = h, c \tag{6}$$

with $T_{fj}$ to be inferred for given $t_j$ from

$$\pm\Delta S = t_j\,\kappa_j(T_{fj}, T_j)\left(\frac{T_j}{T_{fj}} - 1\right), \quad j = h, c. \tag{7}$$

The plus in front of $\Delta S$ applies in case of $j = h$; otherwise, the minus has to be used.

A peculiarity of the CA efficiency (4) is its independence from the dissipations $\kappa_c$ and $\kappa_h$ which is strictly valid only for Newtonian heat transfer [15,3]. For the low-dissipation entropy model (3), the CA efficiency is obtained only for symmetric dissipation $\sigma_h = \sigma_c$ [6].

The low-dissipation model, as well as all endoreversible models, have a reversible limit, i.e., $S_j(t_j) \to 0$ for $t_j \to \infty$. In reality—at least for macroscopic engines—the reversible limit does not exist, because of the unavoidable presence of heat leakage currents or other physical characteristics of the entropy functions. It has been proved recently that if no reversible limit exists, i.e., $S_j(t_j) > 0$ for $t_j \to \infty$, the series expansion of $\eta_{P\max}$ in powers of $\eta_C$ is not possible, and thus the usual "linear response regime" with $T_c \approx T_h$ is not mathematically feasible [15]. Instead, an expansion in powers of $r = T_c/T_h$ can be performed, at least in a sufficiently small neighborhood of $r = 0$, although $r = 0$ (i.e., $T_c = 0$) is not physically accessible.

## II. CYCLES WITH NONISENTROPIC ADIABATS

Adiabats are those branches of the Carnot cycle where no heat is exchanged with the environment and the fluid temperature is changed by external work. If in addition the fluid entropy stays constant during these processes, the adiabat is isentropic. For Carnot cycles during adiabats, the engine is thermally isolated from the heat reservoirs. Thus, for all endoreversible models, the adiabats are isentropic, because of $\kappa = 0$ in Eq. (5). More realistically, also in case of thermal isolation, additional entropy generation is possible which leads to further internal fluid heating during the adiabatic processes, e.g., by friction. This in turn results in a correction for Eqs. (1) and (2) for the heats $Q_j$ absorbed or rejected to the reservoirs. Then the reversible entropy parts $\Delta S$ are different for the hot and cold side [9,10].

The paradigm of the ideal-gas endoreversible heat engine is of basic interest, because it constitutes a guiding principle for the description of general devices. In the appendix of Ref. [15], an exact analytical solution has been presented for the relation between the control parameters $V(t)$ (volume evolution) and fluid temperature $T_f(t)$. The fluid's entropy changes for the hot- and cold-side transitions turned out to

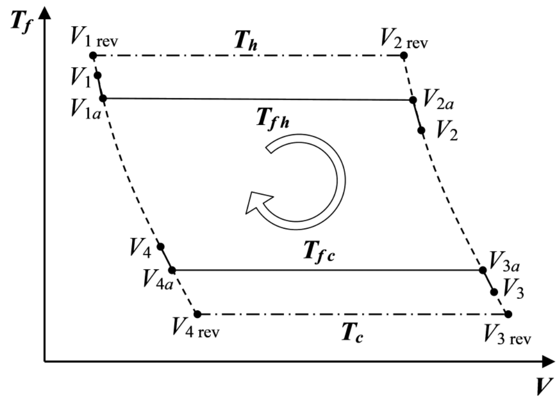


FIG. 1. Fluid temperature $T_f$ and control parameter $V$ (volume) for endoreversible heat engine. Isentropic adiabatic transitions (dashed lines) between hot and cold side. Transitions between corner points $V_1$, $V_2$ and $V_3$, $V_4$ (solid lines) with discontinuous $T_f(t)$ correspond to exact solutions of the entropy minimization following Eq. (9). $V_{la}$ is equivalently adapted and $V_{l\,\mathrm{rev}}$ is ideal Carnot cycle.

be

$$\pm\Delta S_j = mR\log\frac{V(t_j+t_{0j})}{V(t_{0j})} + c_v\log\frac{T_f(t_j+t_{0j})}{T_f(t_{0j})}, \quad j = h, c, \tag{8}$$

with $\Delta S_h = \Delta S_c$ and sign "+" for $j = h$ and "–" for $j = c$ in Eq. (8). Here $R$ denotes the ideal-gas constant, $m$ the mole fraction of the enclosed gas, and $c_v$ its specific heat. $t_{0h}$ and $t_{0c}$ are the starting times of the isothermal transitions with duration $t_h$ and $t_c$, respectively. The corresponding corner points (vertices) of the Carnot cycle will be denoted in the following by $[V_1 = V(t_{0h}), T_f(1) = T_f(t_{0h})]$, $[V_2 = V(t_h + t_{0h}), T_f(2) = T_f(t_h + t_{0h})]$, $[V_3 = V(t_{0c}), T_f(3) = T_f(t_{0c})]$, $[V_4 = V(t_c + t_{0c}), T_f(4) = T_f(t_c + t_{0c})]$; cf. Fig. 1.

The equality $\Delta S_h = \Delta S_c$ is generally valid beyond endoreversible models in case of isentropic adiabats, due to entropy conservation for the working fluid after one full cycle, since entropy is an extensive state function. In the appendix of Ref. [15], the question was raised, how are the $\Delta S_j$ in Eq. (8) related to the reversible $\Delta S$ in Eqs. (1) and (2), which are considered to be the entropies for the ideal lossless Carnot cycle with irreversibilities at the hot- and cold-side transitions turned off. This equivalence was confirmed in case that the initial and final fluid temperatures for the isothermal transitions are equal, i.e., for $T_f(1) = T_f(2)$ and $T_f(3) = T_f(4)$. Then the second term in Eq. (8) disappears with the first one representing the classical expression $\Delta S_{\mathrm{rev}}$ for the ideal Carnot cycle. However, what happens for $T_f(1) \neq T_f(2)$ or $T_f(3) \neq T_f(4)$? In Ref. [15] it was presumed that the $\Delta S$ in Eqs. (1), (2), and (8) are not completely independent from the irreversibilities, because of their common dependence on $T_f(l).T_f(1) \neq T_f(2)$ may arise, when, e.g., the engine's mechanics does not fulfill the volume conditions for an ideal Carnot cycle with $T_{fj} = T_j$: $V_2/V_1 = V_3/V_4$ with $V_3/V_2 = (T_{fh}/T_{fc})^{cv/mR}$. [$T_{fj} \neq T_j$ does not affect the volume ratios $V_2/V_1 = V_3/V_4$, but initial and final volume values $V_3$ and $V_4$ on the cold side, for fixed $V_1$ and $V_2$; cf. Eqs. (10) ff.]

As was pointed out in Sec. I, to derive unambiguous functions $S_j(t_j)$, the detailed protocol $V(t)$ in the intervals $(t_{0j}, t_j + t_{0j})$ for given vertex positions $[V_l, T_f(l)]$ has to be optimized in such a way that the irreversibilities are minimized. This was performed by variation of the entropy expression [15]:

$$S_j = \int_0^{t_j} q_j(t)\left(\frac{1}{T_{fj}(t)} - \frac{1}{T_j}\right)dt = \int_0^{t_j} \kappa_j(T_{fj}(t), T_j)\frac{[T_j - T_{fj}(t)]^2}{T_{fj}(t)\,T_j}\,dt, \tag{9}$$

and resulted in the condition $T_{fj}(t) = \mathrm{const}$, with $T_{fj}$ values determined by Eq. (7). However, by performing variational techniques for $T_f(1) \neq T_f(2)$ or $T_f(3) \neq T_f(4)$, no solution is obtained. The solutions to this problem are discontinuous functions $T_{fj}(t)$ which are out of scope of variational methods.

The actual solutions are depicted in Fig. 1 in the $V$, $T_f$ plane. The vertices at $[V_1, T_f(1)]$ and $[V_2, T_f(2)]$ are connected by a path starting on the left-side adiabat (dashed line) until an optimized temperature $T_{fh}$ is obtained at $V_{1a}$, and then with constant $T_{fh}$ moves on to $V_{2a}$, and from there along the right-side adiabat to $[V_2, T_f(2)]$, and further to $[V_3, T_f(3)]$. Then the path leads back on the same adiabat to the optimized low-side temperature $T_{fc}$ at $V_{3a}$ and moves on to $V_{4a}$ and $[V_4, T_f(4)]$. At $[V_1, T_f(1)]$ the cycle is completed on the left adiabat. Since the adiabats do not contribute any entropy generation, the cycle $[V_l, T_f(l)]$, $l = 1$ to 4, is in fact equivalent to the adapted cycle without back and forth movements $(V_{la}, T_{fj})$, $l = 1$, 2, 3, 4. The preset times $t_j$ for hot- and cold-side transitions $[V_l, T_f(l)] \to [V_{l+1}, T_f(l+1)]$, $l = 1, 3$ are optimally split up, when the time spent along the adiabatic transitions is shortest and the time for the isothermal process along the $T_{fj}$ is largest. Ignoring relaxation times which are very small for an ideal gas, the adiabatic transitions can be considered to be infinitely fast, resulting in discontinuous $T_f(t)$ and the $t_j$ are identical to the transition times in the adapted $(V_{la}, T_{fj})$ cycle with continuous (constant) $T_f(t) = T_{fj}$ on the hot and cold side. For infinitely fast adiabatic transitions, it is not necessary to isolate the engine thermally, since heat transfer from or to the environment cannot take place in zero time.

For vertices $[V_l, T_f(l)]$ of the original cycle which lie outside of the adapted cycle $(V_{la}, T_{fj})$, e.g., for $l = 1, 3$ in Fig. 1, the work lost and gained by the back and forth movement along adiabats within the full cycle compensate exactly, so that all performance data are conserved by the adapted cycle, and for both cycles the minimized entropies $S_j(t_j)$ and optimized $T_{fj}$ are given by Eqs. (6) and (7).

Two points, denoted by $(V_i, T_i)$ and $(\mathrm{V_j}, T_j)$, lying on the same ideal-gas adiabat, satisfy a well-known relation to be inferred from Eq. (8) applied to an adiabat with $\Delta S_a = 0$:

$$\frac{T_i}{T_j} = \left(\frac{V_j}{V_i}\right)^{mR/cv}. \tag{10}$$

Applying this relation to the points $[V_1, T_f(1)]$, $(V_{1a}, T_{fh})$ and $[V_2, T_f(2)]$, $(V_{2a}, T_{fh})$, one obtains $T_f(2)/T_f(1) = [V_{2a}V_1/(V_{1a}V_2)]^{mR/cv}$ and a similar expression for $T_f(4)/T_f(3)$ on the cold side. Thus, Eq. (8) can be written:

$$\Delta S_h = mR\log\frac{V_{2a}}{V_{1a}} = \Delta S_c = mR\log\frac{V_{3a}}{V_{4a}} \tag{11}$$

Furthermore, the adiabats can be extended to the reservoir temperatures $T_h$ and $T_c$ and it can be inferred that the ideal Carnot cycle (dashed-dotted lines in Fig. 1) with corresponding volume vertices $V_{l\,\mathrm{rev}}$ has the same reversible $\Delta S_j$ as in Eq. (8), because of $V_{2\,\mathrm{rev}}/V_{1\,\mathrm{rev}} = V_{2a}/V_{1a}$, $V_{3\,\mathrm{rev}}/V_{4\,\mathrm{rev}} = V_{3a}/V_{4a}$:

$$\Delta S_h = mR \log \frac{V_{2\,\mathrm{rev}}}{V_{1\,\mathrm{rev}}} = \Delta S_c = mR \log \frac{V_{3\,\mathrm{rev}}}{V_{4\,\mathrm{rev}}} = \Delta S_{\mathrm{rev}}. \quad (12)$$

This is the final proof that the $\Delta S$ in Eqs. (1) and (2) are given by the ideal reversible engine with irreversibilities turned off. It should be noted that the $V_{l\,\mathrm{rev}}$ in Eq. (12), contrary to the $V_{la}$ in Eq. (11), are independent from the optimized constant fluid temperatures $T_{fj}$. Thus the concern expressed in Ref. [15] that the $\Delta S$ in Eqs. (1), (2), and (8) are not completely independent from the irreversibilities (9), because of their common dependence on $T_f(l)$, is no longer valid. Consequently, the $\Delta S_j = \Delta S_{\mathrm{rev}}$ are also independent from the $t_j$.

In principle the volume values $V_l$ in Eq. (8) can be chosen at will [27]. The corner points of the cycle are only subjected to the constraint that they are located on the left- and right-hand adiabats in Fig. 1, i.e., $T_f(1)/T_f(4) = (V_4/V_1)^{mR/cv}$, $T_f(2)/T_f(3) = (V_3/V_2)^{mR/cv}$. The vertices of the adapted cycle $V_{la}$ then are located on the same adiabats. The discontinuous hot- and cold-side transitions $[T_f(l), V_l] \rightarrow [T_f(l+1), V_{l+1}]$, $l = 1, 3$, depicted in Fig. 1 by solid lines, are hardly of practical value. Nevertheless they visualize the exact mathematical solution to the entropy minimization problem posed following Eq. (9).

### A. Theory including nonisentropic adiabats

In the case of cycles with nonisentropic adiabats, the generated heat flow $q_a(t)$ in those branches, caused, e.g., by friction, is absorbed solely by the working medium, since heat cannot be exchanged with the environment or reservoirs. The corresponding irreversible entropy production is given by the first term of Eq. (9):

$$S_a(t_a) = \int_{t_{a0}}^{t_{a0}+t_a} \frac{q_a(t)}{T_{fa}(t)}\, dt, \quad (13)$$

and equals the entropy absorption of the fluid during adiabatic process time $t_a$. For given transit time $t_a$, an unequivocal $S_a(t_a)$ is defined by the minimized entropy production with respect to an optimized control parameter evolution $V(t)$ in the interval $(t_{a0}, t_{a0} + t_a)$. Starting from the energy-balance equation for an ideal gas, $dU = c_v dT_{fj} = dQ - dW$:

$$c_v \frac{dT_{f\,a}}{dt} = q_a(t) - mR \frac{dV(t)/dt}{V(t)} T_{f\,a}(t),$$

an expression similar to Eq. (8) holds:

$$S_a(t_a) = mR \log \frac{V(t_a + t_{0a})}{V(t_{0a})} + c_v \log \frac{T_f(t_a + t_{0a})}{T_f(t_{0a})}.$$

For a closed cycle, the change in fluid entropy is zero, and thus

$$\Delta S_h - \Delta S_c + S_{ar}(t_{ar}) + S_{al}(t_{al}) = 0, \quad (14)$$

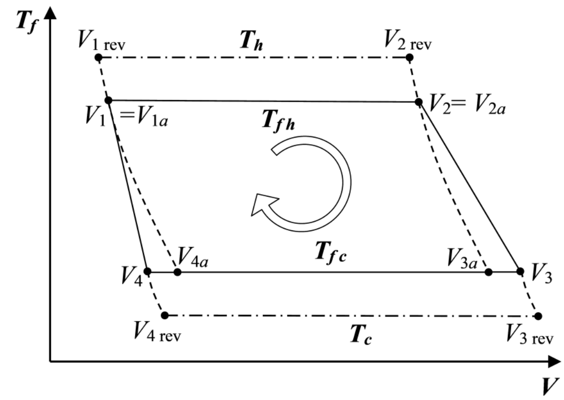


FIG. 2. Analog of Fig. 1 for nonisentropic adiabats (solid lines) resulting in $\Delta S_h < \Delta S_c$ [Eq. (14)]. The adapted cycle $V_{la}$ of Fig. 1 with isentropic adiabats is drawn for comparison.

where $-\Delta S_c$ and $\Delta S_h$ denote the fluid's entropy changes along the quasi-isothermal transitions according to Eq. (8). $S_{ar}$ and $S_{al}$ are the irreversible entropy changes along the right- and left-hand adiabats, respectively, which are given by Eq. (13). Since for nonisentopic transitions $q_a > 0$, the $S_{ar}$ and $S_{al}$ in Eq. (14) always are larger than zero and therefore the equality $\Delta S_h = \Delta S_c$ no longer holds. Instead, $\Delta S_h < \Delta S_c$ is deduced.

In Fig. 2(a) Carnot cycle is visualized with nonisentropic adiabats (solid lines) which deviate from the ideal isentropic adiabats (dashed lines), so that an increased volume extension $V_3$–$V_2$ is needed for the cooldown transition $T_{fh} \rightarrow T_{fc}$ due to the internal heat generation by $q_a$. Similarly, for the left-hand adiabat, a reduced volume compression $V_4$–$V_1$ is used, because the internal heating $q_a$ facilitates the temperature rise $T_{fc} \rightarrow T_{fh}$. Compared to the cycle with isentropic adiabats with $S_a(t_a) = 0$ in Fig. 1, for $S_a(t_a) > 0$ no lossless adiabatic transitions with compensating back and forth movements are possible and thus one cannot choose the corner-point volume values of the cycle $V_l$ at will, since an adapted cycle with $V_{la}$ values and equal performance does not exist. Therefore the vertices $[V_l, T_f(l)]$, $l = 1, 2, 3, 4$ are restricted by the conditions $T_f(1) = T_f(2) = T_{fh}$ and $T_f(3) = T_f(4) = T_{fc}$ in Fig. 2.

Then, by the same reasoning as for Eqs. (10)–(12), it is inferred that

$$\Delta S_h = mR \log \frac{V_2}{V_1} = mR \log \frac{V_{2\,\mathrm{rev}}}{V_{1\,\mathrm{rev}}} =: \Delta S_{h,\,\mathrm{rev}},$$

$$\Delta S_c = mR \log \frac{V_3}{V_4} = mR \log \frac{V_{3\,\mathrm{rev}}}{V_{4\,\mathrm{rev}}} =: \Delta S_{c,\,\mathrm{rev}}. \quad (15)$$

The reversible $\Delta S_{h,\mathrm{rev}}$ and $\Delta S_{c,\mathrm{rev}}$ thus defined are independent from $T_{fh}$ or $T_{fc}$, respectively, since the $\Delta S_{j,\mathrm{rev}}$ only depend on ratios $V_2/V_1$ or $V_3/V_4$ on hot or cold side, but not on the individual $V_l$. If for example $V_1$, $V_2$ are preset values (e.g., by the engine's mechanics), $\Delta S_{h,\mathrm{rev}}$ is fixed. However, the volume ratio $V_3/V_4$, and thus $\Delta S_{c,\mathrm{rev}}$ that develop, depend on the $S_a(t_a)$ according to Eq. (14). Conversely, if the cold-side $V_3$, $V_4$ volumes and thus $\Delta S_{c,\mathrm{rev}}$ are considered to be fixed, the resulting $V_1$, $V_2$, and $\Delta S_{h,\mathrm{rev}}$ $\Delta S_{h,\mathrm{rev}}$ depend on $S_a(t_a)$. In any case, Eqs. (1) and (2) stay valid when $\Delta S$ is replaced by

$\Delta S_{h,\text{rev}}$, and $\Delta S_{c,\text{rev}}$ which are connected by Eq. (14):

$$\begin{aligned}\Delta S_{c,\,\text{rev}} &= \Delta S_{h,\,\text{rev}} + S_{ar}(t_{ar}) + S_{al}(t_{al}),\\ Q_h &= T_h[\Delta S_{h,\,\text{rev}} - S_h(t_h)],\\ Q_c &= T_c[-\Delta S_{c,\,\text{rev}} - S_c(t_c)] \rightarrow\\ Q_c &= T_c[-\Delta S_{h,\,\text{rev}} - S_{ar}(t_{ar}) - S_{al}(t_{al}) - S_c(t_c)]. \quad (16)\end{aligned}$$

In extreme cases for fixed $\Delta S_{c,\text{rev}} > 0$ and fixed volume values $V_3 < V_4$ and for very large nonisentropic adiabats $S_a(t_a)$, $\Delta S_{h,\text{rev}} = \Delta S_h$ becomes negative, which means that right and left adiabats cross each other in Fig. 2 and $V_2 < V_1$. Then output power $P$ after one cycle becomes negative [cf. Eq. (18)] and a cycle can only be completed by delivering external work to the engine.

In the following, $Q_h$ and $Q_c$ in the form (16) will be used as fundamental description for heat converters with either $\Delta S_{h,\,\text{rev}}$ or $\Delta S_{c,\text{rev}}$ used as constant reversible system parameter for the ideal lossless heat engine independent of $t_a$. Equations (16) here have been exemplified by the paradigm of the ideal-gas heat engine, but will be used beyond that special case. Generally, after one full cycle the irreversible entropy production is given by

$$S_{\text{irr}} = -Q_h/T_h - Q_c/T_c = S_h(t_h) + S_c(t_c) + S_{ar}(t_{ar}) + S_{al}(t_{al}). \quad (17)$$

The theory as developed applies equally for the refrigerator mode with device operation in reverse direction absorbing heat $Q_c$ and releasing heat $|Q_h|$ to the hot reservoir. This is also described by Eqs. (16) and (17) with the proviso that the constant $\Delta S_{h,\text{rev}}$ or $\Delta S_{c,\text{rev}}$ changes sign and becomes negative and all irreversibilities stay positive. For example, if $\Delta S_{h,\text{rev}}$ is the system constant, then $\Delta S_{h,\text{rev}} \rightarrow -\Delta S_{h,\text{rev}}$ and $\Delta S_{c,\text{rev}} \rightarrow -\Delta S_{h,\text{rev}} + S_a(t_a)$. If $\Delta S_{c,\text{rev}}$ is the system constant, then $\Delta S_{c,\text{rev}} \rightarrow -\Delta S_{c,\text{rev}}$ and $\Delta S_{h,\text{rev}} \rightarrow -\Delta S_{c,\text{rev}} - S_a(t_a)$. In the refrigerator mode $T_{fh} > T_h$ and $T_{fc} < T_c$ holds and $|\Delta S_{h,\text{rev}}| > |\Delta S_{c,\text{rev}}|$.

### B. Performance optimization with nonisentropic adiabats

The irreversibilities reduce the engine's power output in the generator mode according to Eq. (16):

$$P(t_h, t_c, t_{ar}, t_{al}) = \frac{Q_h + Q_c}{t_h + t_c + t_{ar} + t_{al}} = \frac{(T_\text{h} - T_c)\,\Delta S_{h,\ \text{rev}} - T_\text{h} S_h(t_h) - T_c[S_c(t_c) + S_{ar}(t_{ar}) + S_{al}(t_{al})]}{t_h + t_c + t_{ar} + t_{al}}. \quad (18)$$

The corresponding efficiency $\eta = W/Q_h$ is

$$\eta(t_h, t_c, t_{ar}, t_{al}) = 1 - \frac{T_c}{T_h}\,\frac{\Delta S_{h,\ \text{rev}} + S_c(t_c) + S_{ar}(t_{ar}) + S_{al}(t_{al})}{\Delta S_{h,\ \text{rev}} - S_h(t_h)}. \quad (19)$$

According to Ref. [15], $\eta$ can also be directly expressed by the full irreversible entropy production $S_{\text{irr}}$ without use of the reversible $\Delta S$. Dividing $S_{\text{irr}}$ [left-hand side of Eq. (17)] by $Q_h$ and utilizing $\eta = 1 + Q_c/Q_h$ yields

$$\eta = \eta_C - T_c S_{\text{irr}}/Q_h. \quad (20)$$

$P(t_h, t_c, t_{ar}, t_{al})$ can be maximized with respect to the transit times $t_j$ similar to $P(t_h, t_c)$ in previous works for infinitely fast isentropic adiabats [6,7,15], by solving the equations $\partial P/\partial t_j = 0$ for $t_j$. The solutions $\tau_j \geqslant 0$ yield

$$P_{\max} = P(\tau_h, \tau_c, \tau_{ar}, \tau_{al}),\ \eta_{P\max} = \eta(\tau_h, \tau_c, \tau_{ar}, \tau_{al}). \quad (21)$$

Since now an equation system for four unknown $\tau_j$ arises, instead of two, analytical solutions for cases of practical interest can hardly be obtained. In Ref. [15], extended solutions for endoreversible models with isentropic adiabats for $t_a > 0$ have been obtained, which yield for sufficiently large $t_a$ results for $\eta_{P\max}$ above the CA efficiency, Eq. (4).

Nonisentropic adiabats have been considered in Refs. [9,10] with a relation similar to Eq. (14). The discussion in the present work reveals the identity of $\Delta S_j$ and the reversible ideal entropies $\Delta S_{j,\text{rev}}$. Reference [9] presents an analytical solution for the power-maximization problem (21) in case of a low-dissipation assumption (3) for all four cycle branches. For the refrigerator mode with the same low-dissipation assumptions, only bounds for special maximized refrigerator figures of merit could be deduced [10]. For the adiabats, also constant irreversibilities have been considered [$S_a(t_a) = \text{const} > 0$].

The refrigerator efficiency $\varepsilon$ is defined as heat $Q_c$ absorbed per cycle from the reservoir to be cooled, divided by work input $-W$. This is called coefficient of performance (CoP):

$$\varepsilon = Q_c/(-W) = -Q_c/(Q_c + Q_h) \quad (22)$$

The direct correspondence to the maximization of power output in the generator mode is the minimization of input power $-P = -W/(t_h + t_c + t_{ar} + t_{al})$ in the refrigerator mode [cf. Eq. (18) now with negative $\Delta S_{j,\text{rev}}$]. However, in all literature (with the exception of Ref. [15]) monotonous decreasing irreversibilities $S_j(t_j)$ for increasing $t_j$ have been assumed. Thus, $-P$ in Eq. (18) is monotonously decreasing with the limit zero for $t_j \rightarrow \infty$. Hence, a finite extremum for $-P$ does not exist.

This is the deeper reason for the fundamental difference in performance optimization of refrigerators and generators. As has been pointed out in Ref. [15], physically it is not mandatory that the $S_j(t_j)$ are monotonous decreasing functions, since—at least for macroscopic engines—friction is always present and can increase with lower piston speed, depending on the kind and the roughness of surfaces. A widely used refrigerator figure of merit for performance optimization is the product of $\varepsilon$ and cooling power $q_c = Q_c/t_{\text{cycle}}$, where $t_{\text{cycle}}$ is the cycle time [10,13,28]: $\chi = \varepsilon q_c$. For $t_j \rightarrow \infty$, $t_{\text{cycle}} = \sum_j t_j \rightarrow \infty$, and typically $S_j(t_j) \rightarrow 0$. Thus, by Eqs. (16) and (22): $\varepsilon \rightarrow \varepsilon_C = T_c/(T_h - T_c)$ and $q_c \rightarrow 0$ and $\chi \rightarrow 0$, where $\varepsilon_C$ is the reversible Carnot CoP.

On the other hand, cooling power $q_c$ itself can be an object for maximization and has a finite upper bound, also in case of input power $-P \to +\infty$. For $q_c$ maximization, it is preferable to rewrite Eqs. (16) by use of $\Delta S_{c,\text{rev}}$ instead of $\Delta S_{h,\text{rev}}$:

$$Q_h = T_h[\Delta S_{c,\text{ rev}} - S_h(t_h) - S_{ar}(t_{ar}) - S_{al}(t_{al})],$$
$$Q_c = T_c[-\Delta S_{c,\text{ rev}} - S_c(t_c)]. \tag{23}$$

In terms of Fig. 2, the cold-side control parameters $V_3$ and $V_4$ are fixed, so that $\Delta S_{c,\text{rev}} < 0$ stays constant for all adiabatic process times $t_a$.

For low-dissipation cold-side entropy $S_c(t_c) = \sigma_c/t_c$ and arbitrary functions for the other $S_j(t_j)$, $j = h, ar, al$, cooling power $q_c = Q_c/t_{\text{cycle}}$, $t_{\text{cycle}} = t_h + t_c + t_{ar} + t_{al}$, can be first maximized with respect to $t_c$ with the other $t_j$ held fixed. It can be shown that the simultaneous maximization, e.g., with respect to $t_c$, $t_h$, leads to a degenerate equation system without solution. The optimized time for $t_c$ is

$$t_{c,\text{opt}} = \frac{\sigma_c}{-\Delta S_{c,\text{ rev}}}\left(1 + \sqrt{\frac{-\Delta S_{c,\text{ rev}}}{\sigma_c}t_{ah} + 1}\right),$$
$$t_{ah} = t_h + t_{ar} + t_{al}, \tag{24}$$

and thus $q_c$ maximized with respect to $t_c$ is

$$q_{cm\text{LD}} = \frac{T_c}{t_{ah}}\left[-\Delta S_{c,\text{ rev}} - 2\frac{\sigma_c}{t_{ah}}\left(\sqrt{1 - \Delta S_{c,\text{ rev}}\frac{t_{ah}}{\sigma_c}} - 1\right)\right]. \tag{25}$$

$q_{cm\text{LD}}$ is a monotonous decreasing function of $t_{ah}$ and achieves its absolute maximum for $t_{ah} \to 0$:

$$q_{c,\max} = \lim_{t_{ah}\to 0} q_{cm\text{LD}} = \frac{T_c}{4\sigma_c}\Delta S^2_{c,\text{ rev}}, \tag{26}$$

irrespective of the $S_a(t_a)$ and $S_h(t_h)$ functions. However, $q_h$ and thus also CoP $\varepsilon$ [Eq. (22)], depend on those entropies which in low-dissipation approximation become infinite for $t_{ah} \to 0$. Then, $q_h \to -\infty$ and $\varepsilon \to 0$. Generally for arbitrary $S_a(t_a)$ and $S_h(t_h)$, $q_h$ for the optimized $t_{c,\text{opt}}$ [Eq. (24)], is

$$q_{hm} = \frac{T_h[\Delta S_{c,\text{ rev}} - S_h(t_h) - S_{ar}(t_{ar}) - S_{al}(t_{al})]}{t_{ah} - \frac{\sigma_c}{\Delta S_{c,\text{ rev}}}\left(1 + \sqrt{1 - \Delta S_{c,\text{ rev}}\frac{t_{ah}}{\sigma_c}}\right)}.$$

For $t_{ah} \to 0$, $q_{hm}$ stays finite, if $S_a(0)$ and $S_h(0)$ are finite values (e.g., for constant entropies). Then, $\varepsilon = -1/(1 + q_{hm}/q_{cm\text{LD}}) > 0$. With the help of Eq. (25), the explicit expression for $\varepsilon$ is obtained:

$$1/\varepsilon = -1 + \frac{T_h[\Delta S_{c,\text{ rev}} - S_h(t_h) - S_{ar}(t_{ar}) - S_{al}(t_{al})]}{T_c\left[\Delta S_{c,\text{ rev}} + \frac{\sigma_c}{t_{ah}}\left(\sqrt{1 - \Delta S_{c,\text{ rev}}\frac{t_{ah}}{\sigma_c}} - 1\right)\right]}, \tag{27}$$

and the limit for $t_{ah} \to 0$ yields

$$\varepsilon(0) = -\Delta S_{c,\text{ rev}}T_c/[-\Delta S_{c,\text{ rev}}(2T_h - T_c) + T_h(S_h(0) + S_{ar}(0) + S_{al}(0))].$$

A further standard entropy model is the endoreversible model of Eq. (6). For refrigerators, $\Delta S = \Delta S_{j,\text{rev}} < 0$ and the hot-side entropy $S_h(t_h)$ experiences a singularity due to its compression stroke, instead of the cold-side entropy $S_c(t_c)$. The case of $S_c(t_c)$ singularity was treated in Ref. [15]. Again, maximizing cooling power $q_c = Q_c/t_{\text{cycle}}$ with respect to $t_c$ by use of Eqs. (23) and (6) for arbitrary entropies $S_h(t_h)$ and $S_a(t_a)$ and specializing to constant heat conductance $\kappa_c$ for $S_c(t_c)$, yields

$$t_{c,\text{opt}} = \sqrt{\frac{-\Delta S_{c,\text{ rev}}}{\kappa_c}t_{ah}},$$
$$q_{cm\text{CA}} = T_c\Bigg/\left(\sqrt{1/\kappa_c} + \sqrt{\frac{t_{ah}}{-\Delta S_{c,\text{ rev}}}}\right)^2. \tag{28}$$

One might conclude that the maximum of $q_c$ is achieved for $t_{ah} \to 0$ with $q_{c,\max} = T_c\kappa_c$. However, usually the hot-side entropy is also given by an endoreversible $S_h(t_h)$ [Eq. (6), corresponding to $S_c(t_c)$]. Because of the refrigerator compression stroke, $S_h(t_h)$ has a singularity for $t_h \to -\Delta S_{h,rev}/\kappa_h$ and $t_h$ cannot become smaller, since otherwise $S_h(t_h) < 0$ or the condition of constant $\Delta S$ in Eq. (7) would be violated with $T_{fh} \to \infty$ [15]. The limit of (28) to the smallest possible $t_h = -\Delta S_h/\kappa_h$ has to take into account the relation (14) between $\Delta S_h$ and $\Delta S_c$ where $\Delta S_h$ depends on the $t_a$:

$$q_{cm} = -T_c\Delta S_c\Bigg/\left(\sqrt{\frac{-\Delta S_c}{\kappa_c}} + \sqrt{\frac{-\Delta S_c}{\kappa_h} + t_{ar} + t_{al} + \frac{S_{ar}(t_{ar}) + S_{al}(t_{al})}{\kappa_h}}\right)^2. \tag{29}$$

Here $\Delta S_j = \Delta S_{j,\text{rev}}$ has been set according to Eqs. (15). The nonisentropic adiabats $S_a(t_a)$ are not of the form (6), but can be assumed to be of the low-dissipation form (3). Then the limit $t_a \to 0$ leads to $q_{cm} \to 0$. In order to maximize $q_{cm}$ with respect to $t_{ar}$ and $t_{al}$, the conditions hold: $S'_{ar}(t_{ar}) = -\kappa_h$, $S'_{al}(t_{al}) = -\kappa_h$, i.e., $t_a = \sqrt{\sigma_a/\kappa_h}$ and $t_a + S_a(t_a)/\kappa_h = 2\sqrt{\sigma_a/\kappa_h}$. Thus,

$$q_{c,\max} = -T_c\Delta S_c\Bigg/\left(\sqrt{\frac{-\Delta S_c}{\kappa_c}} + \sqrt{\frac{-\Delta S_c}{\kappa_h} + 2\sqrt{\sigma_{ar}/\kappa_h} + 2\sqrt{\sigma_{al}/\kappa_h}}\right)^2. \tag{30}$$

Provided that $S_h(t_h)$ is not of the endoreversible form (6), an endoreversible part of the form (6) is present—at least for macroscopic engines—in addition to other parts, e.g., for friction. Then again the endoreversible part causes a finite limit for the smallest $t_h \to -\Delta S_{h,\text{ rev}}(t_a)/\kappa_h > 0$ by its singularity in $S_h(t_h)$. Therefore, the maximum cooling power achievable should be of the form (29) or (30) rather than just $T_c\kappa_c$, obtained for $t_h, t_a \to 0$ from Eq. (28). By the same reasoning, the finite limit for $t_h > 0$ can be applied to alter the cold-side low-dissipation result (26) in an extended theory.

The ejected heat flow $q_h < 0$ for the endoreversible model is calculated by Eq. (23) with $t_c = t_{c,\text{opt}}$ from Eq. (28):

$$q_{hm\text{CA}} = \frac{T_h\,\kappa_h\,t_h\,[\Delta S_c - S_a(t_a)]}{[t_a + t_h + \sqrt{-\Delta S_c(t_a + t_h)/\kappa_c}]\,[\Delta S_c - S_a(t_a) + \kappa_h t_h]}, \tag{31}$$

where $S_a(t_a) = S_{ar}(t_{ar}) + S_{al}(t_{al})$ and $t_a = t_{ar} + t_{al}$. The limit $t_h \to -\Delta S_h/\kappa_h = -[\Delta S_c - S_a(t_a)]/\kappa_h$ leads to $q_{hm\text{CA}} \to -\infty$ with CoP $\varepsilon = -1/(1 + q_{hm\text{CA}}/q_{cm\text{CA}}) \to 0$. For general $t_h$, the efficiency $\varepsilon$ is obtained from Eqs. (28) and (31).

## III. STEADY-STATE HEAT ENGINES

Steady-state heat engines do not operate in cycles with alternating engine connections to the heat reservoirs. Instead the engine is constantly connected to both reservoirs and the heat flows $q_h$ and $q_c$ at the hot and cold side are constant in time, and insofar different from Eq. (5). Examples are mechanical turbines and thermoelectric and thermionic converters [29] (Sec. IV). Dividing Eqs. (16) by the cycle time $t_{\text{cycle}} = t_h + t_c + t_{ar} + t_{al}$ leads to the analogous equations for average values per cycle with entropy *rates* defined for $j = h$, $c$, $ar$, $al$ by $s_j = S_j(t_j)/t_{\text{cycle}}$, and reversible entropies $\Delta s_j = \Delta S_j/t_{\text{cycle}}$ and heat *flows* $q_j = Q_j/t_{\text{cycle}}$ for $j = h, c$:

$$q_h = T_h(\Delta s_h(p) - s_h(p)), \quad q_c = T_c(-\Delta s_c(p) - s_c(p)),$$
$$\Delta s_c(p) = \Delta s_h(p) + s_a(p), \quad s_a(p) = s_{ar}(p) + s_{al}(p). \tag{32}$$

The entropy rates thus defined still depend for averaged Carnot cycles on the $t_j$ and, contrary to $\Delta S_j$, also the reversible $\Delta s_j$ depend on $t_j$. For genuine steady-state engines, $t_j$ is not defined and $s_j(p)$ and $\Delta s_j(p)$ in Eq. (32) express the dependence on an engine-specific parameter set $p$ which may include reservoir temperatures $T_c$ and $T_h$. For power generators, $\Delta s_j > 0$ and for refrigerators, $\Delta s_j < 0$ with unaltered sign for the $s_j$.

The total irreversible entropy production rate $s_{\text{irr}}$ is given by the sum of entropy loss per unit time of the hot reservoir $-q_h/T_h$ and entropy gain of the cold reservoir $-q_c/T_c$, since the steady-state engine itself cannot accumulate entropy or heat. Thus, by Eq. (32),

$$s_{\text{irr}} = -q_h/T_h - q_c/T_c = s_h + s_c + s_a. \tag{33}$$

Generally, the sign of $s_a$ is not fixed and $s_a < 0$ may occur, as will be the case for the thermoelectric converter in Sec. IV. Similar to Eq. (20), the efficiency $\eta$ of the heat engine can be expressed for steady state by $s_{\text{irr}}$ without use of the $\Delta s$:

$$\eta = \eta_C - T_c s_{\text{irr}}/q_h. \tag{34}$$

For the model (32), the endoreversibility assumption is possible in a similar way as for Carnot engines with Eq. (5). Power maximization for that case has been done first in a somewhat obscure way, in Ref. [20], where thermodynamic cycles are mentioned, but no cycle times or $t_j$ were defined. The maximized work output thus corresponds to maximized power, since in effect a steady-state heat engine was assumed. Heat transfer similar to (5) was applied only on the hot side with constant fluid temperature $T_{fh}$ and $\kappa_h$. Thus, $\kappa_c = \infty$. Maximizing work- (power-) output with respect to $T_{fh}$ led to $T_{fh} = \sqrt{(T_h T_c)}$ and $\eta_{CA}$ in Eq. (4). So, the problem was solved only for the extremely asymmetric case with dissipation ratio $\kappa_h/\kappa_c = 0$. Curzon and Ahlborn in their work [1] used the Carnot cycle with optimized $t_j$, and with $\kappa_j$ and $T_{fj}$ constant in time on both sides. With the endoreversibility requirement $Q_h/T_{fh} = -Q_c/T_{fc}$, the $\eta_{CA}$ was obtained. Since $\eta_{CA}$ is completely independent from the $\kappa_h$ and $\kappa_c$, the originally strongly simplifying assumptions in Ref. [20] could be successful.

For the general steady-state engine (32), the power-maximization problem in the case of endoreversibility can be solved along similar lines as in Ref. [1]. An ideal steady-state engine without irreversible entropy production can be assumed to operate between the temperature levels $T_{fh}$ on the hot side and $T_{fc}$ on the cold side, in the same way as for the cyclic engine in Secs. I and II. However, the $T_{fj}$ do not necessarily denote temperatures of a working fluid, but now are conceived to be mere contact temperatures of an internal heat engine which are independent of time. They are connected by heat conductances $\kappa_h$ and $\kappa_c$ to the reservoirs $T_h$ and $T_c$ as single source of irreversibility. If in addition, the internal engine is no longer considered to be lossless, but includes internal irreversible entropy generations $s_{ij}$, $j = h, c,$ $a$ in the form of Eqs. (32), the system may be called pseudo-endoreversible:

$$q_h = T_{fh}(\Delta s_{\text{i}h} - s_{\text{i}h}), \quad q_c = T_{fc}(-\Delta s_{\text{i}c} - s_{\text{i}c}),$$
$$\Delta s_{\text{i}c} = \Delta s_{\text{i}h} + s_{\text{i}a}. \tag{35}$$

The internal reversible entropy parts $\Delta s_{ij}$ can differ from the $\Delta s_j$ of the complete system in Eqs. (32). The external heat flows $q_j$, however, are the same for the complete engine in Eqs. (32) and for the internal engine in Eqs. (35):

$$q_h = \kappa_h(T_h - T_{fh}), \quad q_c = \kappa_c(T_c - T_{fc}), \tag{36}$$

with generally temperature-dependent $\kappa_j\,(T_{fj}, T_j)$. In the case of an ideal internal engine, the $s_i j$ are zero and $\Delta s_{ic} = \Delta s_{ih} = \Delta s$. Thus, $q_h = T_{fh}\Delta s$, $q_c = -T_{fc}\Delta s$, and the usual endoreversibility condition $q_h/T_{fh} = -q_c/T_{fc}$ is fulfilled [1].

Using (35) for the $T_{fj}$, $j = h, c$, Eqs. (36) yield $q_j = \kappa_j T_j(\pm\Delta s_{ij} - s_{ij})/(\pm\Delta s_{ij} + \kappa_j - s_{ij})$ with $\pm =$"+" for $j = h$ and "–" for $j = c$. Inserting these expressions for $q_j$ into Eqs. (32), the $s_j$ irreversibilities for the complete engine can be inferred:

$$s_j = \frac{\Delta\hat{s}_j^2}{\kappa_j(T_{fj}, T_j) \pm \Delta\hat{s}_j}, \quad j = h, c$$
$$\Delta\hat{s}_h = \Delta s_{\text{i}h} - s_{\text{i}h}, \Delta\hat{s}_c = \Delta s_{\text{i}c} + s_{\text{i}c}. \tag{37}$$

The $\Delta\hat{s}_j$ can be shown to be identical to the $\Delta s_j$ of Eq. (32). From Eqs. (35) $q_j/T_{fj} = \pm\Delta s_{ij} - s_{ij} = \pm\Delta\hat{s}_j$, where $q_j/T_{fj}$ are the entropy flows to or from the internal engine. It can be shown that $q_j/T_{fj} = \pm\Delta s_j$ and therefore $\Delta\hat{s}_j = \Delta s_j$. This is supported by summing up all sources of irreversible entropy production. For the heat conductances $\kappa_j$ in analogy to Eq. (9), the entropy production rates are

$$s_{\kappa j} = q_j\left(\frac{1}{T_{fj}} - \frac{1}{T_j}\right) = \kappa_j \frac{(T_j - T_{fj})^2}{T_{fj}\,T_j}, \quad j = h, c. \tag{38}$$

The total irreversible entropy production of the internal engine is obtained in the same way as in Eq. (33):

$$s_{\text{i}\,ir} = -q_h/T_{fh} - q_c/T_{fc} = s_{\text{i}h} + s_{\text{i}c} + s_{\text{i}a}, \tag{39}$$

and the sum of Eqs. (38) and (39) gives the total irreversibility of the full system in Eq. (33): $s_{\kappa h} + s_{\kappa c} + s_{i,ir} = s_{\text{irr}} = s_h + s_c + s_a$. Thus, the $s_{\kappa j}$ and the internal $s_{\text{i},ir}$ have to be identified with the $s_j$ and $s_a$ entropies of the complete system in Eqs. (32):

$$s_h = s_{\kappa h}, s_c = s_{\kappa c}, s_a = s_{i,ir}. \quad (40)$$

Equations (32) with the expressions (38) for $s_j = s_{\kappa j}$ yield

$$\pm\Delta s_j = q_j/T_j + s_j = q_j/T_{fj} = \kappa_j(T_j/T_{fj} - 1), \quad (41)$$

which proves the relation $\pm\Delta s_j = q_j/T_{fj} = \pm\Delta\hat{s}_j$ with the help of Eq. (35). The difference $\Delta s_c$–$\Delta s_h = s_a$ leads to a "pseudo-endoreversibility condition" for the case of $s_a = s_{i,ir} \neq 0$:

$$s_a = -q_h/T_{fh} - q_c/T_{fc} = -\kappa_h(T_h/T_{fh} - 1) - \kappa_c(T_c/T_{fc} - 1) \quad (42)$$

In the first part of Eq. (41), replacing $q_j$ by $\pm\Delta s_j T_{fj}$ leads to $s_j = \pm\Delta s_j(1–T_{fj}/T_j)$, and by eliminating $T_{fj}/T_j$ with the help of the second part of Eq. (41) again Eq. (37) is confirmed. In the case of $s_a = s_{i,ir} = 0$ with $s_{ij} = 0$, the relations hold: $\Delta s_c = \Delta s_h = \Delta s_{ic} = \Delta s_{ih} = \Delta s$ for a fully endoreversible model description.

Equation (37) for $s_j$ can be compared with Eq. (6) for endoreversible Carnot cycles. The essential difference is the missing factor $t_j$ for the isothermal transit time. For the Carnot cycle, $T_{fj}$ is adapted for different $t_j$ by Eq. (7), so that $\Delta S$ stays constant. This is no longer the case in steady state for the $\Delta s_j$ in Eqs. (37) and (41), and $\Delta s_j$ directly depends on the contact temperatures $T_{fj}$ of the internal engine.

The power output $P = q_h + q_c$ to be maximized can be expressed by (36) with $T_{fh}$, and $T_{fc}$ as variables to be optimized, which however are not independent due to the pseudo-endoreversibility condition (42): $q_h/T_{fh} = -q_c/T_{fc}–s_a$ which can be used in (36) in order to eliminate $T_{fc}$ by

$$T_{fc} = \frac{\kappa_c T_c}{\kappa_c + \kappa_h - s_a - \kappa_h T_h/T_{fh}}.$$

The right-hand side can still depend on $T_{fc}$ for temperature-dependent $\kappa_j$ and also $s_a$ may depend on the $T_{fj}$. Nevertheless, $P = q_h + q_c$ expressed in this way is correct. However, when maximizing $P$ with respect to $T_{fh}$, unspecified temperature dependences of $\kappa_j$ and $s_a$ cannot be taken into account. For constant $\kappa_j$ and $s_a$, the optimized $T_{fh}$ is

$$T_{fh} = \frac{\kappa_c\sqrt{T_h T_c} + \kappa_h T_h}{\kappa_c + \kappa_h - s_a}, \quad (43)$$

which includes the result of Ref. [20] for $\kappa_c \to \infty$, even for internal irreversibility $s_a > 0$. When utilizing Eq. (43) for $P_{\max}$, the result emerges:

$$P_{\max} = \frac{(\sqrt{T_h} - \sqrt{T_c})^2 - s_a(T_h/\kappa_c + T_c/\kappa_h)}{1/\kappa_h + 1/\kappa_c - s_a/(\kappa_c\kappa_h)}. \quad (44)$$

Also for $s_a = 0$, this steady-state result differs essentially in the denominator from that for the endoreversible cycle [1,15]:

$$P_{\max CA} = \frac{(\sqrt{T_h} - \sqrt{T_c})^2}{(\sqrt{1/\kappa_h} + \sqrt{1/\kappa_c})^2}.$$

It can be shown that $P_{\max}$ in Eq. (44) is a monotonous decreasing function for increasing $s_a$, and $P_{\max}$ will become negative (i.e., invalid) before the singularity for zero denominator is reached.

For $\eta_{P\max} = 1 + q_c/q_h$, one obtains

$$\eta_{P\max} = \frac{(1 - \sqrt{T_c/T_h})^2 - s_a[1/\kappa_c + (T_c/T_h)/\kappa_h]}{1 - \sqrt{T_c/T_h} - s_a/\kappa_c},$$

which coincides with the CA efficiency (4), if $s_a = 0$.

For maximized power, the variables $q_j$, $\Delta s_j$, and $s_j$ can be expressed solely by the $\kappa_j$, $T_j$, and $s_a$ by eliminating the $T_{fj}$ variables. The relation $q_h/T_{fh} = -q_c/T_{fc}–s_a$ from (42) can be solved with the help of Eqs. (36) and (43) for $T_{fc}$:

$$T_{fc} = \frac{\kappa_h\sqrt{T_h T_c} + \kappa_c T_c}{\kappa_c + \kappa_h - s_a}.$$

Thus, for the heat flows $q_j$ and $\pm\Delta s_j = q_j/T_{fj}$,

$$q_j = \frac{T_j - \sqrt{T_c T_h} - s_a T_j\,\kappa_j/(\kappa_c\kappa_h)}{1/\kappa_c + 1/\kappa_h - s_a/(\kappa_c\kappa_h)},$$

$$\Delta s_j = \frac{\sqrt{T_h} - \sqrt{T_c} \mp s_a\sqrt{T_j}\,\kappa_j/(\kappa_c\kappa_h)}{\sqrt{T_c}/\kappa_h + \sqrt{T_h}/\kappa_c}, \quad j = h, c.$$

It is easily verified that $\Delta s_c$–$\Delta s_h = s_a$ is satisfied, as required by Eq. (32). Now the $s_j$ from Eq. (37) for maximized power read

$$s_h = \frac{[(1 - s_a/\kappa_c)\sqrt{T_h} - \sqrt{T_c}]^2}{\sqrt{T_h}(1 + \kappa_h/\kappa_c - s_a/\kappa_c)\,(\sqrt{T_c}/\kappa_h + \sqrt{T_h}/\kappa_c)}$$

$$s_c = \frac{[(1 - s_a/\kappa_h)\sqrt{T_c} - \sqrt{T_h}]^2}{\sqrt{T_c}(1 + \kappa_c/\kappa_h - s_a/\kappa_h)\,(\sqrt{T_c}/\kappa_h + \sqrt{T_h}/\kappa_c)}.$$

Since the heat engine in steady state is connected simultaneously to both heat reservoirs $T_h$ and $T_c$, it is important to take into account leakage heat currents—caused, e.g., by the engine's housing—which contribute to irreversible entropy production. The leakage heat current $\lambda$ can be described generally by a temperature-dependent heat conductance $\kappa_L(T_h, T_c)$:

$$\lambda(T_h, T_c) = \kappa_L(T_h, T_c)\,(T_h - T_c). \quad (45)$$

The $q_h$ and $q_c$ from Eqs. (36) are thus altered to $q'_h$, $q'_c$:

$$q'_h = \kappa_h(T_h - T_{fh}) + \kappa_L(T_h - T_c),$$
$$q'_c = \kappa_c(T_c - T_{fc}) - \kappa_L(T_h - T_c).$$

Again, generated power is $P = q'_h + q'_c = q_h + q_c$, since the heat leakage currents on hot and cold side compensate exactly. Therefore, the procedure for maximizing $P$ leads to the same result for $T_{fh}$ and $P_{\max}$ as in Eqs. (43) and (44). However, the result for efficiency $\eta_{P\max L} = P_{\max}/q'_h$ is reduced, because of increased heat absorption in $q'_h$:

$$\eta_{P\max L} = \frac{\eta_{CA}^2 - s_a[1/\kappa_c + (T_c/T_h)/\kappa_h]}{\eta_{CA} + \kappa_L\eta_C(1/\kappa_h + 1/\kappa_c) - s_a(\kappa_h + \kappa_L\eta_C)/(\kappa_h\kappa_c)} \quad (46)$$

For $\kappa_L \to 0$ and $s_a \to 0$, $\eta_{CA}$ of Eq. (4) is obtained. Generally $\eta_{P\max L}$ is no longer independent from the dissipations $\kappa_c$ and $\kappa_h$, neither for $s_a = 0$.

Equations (32) with inclusion of the additional irreversible heat leakage (45), read

$$q'_h = T_h(\Delta s_h - s'_h), \quad q'_c = T_c(-\Delta s_c - s'_c),$$

where

$$s'_h = s_h - \lambda(T_h, T_c)/T_h, s'_c = s_c + \lambda(T_h, T_c)/T_c. \quad (47)$$

It is obvious from Eq. (47) that for sufficiently large $\lambda(T_h, T_c)$, $s'_h$ can become negative, whereas $s'_c$ is increased by a larger amount, since $T_h > T_c$. This does not violate the second law of thermodynamics, since the sum of $s'_h$ and $s'_c$ plus internal $s_a$ constitutes the overall entropy generation rate $s'_{\rm irr} = s'_h + s'_c + s_a$ and for the same time points only $s'_{\rm irr} \geqslant 0$ is required. In case of the Carnot cycle, $S_c(t_c)$, $S_h(t_h) \geqslant 0$ is required, since both conditions apply separately, because those entropies are generated at different times, when the engine is either connected to the cold or hot reservoir. From Eqs. (45) and (47),

$$s'_{\rm irr} = s_{\rm irr} + \lambda/T_c - \lambda/T_h = s_{\rm irr} + \kappa_L(T_h - T_c)^2/T_cT_h \geqslant 0, \quad (48)$$

and the $\kappa_L$ -entropy term is always a positive contribution.

In the refrigerator or heat-pump mode, the heat engine works in the reverse direction with $\Delta s_j \to -\Delta s_j$ for either $j = h$ or $j = c$ [cf. discussion following Eq. (17)] and unaltered sign for $s_{\rm irr}$, $s_a$, and $s'_{\rm irr}$. The engine then ejects heat $q'_h < 0$ to the $T_h$ reservoir and absorbs heat $q'_c > 0$ from the $T_c$ reservoir. Thus, necessarily $|\Delta s_c| > s'_c$ and the size of $\lambda(T_h, T_c)$ is limited by this condition, or equivalently by $q_c > \lambda(T_h, T_c)$.

## IV. THERMOELECTRIC CONVERTERS

In this section the theory of thermoelectric (TE) converters will be treated with special consideration of reversible and irreversible entropy production rates in the form of Eq. (32). Both one-dimensional (1D) and three-dimensional (3D) device theory will be considered for general position- and temperature-dependent material parameters. The definition of reversible entropy production as part of total entropy generation so far has only been given for constant material properties (CMP) in 1D, e.g., Refs. [30,31]. The thermal transconductance is often set to zero in the CMP literature and thermal contact resistances and heat leakage currents are included by an additional equivalent circuit. The present approach includes thermal and electrical contact and bulk resistances by taking into account arbitrary device profiles for thermal and electrical conductivities. The effect of inhomogeneous Seebeck coefficient in the device volume gives rise to additional Thomson-Peltier heating or cooling and is of particular importance with respect to reversible and irreversible entropies.

### A. General 3D TE device theory

The starting point for the theory is a steady-state equation for the total heat flux (heat-flow density), which following the Onsager–deGroot–Callen theory [22–24,32–34] includes the Fourier heat flow proportional to the temperature gradient $\nabla T(x)$ and heat transport by electron particle flow (Peltier heat) in an arbitrary volume $V$. With electric current density $\boldsymbol{j}$ $(x)$ the total heat flux at position $x$ is given by

$$\boldsymbol{q}(x) = -k(x, T(x))\ \nabla T(x) + \ T(x)\ \boldsymbol{j}(x)\ \alpha(x, T(x))\ . \quad (49)$$

The heat-flux vector $\boldsymbol{q}$ $(x)$ here denotes the heat flow per unit area at location $x$, contrary to the heat flows $q_j$, $j = h, c$ in Sec. III. The symbol $x$ denotes the spatial coordinates $(x, y, z)$ in the 3D case within the device volume $V$, or only $x$ in the 1D case. The electric current flux vector $\boldsymbol{j}$ is associated with the Peltier heat flux $T\boldsymbol{j}\alpha$ in the volume. Generally, the material properties of thermal conductivity $k$, electric resistivity $\rho$, and thermopower (Seebeck coefficient) $\alpha$ of the material simultaneously depend on location $x$ and temperature $T(x)$ at that location, i.e., $k(x, T(x))$, $\rho(x, T(x))$, and $\alpha(x, T(x))$ for the description of different materials at different locations in the volume [35–37]. The individual materials only depend on $T$. The divergence of the heat flux turns out to be

$$\nabla \cdot \boldsymbol{q}(x) = \rho(x, T(x))\ \boldsymbol{j}(x)^2 + \boldsymbol{j}(x)\ \alpha(x, T(x)) \cdot \nabla T(x). \quad (50)$$

The first term on the right-hand side is the electric Joule heating $\rho \boldsymbol{j}^2$. The second term is the generated electric power density, which in part is converted into Joule heat. Inserting (49) in Eq. (50) leads to the heat balance or thermoelectric equation:

$$\nabla(-k(x, T)\ \nabla T(x)) = \rho(x, T)\ \boldsymbol{j}(x)^2 - T(x)\ \nabla(\boldsymbol{j}(x)\ \alpha(x, T)) \quad (51)$$

This can be interpreted as a classical Fourier heat-conduction equation with the divergence of the Fourier heat flux on the left-hand side and Joule heat and Thomson–Peltier heat generation or cooling terms on the right-hand side. Usually electric current conservation requires $\nabla \boldsymbol{j}(x) = 0$. In Refs. [35–37] a more general theory has been presented for the inclusion of arbitrarily distributed electric sources and sinks from external circuits, e.g., for the description of cascaded TE converters. Then $\nabla \boldsymbol{j}(x) = c(x)$ is a prescribed function. This current condition together with Eq. (51) can be condensed into two partial differential equations for the fields of electrochemical potential $\varphi(x)$ and $T(x)$, which for appropriate boundary conditions defines the solutions $T(x)$ and $\boldsymbol{j}$ $(x)$ uniquely [36]. $\varphi(x)$ is related to $\boldsymbol{j}(x)$ by $-\nabla\varphi = \boldsymbol{E} = \rho \boldsymbol{j} + \alpha \nabla T$. The genuine local electric field $\rho \boldsymbol{j}$, arising from ohmic voltage drop, cannot always be expressed as a gradient in the 3D case, since rot $(\rho \boldsymbol{j})$ may differ from zero, contrary to the $\boldsymbol{E}$ field. The mentioned solution strategy for $\varphi(x)$ and $T(x)$ was not used in Refs. [35–37], since the product $\boldsymbol{j}$ $\alpha(x)$ was considered as single vector function to be optimized for maximization of generator or refrigerator performance (output power, cooling power, efficiencies) with given TE figure of merit $Z = \alpha^2/(k\rho)$. Thus, the more general problem of simultaneous optimization of material distribution and electric current distribution with $\nabla$ $\boldsymbol{j}$ $(x) \neq 0$ in 3D was treated.

In the following, electric current conservation $\nabla \boldsymbol{j}(x) = 0$ is assumed. The general 3D device volume $V$ has by definition on its surface $\partial V$ two disjoint thermal and electric contact areas $a_h$ and $a_c$ of arbitrary shape, connected to hot and cold heat reservoirs of temperature $T_h$ and $T_c$, respectively. The remaining parts of $\partial V$ constitute the device sidewalls $\partial V_S$ with zero boundary condition for heat flow through the sidewalls:

$$\boldsymbol{q}(a)\boldsymbol{n}(a) = 0 \quad \text{for} \quad a \in \partial V_S. \quad (52)$$

$\boldsymbol{n}$ $(a)$ denotes the unit outward vector normal to the sidewall. Dirichlet conditions are required on the contact areas $a_h$, $a_c$ : $T(a) = T_h$ for $a \in a_h$, $T(a) = T_c$ for $a \in a_c$. Similarly, for the electric current $\boldsymbol{j}(x)$ the boundary conditions hold:

$$\boldsymbol{j}(a)\boldsymbol{n}(a) = 0 \quad \text{for } a \in \partial V_{S,}$$
$$i = -\int_{ah} \boldsymbol{j}(a) d\boldsymbol{a} = \int_{ac} \boldsymbol{j}(a) d\boldsymbol{a}, \tag{53}$$

with $i$ the electric current entering at contact $a_h$ and leaving at $a_c$. Here $d\boldsymbol{a}$ is an infinitesimal surface element of areas $a_h$ or $a_c$ directed in normal outward direction. In addition it is assumed that the contact region $a_h$ and $a_c$ are electric equipotential surfaces for the applied outside voltages, i.e., contacts of metallic character. By use of Eq. (49), the heat inflow $q_h$ through contact area $a_h$ and heat outflow $q_c$ through area $a_c$ can be written as

$$q_h = -\int_{ah} \boldsymbol{q}(a) \cdot d\boldsymbol{a} = \int_{ah} [k(a, T_h)\, \nabla T(a) - T_h\, \boldsymbol{j}(a)\, \alpha(a, T_h)]\, d\boldsymbol{a}, \tag{54}$$

$$q_c = -\int_{ac} \boldsymbol{q}(a) \cdot d\boldsymbol{a} = \int_{ac} [k(a, T_c)\, \nabla T(a) - T_c\, \boldsymbol{j}(a)\, \alpha(a, T_c)]\, d\boldsymbol{a}. \tag{55}$$

The sign convention for $q_j$ in Eqs. (54) and (55) is chosen in such a way to coincide with Sec. III for general steady-state engines, i.e., $q_h$ is positive and $q_c$ is negative in the generator mode.

In the generator mode the generated electric power $P_{el}$ converted from heat to electricity is again given by $P_{el} = q_h + q_c$, or with the help of Eqs. (50), (52), (54), and (55):

$$P_{el} = q_h + q_c = -\int_{\partial V} \boldsymbol{q}(a)\, d\boldsymbol{a} = -\int_V \nabla \boldsymbol{q}(x)\, d^3x = \int_V [-\boldsymbol{j}(x)\alpha(x, T(x))\, \nabla T(x) - \rho(x, T(x))\boldsymbol{j}(x)^2]\, d^3x. \tag{56}$$

The generator efficiency $\eta$ is defined by the ratio of $P_{el}$ and heat inflow $q_h$ from the hot-side $T_h$ reservoir:

$$\eta = \frac{P_{el}}{q_h} = \frac{\int_V \left[-\boldsymbol{j}(x)\alpha(x, T(x))\, \nabla T(x) - \rho(x, T(x))\boldsymbol{j}(x)^2\right]\, d^3x}{\int_{ah} [k(a, T_h)\, \nabla T(a) - T_h\, \boldsymbol{j}(a)\, \alpha(a, T_h)]\, d\boldsymbol{a}}. \tag{57}$$

For the cooling mode, the electric current density $\boldsymbol{j}$ is reversed and the heat flux $\boldsymbol{q}$ enters through the $a_c$ contact and leaves through the $a_h$ contact. On average $\boldsymbol{q}$ then is in opposite direction to the Fourier heat flux $-k\nabla T$ by reason of the dominating Peltier heat flux $T\boldsymbol{j}\alpha$.

For the description of entropy production, the concept of entropy current density $\boldsymbol{j_s}(x) = \boldsymbol{q}(x)/T(x)$ can be formally introduced [24,32–34]. However, it should be noticed that the current $\boldsymbol{j_s}$ is not governed by a continuity equation, as, e.g., for electric charge, since $\nabla \boldsymbol{j_s}(x,t) \neq -\partial s(x,t)/\partial t$, where $s(x,t)$ is the local entropy density. In steady state $\partial s/\partial t = 0$, whereas $\nabla \boldsymbol{j_s}(x) \neq 0$ can hold and contributes to overall entropy generation. The situation can rather be compared with the heat conduction equation $c_v \partial T(x,t)/\partial t + \nabla(-k\nabla T(x,t)) = H_{\text{gen}}(x,t)$, with $c_v$ as material's specific heat capacity and $H_{\text{gen}}$ a heat generation density at position $x$. In steady state $c_v \partial T/\partial t = 0$ and $H_{\text{gen}}(x)$ is the analog to an entropy generation rate per unit volume denoted by $\nabla \boldsymbol{j_s}(x)$ and whose integral over volume $V$ gives the total irreversible entropy generation rate including heat flows from the reservoirs to the TE engine. The TE engine itself does not change its entropy content with time.

Thus, with the help of Eqs. (49) and (50), the irreversible entropy production rate of the TE device is given by

$$\begin{aligned} s_{\text{irr}} &= \int_V \nabla \boldsymbol{j_s}(x)\, d^3x \\ &= \int_V \nabla \frac{\boldsymbol{q}(x)}{T(x)}\, d^3x = \int_V \left[\frac{\rho\, \boldsymbol{j}(x)^2}{T(x)} + k\left(\frac{\nabla T(x)}{T(x)}\right)^2\right] d^3x \\ &= \int_{\partial V} \frac{\boldsymbol{q}(a)}{T(a)} d\boldsymbol{a} = -\frac{q_h}{T_h} - \frac{q_c}{T_c}. \end{aligned} \tag{58}$$

This result is valid for general spatial and temperature-dependent material functions $k(x, T(x))$, $\rho(x, T(x))$. An expression similar to the second line of Eq. (58) has been presented for the 1D case in Refs. [38,39]. For the surface integral form of $s_{\text{irr}}$ in (58), Eqs. (54) and (55) have been used for the heat flows $q_j$. This form is equivalent to Eq. (33) for general steady-state heat engines. The contribution $T\ \boldsymbol{j}\ \alpha(a, T)$ in the surface integrals of (54) and (55) can be made to disappear by a thin metallic layer with $\alpha(a, T) = 0$ at the contact boundaries. However, this will be nearly compensated by altered $k(a, T)\nabla T(a)$ with unknown $\nabla T(a)$. The determination of $\nabla T(a)$ requires solution of the thermoelectric Eq. (51) for $T(x)$.

A methodology for the solution $T(x)$ of Eq. (51) satisfying $\nabla \boldsymbol{j}(x) = 0$ can start by scaling the electric contact current $i$ with an arbitrary dimensionless factor $\mu$. Since the internal current density $\boldsymbol{j}(x)$ influences the temperature distribution $T(x)$, the knowledge of the scaling of $\boldsymbol{j}(x)$ with $\mu$ or $i$ is also required. In cases of sufficiently symmetric volume $V$ and material distributions in it, $\boldsymbol{j}(x)$ is proportional to $i$ and can be written as $\boldsymbol{j}(x) = \mu \boldsymbol{u}(x)$ with a normalized current distribution $\boldsymbol{u}(x)$ with $\nabla \boldsymbol{u}(x) = 0$ corresponding to a complete solution of the partial differential equation system for $T(x)$, $\varphi(x)$. In particular for 1D geometries with inhomogeneous material distribution, $\boldsymbol{j}(x) = \mu \boldsymbol{u}$ is always valid, since then $\boldsymbol{j}(x)$ is constant everywhere. In the most general case, $\boldsymbol{j}(x) = \Sigma_{n=0} \mu^n \boldsymbol{u}_n(x)$ with $\boldsymbol{u}_0(x) \neq 0$, i.e., there may be internal eddy currents, also for zero contact current $i$. The temperature $T(x)$ in (51) can be expanded in powers of $\mu$:

$$T(x) = \sum_{n=0}^{\infty} t_n(x)\, \mu^n, \tag{59}$$

where $t_0(x)$ corresponds to the solution of Eq. (51) for $i, \boldsymbol{j} = 0$, i.e., to the temperature distribution for pure Fourier heat flux: $-k[x, t_0(x)]\nabla t_0(x)$. Then, following Eqs. (52) and (53), $t_0(x)$ satisfies the boundary conditions $\nabla t_0(a)\boldsymbol{n}(a) = 0$ for $a \in \partial V_S, t_0(a) = T_h$ for $a \in a_h, t_0(a) = T_c$ for $a \in a_c$. Since the expansion (59) is valid for a continuous region of $\mu$, all other $t_n(x)$ satisfy $\nabla t_n(a)\boldsymbol{n}(a) = 0$ for $a \in \partial V_S$ and $t_n(a) = 0$ for $a \in a_h, a_c$, i.e., $t_n$ for $n \geqslant 1$ has only zero boundary conditions.

In the following, $\boldsymbol{j}(x) = \mu \boldsymbol{u}(x)$ will be assumed for TE devices with sufficient symmetry. Inserting the $T(x)$ expansion (59) into Eqs. (54) and (55) and sorting terms with respect to powers of $\mu$, only consideration of the $\nabla T(a)$ terms is necessary. For the contact heat flows $q_j$, coefficients $q_{j,n}$ arise with $q_j = \Sigma_{n=0} q_{j,n}\mu^n$ for $j = h, c$:

$$q_{j,0} = \int_{aj} k(a, T_j)\, \nabla t_0(a)\, d\boldsymbol{a}$$

$$q_{j,1} = \int_{aj} (k(a, T_j)\, \nabla t_1(a) - T_j\, \boldsymbol{u}(a)\, \alpha(a, T_j))\, d\boldsymbol{a}$$

$$q_{j,m} = \int_{aj} k(a, T_j)\, \nabla t_m(a)\, d\boldsymbol{a} \quad \text{for m} \geqslant 2. \tag{60}$$

The surface gradient terms $\nabla t_m(a)$ in the above integrals are unknown and have to be determined by solution of a recursive equation system by sorting Eq. (51) in powers of $\mu$ by utilizing Eq. (59). In the case of temperature-independent material parameters $k(x)$, $\rho(x)$, and $\alpha(x)$, this can be easily done:

$$\begin{aligned}
&\nabla(-k(x)\, \nabla t_0(x)) = 0 \quad \text{for } n = 0,\\
&\nabla(-k(x)\, \nabla t_1(x)) = -t_0(x)\, \boldsymbol{u}(x)\, \nabla\alpha(x) \quad \text{for } n = 1,\\
&\nabla(-k(x)\, \nabla t_2(x)) = -t_1(x)\, \boldsymbol{u}(x)\, \nabla\alpha(x)\\
&\qquad\qquad + \rho(x)\, \boldsymbol{u}(x)^2 \quad \text{for } n = 2,\\
&\nabla(-k(x)\, \nabla t_n(x)) = -t_{n-1}(x)\, \boldsymbol{u}(x)\, \nabla\alpha(x) \quad \text{for n} > 2.
\end{aligned} \tag{61}$$

For Seebeck functions $\alpha(x, T(x))$ with additional $T$ dependence and still only spatially dependent $\rho(x)$ and $k(x)$, the right-hand sides of the recursive equation system (61) for the coefficient functions $t_m(x)$ become much more complicated. In order to express $T\nabla\alpha(x, T(x))$ in the last term of Eq. (51),

$$\begin{aligned}
\boldsymbol{j}T(x)\nabla a(x, T(x)) = \boldsymbol{j}T(x)[\nabla_1 a(x, T(x))\\
+\partial a(x, T)/\partial T\, \nabla T(x)],
\end{aligned} \tag{62}$$

by a power series in $\mu$, the terms with $\alpha(x, T(x))$ have to be first expanded in powers of $T(x)–t_0(x) = \Sigma_{n=1} t_n(x)\mu^n$:

$$\begin{aligned}
&\frac{\partial}{\partial T}\alpha\left(x, t_0(x) + \sum_{n=1}^{\infty} t_n(x)\, \mu^n\right)\\
&= \sum_{\nu=0}^{\infty} b_\nu[x, t_0(x)] \left[\sum_{n=1}^{\infty} t_n(x)\, \mu^n\right]^\nu,
\end{aligned}$$

where $b_\nu[x, t_0(x)] = \alpha^{(\nu+1)}[x, t_0(x)]/\nu!$ and $\alpha^{(m)}(x, T)$ denotes the $m$th derivative of $\alpha(x, T)$ with respect to $T$. By use of

$$\left[\sum_{n=1}^{\infty} t_n(x)\, \mu^n\right]^\nu = \sum_{m=0}^{\infty} a_{\nu\, m}(x)\, \mu^m \text{ with } a_{00} = 1, a_{0m} = 0$$

for $m > 0$, $a_{\nu m} = 0$ for $m < \nu$ and else $a_{\nu\, m}(x) = \sum_{\substack{\lambda1,\lambda2,\ldots,\lambda\nu \geqslant 1\\ \lambda1+\lambda2+\ldots+\lambda\nu = m}}^{m+1-\nu} t_{\lambda1}(x)\, t_{\lambda2}(x) \ldots t_{\lambda\nu}(x)$, one obtains

$$\alpha^{(1)}\left(x, \sum_{n=0}^{\infty} t_n(x)\, \mu^n\right) = \sum_{m=0}^{\infty} A_m(x)\mu^m,$$

$$A_m(x) = \sum_{\nu=0}^{m} b_\nu\, a_{\nu\, m}(x).$$

Hence,

$$\nabla\alpha(x, T(x)) = \nabla_1\alpha(x, T(x)) + \nabla T(x) \sum_{m=0}^{\infty} A_m(x)\mu^m.$$

The last term in (62) is a product of three power series in $\mu$:

$$\begin{aligned}
&\boldsymbol{j}(x)T(x)\alpha^{(1)}\nabla T(x)\\
&= \mu\, \boldsymbol{u}(x) \sum_{n=0}^{\infty} t_n(x)\mu^n \sum_{m=0}^{\infty} A_m(x)\mu^m \sum_{p=0}^{\infty} \nabla t_p(x)\mu^p\\
&= \mu\, \boldsymbol{u}(x) \sum_{m=0}^{\infty} \boldsymbol{B}_{T,m}(x)\mu^m,
\end{aligned}$$

$$\boldsymbol{B}_{T,m}(x) = \sum_{n=0}^{m} \sum_{p=0}^{n} t_p(x)\nabla t_{n-p}(x)\, A_{m-n}(x). \tag{63}$$

Quite similarly follows for the term $\nabla_1\alpha(x, T)$:

$$\nabla_1\alpha(x, T(x)) = \sum_{m=0}^{\infty} \boldsymbol{A}_{x,m}(x)\mu^m,$$

$$\boldsymbol{A}_{x,m}(x) = \sum_{\nu=0}^{m} \boldsymbol{b}_{x,\nu}\, a_{\nu\, m}(x),$$

$\boldsymbol{b}_{x,\nu} = \nabla_1\alpha^{(\nu)}(x, t_0(x))/\nu!$, and thus

$$\begin{aligned}
\boldsymbol{j}(x)\, T(x)\, \nabla_1\alpha(x, T(x)) &= \mu\, \boldsymbol{u}(x) \sum_{n=0}^{\infty} t_n(x)\mu^n \sum_{m=0}^{\infty} \boldsymbol{A}_{x,m}(x)\mu^m\\
&= \mu\, \boldsymbol{u}(x) \sum_{m=0}^{\infty} \boldsymbol{B}_{x,m}(x)\mu^m,
\end{aligned}$$

$$\boldsymbol{B}_{x,m}(x) = \sum_{n=0}^{m} t_n(x)\, \boldsymbol{A}_{x,m-n}(x). \tag{64}$$

With $\boldsymbol{B}_n(x) = \boldsymbol{B}_{x,n}(x) + \boldsymbol{B}_{T,n}(x)$, Eq. (62) reads $\boldsymbol{j}T(x)\nabla\alpha = \boldsymbol{j}\Sigma_{n=0}\boldsymbol{B}_n(x)\mu^n$ and the equation system for the $t_m(x)$ is

$$\begin{aligned}
&\nabla(-k(x)\, \nabla t_0(x)) = 0 \quad \text{for } n = 0,\\
&\nabla(-k(x)\, \nabla t_1(x)) = -\boldsymbol{u}(x)\, \boldsymbol{B}_0(x) \quad \text{for } n = 1,\\
&\nabla(-k(x)\, \nabla t_2(x)) = -\boldsymbol{u}(x)\, \boldsymbol{B}_1(x) + \rho(x)\, \boldsymbol{u}(x)^2 \quad \text{for } n = 2,\\
&\nabla(-k(x)\, \nabla t_n(x)) = -\boldsymbol{u}(x)\, \boldsymbol{B}_{n-1}(x) \quad \text{for } n \geqslant 2.
\end{aligned} \tag{65}$$

The $\boldsymbol{B}_n(x)$ vector functions only contain the coefficients $t_m(x)$ and $\nabla t_m(x)$ up to order $n$ so that the system (65) is a recursive one. The low-order functions $A_m(x)$ and $\boldsymbol{B}_{T,m}(x)$ can be derived from Eqs. (63):

$$A_0(x) = b_0(x, t_0(x)), \quad A_1(x) = b_1 t_1(x),$$
$$A_2(x) = b_1 t_2 + b_2 t_1^2, \quad A_3(x) = b_1 t_3 + 2b_2 t_1 t_2 + b_3 t_1^3,$$
$$B_{T,0}(x) = t_0(x)\nabla t_0(x) A_0(x),$$
$$\boldsymbol{B}_{T,1}(x) = (t_0\nabla t_1 + t_1\nabla t_0) A_0(x) + t_0\nabla t_0 A_1(x),$$
$$\boldsymbol{B}_{T,2}(x) = (t_0\nabla t_2 + t_1\nabla t_1 + t_2\nabla t_0) A_0(x) + (t_0\nabla t_1 + t_1\nabla t_0) A_1(x) + t_0\nabla t_0 A_2(x),$$

and for $\boldsymbol{A}_{x,m}(x)$, $\boldsymbol{B}_{x,m}(x)$ from Eqs. (64):

$$\boldsymbol{A}_{x,0}(x) = b_{x,0}(x, t_0(x)), \quad \boldsymbol{A}_{x,1}(x) = \boldsymbol{b}_{x,1} t_1(x),$$
$$\boldsymbol{A}_{x,2}(x) = \boldsymbol{b}_{x,1} t_2 + \boldsymbol{b}_{x,2} t_1^2,$$
$$\boldsymbol{A}_{x,3}(x) = \boldsymbol{b}_{x,1} t_3 + 2\boldsymbol{b}_{x,2} t_1 t_2 + \boldsymbol{b}_{x,3} t_1^3$$
$$\boldsymbol{B}_{x,0}(x) = t_0(x)\boldsymbol{A}_{x,0}(x), \quad \boldsymbol{B}_{x,1}(x) = t_1\boldsymbol{A}_{x,0}(x) + t_0\boldsymbol{A}_{x,1}(x),$$
$$\boldsymbol{B}_{x,2}(x) = t_2\boldsymbol{A}_{x,0}(x) + t_1\boldsymbol{A}_{x,1}(x) + t_0\boldsymbol{A}_{x,2}(x).$$

In particular, the result is obtained for $\boldsymbol{B}_0(x)$ and $\boldsymbol{B}_1(x)$:

$$\begin{aligned}
\boldsymbol{B}_0(x) &= t_0(x)[\nabla t_0(x)\partial\alpha(x, t_0)/\partial T + \nabla_1 a(x, t_0)] \\
&= t_0(x)\nabla a(x, t_0), \\
\boldsymbol{B}_1(x) &= (t_0\nabla t_1 + t_1\nabla t_0)\partial\alpha(x, t_0)/\partial T \\
&\quad + t_0 t_1\nabla t_0\nabla^2\alpha(x, t_0)/\partial T^2 + \\
&\quad + t_1(x)\nabla_1\alpha(x, t_0) + t_0(x)t_1(x)\partial[\nabla_1\alpha(x, t_0)]/\partial T = \\
&= \nabla[t_0 t_1\partial\alpha(x, t_0)/\partial T] + t_1(x)[\nabla_1\alpha(x, t_0) \\
&\quad + t_0(x)\nabla_1\partial\alpha(x, t_0)/\partial T].
\end{aligned} \tag{66}$$

If $\alpha(x, T) = \alpha(x)$ is temperature independent, the functions $A_m(x)$ and $\boldsymbol{B}_{T,m}(x)$ are equal to zero and $\boldsymbol{A}_{x,m}(x) = 0$ for $m > 0$ with $\boldsymbol{A}_{x,0}(x) = \nabla\alpha(x)$. Thus $\boldsymbol{B}_m(x) = t_m(x)\nabla\alpha(x)$ and the equation system (61) is recovered.

The series of $P_{el} = q_h + q_c$ in powers of $\mu$ is given by $P_{el} = \Sigma_{n=0} P_n\mu^n = \Sigma_{n=0}(q_{h,n} + q_{c,n})\mu^n$ and is closely related to a relation between hot- and cold-side temperature gradients $\nabla t_m(a)$ which is obtained by Eq. (56) after partial integration of the volume integral term and use of Eqs. (54) and (55):

$$\begin{aligned}
&\int_V -\boldsymbol{j} a(x, T)\nabla T\, d^3x \\
&\quad = \int_V \boldsymbol{j}\nabla a(x, T) T\, d^3x - \int_{\partial V} \boldsymbol{j} a(a, T) T(a) d\boldsymbol{a}, \\
&\int_{\partial V} k(a, T)\nabla T(a)\, d\boldsymbol{a} \\
&\quad = \int_V [\boldsymbol{j}\,\nabla\alpha(x, T)\, T(x) - \rho(x, T)\boldsymbol{j}(x)^2]\, d^3x.
\end{aligned} \tag{67}$$

Expansion of (67) in powers of $\mu$ with $\boldsymbol{j}(x) = \mu\boldsymbol{u}(x)$ for temperature-independent function $\rho(x)$, or equivalently by integration of the equation system (65) over $V$ and utilizing (60), leads with $\int_{\partial V} = \Sigma_j \int_{aj}$ to

$$\begin{aligned}
\sum_{j=h,c} q_{j,0} &= \sum_{j=h,c} \int_{a\,j} k(a, T_j)\nabla t_0(a)\, d\boldsymbol{a} = 0, \\
\sum_{j=h,c} q_{j,1} &= \sum_{j=h,c} \int_{aj} k(a, T_j)\nabla t_1(a)\, d\boldsymbol{a} - \int_{aj} T_j\,\boldsymbol{u}\,\alpha(a, T_j)\, d\boldsymbol{a} \\
&= \int_V \boldsymbol{u}\,\boldsymbol{B}_0(x)\, d^3x - \int_{\partial V} T_j\,\boldsymbol{u}\,\alpha(a, T_j)\, d\boldsymbol{a} \\
&= -\int_V \boldsymbol{u}\,\alpha(x, t_0(x))\,\nabla t_0(x)\, d^3x \\
\sum_{j=h,c} q_{j,2} &= \sum_{j=h,c} \int_{aj} k(a, T_j)\nabla t_2(a)\, d\boldsymbol{a} \\
&= \int_V [\boldsymbol{u}\,\boldsymbol{B}_1(x) - \rho(x)\boldsymbol{u}(x)^2]\, d^3x \\
\sum_{j=h,c} q_{j,n} &= \sum_{j=h,c} \int_{aj} k(a, T_j)\nabla t_n(a)\, d\boldsymbol{a} \\
&= \int_V \boldsymbol{u}\,\boldsymbol{B}_{n-1}(x)\, d^3x \quad \text{for } n \geqslant 3.
\end{aligned} \tag{68}$$

It is interesting to note that in the special case of merely temperature-dependent $\alpha(x, T) = \alpha(T)$ and spatially-dependent $\rho(x)$, $P_{el}$ in Eq. (56) can be calculated exactly to all orders in $i$, since the series will end with the second-order term, whereas for $\alpha(x)$ the series usually includes all powers of $i$ (or $\mu$). For $\alpha(T)$ the first term in the volume integral of Eq. (56) can be written as a divergence:

$$\boldsymbol{j}(x)\alpha(T(x))\,\nabla T(x) = \nabla\left[\boldsymbol{j}(x)\int_0^{T(x)} \alpha(\tilde{T})\, d\tilde{T}\right],$$

and thus

$$\begin{aligned}
&\int_V -\boldsymbol{j}(x)\alpha(T(x))\,\nabla T(x)\, d^3x \\
&\quad = -\sum_{j=h,c} \int_0^{T_j} \alpha(\tilde{T})\, d\tilde{T} \int_{aj} \boldsymbol{j}(a)\, d\boldsymbol{a} \\
&\quad = \sum_{j=h,c} \pm\, i \int_0^{T_j} \alpha(\tilde{T})\, d\tilde{T} \\
&\quad = i \int_{T_c}^{T_h} \alpha(\tilde{T})\, d\tilde{T},
\end{aligned}$$

where Eq. (53) for the contact currents has been used. Therefore, for $P_{el}$,

$$P_{el} = i \int_{T_c}^{T_h} \alpha(\tilde{T})\, d\tilde{T} - \mu^2 \int_V \rho(x)\boldsymbol{u}(x)^2\, d^3x. \tag{69}$$

Here $\mu^2 = i^2/[\int_{aj} \boldsymbol{u}(a) d\boldsymbol{a}]^2$. Comparing the result (69) with the $P_{el}$ coefficents for the powers of $\mu$ in Eq. (68), it is obvious that all volume integrals over the $\boldsymbol{u}$ $\boldsymbol{B}_m(x)$ functions have to disappear for $m > 0$. Indeed, by writing the integrands $\boldsymbol{B}_m(x)$ as a divergence of a function that is zero on the volume boundary $\partial V$, according to Eq. (66), $\boldsymbol{B}_1(x) = \nabla[t_0 t_1\partial\alpha(t_0)/\partial T]$ and it can be shown that the higher-order $\boldsymbol{B}_m(x)$ are of a similar form with at least one factor $t_n(x)$, $n > 0$, in the boundary integrand, where $t_n(a) = 0$. A nonzero contribution is obtained only for $P_1$ in Eq. (68). With $\boldsymbol{B}_0(x) = t_0(x)\nabla\alpha(t_0(x))$, the second part of Eq. (68) reduces to the leading term of Eq. (69).

Following the general Eqs. (32) for steady-state heat engines, a definition has to be given for the reversible entropies $\Delta s_j$ of the TE converter. From the TE-entropy definition in Eq. (58), reversible entropies can be extracted by expanding $s_{\rm irr}$ in powers of the current scaling factor $\mu$. According to the last term in Eq. (51), the classical local Peltier heat generation or cooling is a reversible process in the sense of equal amounts of heat generated or absorbed by reversing the current $\boldsymbol{j}$ with unaltered magnitude. For infinitesimal $\boldsymbol{j}$, the Joule heat [first right-hand term in Eq. (51)] is negligible as second-order effect. The change of the temperature field $T(x)$ for infinitesimal $\boldsymbol{j}$ also results in a second-order effect for the Thomson-Peltier heat in the last term of Eq. (51). Expanding the third line in Eq. (58) up to first order in $\mu$ yields

$$s_{\rm irr} = s_{irr,0} + \mu\, s_{irr,1} = -\frac{q_{h,0}}{T_h} - \frac{q_{c,0}}{T_c} + \mu\left(-\frac{q_{h,1}}{T_h} - \frac{q_{c,1}}{T_c}\right),$$

where $q_{j,n}$ is defined in Eq. (60). The zero-order term of $s_{\rm irr}$ can be interpreted as arising from a heat leakage current $\lambda(T_h,T_c) = \kappa_L(T_h,T_c)(T_h–T_c)$ formed by the conserved Fourier heat flow $\lambda = q_{h,0} = –q_{c,0}$ [cf. first line in Eq. (68)] in the same way as explained in Eqs. (45)–(48). The corresponding heat conductance $\kappa_L$ is $\kappa_L(T_h,T_c) = q_{h,0}/(T_h–T_c)$ and $s_{irr,0}$ can also be written as

$$s_{\rm irr,0} = q_{h,0}(T_h - T_c)/T_cT_h = \kappa_L(T_h - T_c)^2/T_cT_h \geqslant 0.$$

The linear $s_{irr,1}$ term has to be considered as reversible entropy production, since it is proportional to $\mu$ and therefore to $i$. We are thus led to define, following Eqs. (32),

$$\Delta s_h = \mu\, q_{h,1}/T_h, \quad \Delta s_c = -\mu\, q_{c,1}/T_c,$$
$$\Delta s_c - \Delta s_h = s_a = \mu\, s_{\rm irr,1}. \tag{70}$$

It is important to note that $s_a$ is not restricted to positive values for the TE converter, since $\Delta s_j$ and $s_a$ change sign for reversed current $\mu\to-\mu$. As elucidated following Eq. (47), not all terms contributing to $s_{\rm irr}$ at the same time point are necessarily positive. Only for the total sum, $s_{\rm irr} > 0$ is required. In Sec. III, pseudo-endoreversible heat engines connected by external heat conductances to the reservoirs have been discussed with an internal engine undergoing irreversible entropy production $s_a$. In that case $\Delta s_c–\Delta s_h = s_a > 0$ is necessarily valid. The present description of TE converters does not use external conductances to connect to the environment, since those elements are now included in the "internal" engine.

According to Eq. (60), the $\Delta s_j$ can be expressed as

$$\Delta s_j = \pm\mu \int_{aj} (k(a,T_j)\,\nabla t_1(a)/T_j - \boldsymbol{u}(a)\,\alpha(a,T_j))\,d\boldsymbol{a},$$
$$s_a = -\mu \sum_{j=h,c} \int_{aj} (k(a,T_j)\,\nabla t_1(a)/T_j - \boldsymbol{u}(a)\,\alpha(a,T_j))\,d\boldsymbol{a}.$$

For $k(x,T) = k(x)$ and by use of Eqs. (65), $s_a$ can also be presented by the volume integral:

$$s_a = -\mu \int_V \nabla\,[k(x)\nabla t_1(x)/t_0(x) - \boldsymbol{u}(x)\,\alpha(x,t_0(x))]\,d^3x$$
$$= -\mu \int_V [\boldsymbol{u}\,\boldsymbol{B}_0(x)/t_0(x) - k(x)\nabla t_1(x)\nabla t_0(x)/t_0(x)^2$$
$$- \boldsymbol{u}\,\nabla\alpha(x,t_0(x))]\,d^3x.$$

Because of Eq. (66), $\boldsymbol{B}_0(x) = t_0(x)\nabla\alpha(x,t_0(x))$, and thus,

$$s_a = \mu \int_V k(x)\nabla t_1(x)\nabla t_0(x)/t_0(x)^2\,d^3x.$$

The quadratic term $\mu^2 q_{j,2}$ of $q_j$ is proportional to $i^2 = \mu^2[\int_{aj}\boldsymbol{u}(a)d\boldsymbol{a}]^2$ with the electric contact current $i$ of Eq. (53). Thus, $\mu^2 q_{j,2} = –i^2 r_j$ can be defined with $r_j$ of Ohmic dimension. Following Eq. (60), the $r_j$ can be expressed as

$$r_j = -\int_{aj} k(a,T_j)\,\nabla t_2(a)\,d\boldsymbol{a}\Big/\left[\int_{aj}\boldsymbol{u}(a)\,d\boldsymbol{a}\right]^2,$$

and for $r_h + r_c$ by Eq. (68):

$$r = \sum_{j=h,c} r_j$$
$$= \int_V [\rho(x)\boldsymbol{u}(x)^2 - \boldsymbol{u}\,\boldsymbol{B}_1(x)]\,d^3x\Big/\left[\int_{aj}\boldsymbol{u}(a)\,d\boldsymbol{a}\right]^2. \tag{71}$$

The contact heat flows $q_h$ and $q_c$ can be generally represented with the help of Eqs. (70) and (71):

$$q_h = +q_{h,0} + \Delta s_hT_h - i^2r_h + \sum_{n=3}^{\infty}\mu^n q_{h,n}$$
$$q_c = -q_{h,0} - \Delta s_cT_c - i^2r_c + \sum_{n=3}^{\infty}\mu^n q_{c,n}. \tag{72}$$

From $s_h = \Delta s_h–q_h/T_h$ and $s_c = –\Delta s_c–q_c/T_c$ and by again utilizing Eqs. (70) and (71),

$$s_j = -\frac{q_{j,0}}{T_j} + \frac{i^2\,r_j}{T_j} - \frac{1}{T_j}\sum_{n=3}^{\infty}\mu^n q_{j,n} \quad \text{for } j = h, c. \tag{73}$$

The relation (33), $s_{\rm irr} = –q_h/T_h–q_c/T_c = s_h + s_c + s_a$ stays valid. Here $s_a < 0$ can never cause $s_{\rm irr} < 0$, because according to the second line of Eq. (58), $s_{\rm irr} \geqslant 0$ and $s_{\rm irr}$ is only zero for $\boldsymbol{j} = 0$ and $T(x) = T_h = T_c$. The $q_{j,n}$ are given by Eq. (60) for general position- and temperature-dependent material functions $k(x,T)$ and $\alpha(x,T)$. The generated power $q_h + q_c$ is, by Eq. (72),

$$P_{el} = \Delta s_hT_h - \Delta s_cT_c - i^2r + \sum_{n=3}^{\infty}\mu^n(q_{h,n} + q_{c,n}). \tag{74}$$

An important conclusion can be drawn from Eqs. (60) and (61) or (65). For constant Seebeck $\alpha(x,T) = \alpha$, the $t_m(x)$ are determined by homogeneous Eqs. (61) with the exception of $t_2(x)$. Thus, by the zero boundary conditions of $t_m(x)$ for $m > 0$, $t_m(x) = 0$ for $m \geqslant 1$ and $m \neq 2$. Therefore $q_{j,m} = 0$ for $m > 2$, and Eqs. (72)–(74) for $q_j$, $s_j$, $s_{\rm irr}$, and $P_{el}$ reduce to quadratic expressions in $\mu$. The linear parts

$q_{j,1}$ of $q_j$ by Eqs. (60) and (53) then turn out to be $q_{j,1} = -\alpha T_j \int_{aj} \boldsymbol{u}(a) d\boldsymbol{a} = \pm i\alpha T_j/\mu$, and thus by utilizing Eq. (70),

$$\Delta s_h = \Delta s_c = \Delta s = i\,\alpha, \tag{75}$$

i.e., $s_a = 0$ for homogeneous distribution of the Seebeck coefficient $\alpha$ within the device volume. It is a major result that the difference of $\Delta s_h$ and $\Delta s_c$ is caused by the inhomogeneity of $\alpha$, where for $k(x)$ and $\rho(x)$ in Eq. (61) or (65) arbitrary positive functions have been used. For simplicity in Eqs. (61) and (65), no temperature dependence of $k$ and $\rho$ has been assumed, but the thesis is here established that the result (75) also holds for general $k(x, T)$ and $\rho(x, T)$ functions. $P_{el}$ reduces for constant $\alpha$ to

$$P_{el} = i\alpha(T_h - T_c) - i^2 r,$$
$$r = \int_V \rho(x)\boldsymbol{u}(x)^2\, d^3x \Big/ \left[\int_{aj} \boldsymbol{u}(a)\, d\boldsymbol{a}\right]^2. \tag{76}$$

The expression for $r$ in Eq. (76) also applies in the case of nonconstant temperature-dependent $\alpha(T)$, since then in the defining Eq. (71) the volume integral over $\boldsymbol{u}\ \ \boldsymbol{B}_1(x)$ is zero.

### B. Analytical 1D TE device theory

In the following, TE-device theory is considered analytically for electrical- and heat current flows in parallel in a 1D-TE leg with constant cross-section area $A$. The material parameters are assumed to depend only on the 1D dimension $x$ and temperature $T(x)$. The theory of Sec. IV A is thus considerably simplified, since the electric current density $\boldsymbol{j}$ is now constant by $\nabla \boldsymbol{j}(x) = 0$. The normalized current density $\boldsymbol{u}\,(x)$ can be set to $u = 1\ \text{Amp/m}^2$ and is kept in the following equations for dimensional reasons. The TE leg length is $L$ with $x = 0$ at the hot-side contact area and $x = L$ at the cold-side area.

The contact heat flows in Eqs. (54) and (55) then read

$$q_h = A\left[-k(0, T_h)\,\frac{d\,T(0)}{dx} + T_h\,\boldsymbol{j}\,\alpha(0, T_h)\right],$$
$$q_c = A\left[k(L, T_c)\,\frac{d\,T(L)}{dx} - T_c\,\boldsymbol{j}\,\alpha(L, T_c)\right].$$

The heat-flow coefficients $q_{j,n}$ from Eq. (60) reduce to

$$q_{j,m} = \mp A\, k(a_j, T_j)\,\frac{d\,t_m(a_j)}{dx} \quad \text{for } m = 0, 2, 3, \ldots,$$
$$q_{j,1} = A\left[\mp k(a_j, T_j)\,\frac{d\,t_1(a_j)}{dx} \pm u\,T_j\alpha(a_j, T_j)\right] \quad \text{for } m = 1. \tag{77}$$

Here the upper sign applies for $j = h$ and the lower sign for $j = c$. The contact locations $x = 0,\ L$ are correspondingly characterized by $a_j = 0, L$.

An explicit solution for the $q_{j,1}$ and $q_{j,2}$ coefficients is required, in order to find the reversible entropies of Eq. (70) and resistances $r_j$ of Eq. (71) for the 1D case. For general Seebeck function $\alpha(x, T)$, this amounts to solving the equation system (65) for the $t_0(x)$, $t_{1(x)}$, and $t_2(x)$ functions. For $t_0(x)$ with boundary conditions $t_0(0) = T_h$, and $t_0(L) = T_c$, the solution is obtained by double integration. The first integration yields $q_{h,0} = -Ak(x)dt_0(x)/dx = \text{const}$, i.e., the pure Fourier heat flow arising for $\boldsymbol{j} = 0$. Integrating $q_{h,0}/k(x)$ results in

$$t_0(x) = \frac{K\,(T_c - T_h)}{K(x)} + T_h, \quad \frac{1}{K(x)} = \int_0^x \frac{d\,\tilde{x}}{k(\tilde{x})}, \quad K = K(L)$$
$$q_{h,0} = AK(T_h - T_c), \tag{78}$$

where $1/K(x)$ is the total heat resistance in the interval $(0, x)$. $K(L)$ is the heat conductance of the full TE leg per unit area.

For the higher-order terms $t_m(x)$, one obtains from (65)

$$k(x)t_m'(x) = k(x)g_m(x) + k(0)t_m'(0), \tag{79}$$

with

$$g_m(x) = \frac{1}{k(x)}\int_0^x uB_{m-1}(\tilde{x})\, d\,\tilde{x} \quad \text{for } m = 1, 3, 4, \ldots,$$
$$g_2(x) = \frac{1}{k(x)}\int_0^x \left[uB_1(\tilde{x}) - \rho(\tilde{x})u^2\right] d\,\tilde{x} \quad \text{for } m = 2. \tag{80}$$

The prime on $t_m'(x)$ denotes the derivative with respect to $x$. The unknown $t_m'(0)$ in Eq. (79) has to be determined from the zero boundary conditions for $t_m(x)$, $m > 0$, in particular $t_m(L) = 0$. Integrating Eq. (79) leads to

$$t_m(x) = \int_0^x g_m(\tilde{x})\, d\,\tilde{x} + \frac{k(0)t_m'(0)}{K(x)},$$

and thus by $t_m(L) = 0$:

$$t_m(x) = \int_0^x g_m(\tilde{x})\, d\,\tilde{x} - \frac{K}{K(x)}\int_0^L g_m(\tilde{x})\, d\,\tilde{x},$$
$$k(x)t_m'(x) = k(x)g_m(x) - K\int_0^L g_m(\tilde{x})\, d\,\tilde{x}. \tag{81}$$

Hence, at the contacts for $x = 0,\ L$,

$$k(0)t_m'(0) = -K\int_0^L g_m(\tilde{x})\, d\,\tilde{x},$$
$$k(L)t_m'(L) = k(L)g_m(L) - K\int_0^L g_m(\tilde{x})\, d\,\tilde{x}. \tag{82}$$

Equations (82) for $m = 1, 2$ can be inserted in Eq. (77) to obtain general 1D expressions for the $\Delta s_j$ and $r_j$ in Eqs. (70) and (71).

For $\Delta s_j$, it is found from Eqs. (70), (77), and (82) with $\mu = i/(Au)$ that

$$\Delta s_h = \frac{\mu\, q_{h,1}}{T_h} = i\alpha(0, T_h) + \frac{i}{u\,T_h}K\int_0^L g_1(\tilde{x})\, d\,\tilde{x}$$
$$\Delta s_c = -\frac{\mu\, q_{c,1}}{T_c}$$
$$= i\alpha(L, T_c) + \frac{i}{u\,T_c}\left[K\int_0^L g_1(\tilde{x})\, d\,\tilde{x} - k(L)g_1(L)\right]$$
$$s_a = \Delta s_c - \Delta s_h =$$
$$= \frac{i\,K}{u}\int_0^L g_1(\tilde{x})\, d\,\tilde{x}\left(\frac{1}{T_c} - \frac{1}{T_h}\right)$$
$$- \frac{i\,k(L)}{uT_c}g_1(L) + i[\alpha(L, T_c) - \alpha(0, T_h)]. \tag{83}$$

If $\alpha = \text{const}$, $B_m(x) = 0$ in Eq. (66) and thus also $g_1(x) = 0$. Hence, Eqs. (75) are recovered with $s_a = 0$.

From Eq. (71) we find for $r_j$

$$r_h = \frac{k(0)t_2'(0)}{Au^2} = \frac{-K}{Au^2}\int_0^L g_2(\tilde{x})\, d\tilde{x},$$

$$r_c = \frac{k(L)t_2'(L)}{Au^2} = \frac{1}{Au^2}\left[-k(L)g_2(L) + K\int_0^L g_2(\tilde{x})\, d\tilde{x}\right]$$

$$= \frac{1}{Au^2}\left[\int_0^L \left[\rho(\tilde{x})u^2 - uB_1(\tilde{x})\right] d\tilde{x} + K\int_0^L g_2(\tilde{x})\, d\tilde{x}\right],$$

and therefore

$$r = r_h + r_c = -k(L)g_2(L)/(Au^2), \tag{84}$$

or

$$r = \frac{1}{A}\int_0^L [\rho(\tilde{x}) - B_1(\tilde{x})/u]\, d\tilde{x}.$$

Again, as in the 3D case with Eqs. (71) and (74), the Joule losses, defined as second-order effect in $i$, cannot be attributed solely to $\rho(x)$, but depend in addition on the inhomogeneity of $\alpha(x,T)$ by the $B_1(x)$ term. For $\alpha = \text{const}$, $B_1(x) = 0$.

The full evaluation of (83) and (84) for general $\alpha(x,T)$ leads by Eqs. (66) to complicated expressions. In the following, two special cases will be treated, which are of particular interest: only spatially dependent Seebeck $\alpha(x)$ and merely temperature-dependent $\alpha(T)$. In both cases a suitable choice of the profiles $\rho(x)$ and $k(x)$ allows for the inclusion of electrical and thermal series resistances at the device contact areas. Thus, no additional equivalent circuit components are required for a general description, contrary to previous literature with otherwise constant material properties (CMP model) and neglect of bulk heat conductance.

#### *1. Results for spatially dependent Seebeck coefficient*

The function $g_1(x)$ in Eqs. (83) is given by Eqs. (80), (78), and (66) with $B_0(x) = t_0(x)d\alpha(x)/dx$. One obtains

$$g_1(x) = \frac{u}{k(x)}\left[K\,\Delta T\int_0^x \frac{\alpha(\tilde{x}) - \alpha(x)}{k(\tilde{x})}\, d\tilde{x} + T_h(\alpha(x) - \alpha(0))\right],$$

and thus

$$\int_0^L g_1(x)dx = uT_h\int_0^L \frac{\alpha(x) - \alpha(0)}{k(x)}\, dx + uK\,\Delta T\, D_{\alpha,k}, \tag{85}$$

with

$$D_{\alpha,k} = \int_0^L\int_0^x \frac{\alpha(\tilde{x}) - \alpha(x)}{k(\tilde{x})k(x)}\, d\tilde{x}\, dx.$$

The double-integral $D_{\alpha,k}$ depends solely on the profiles $\alpha(x)$ and $k(x)$ in the same way as the first integral in (85). Thus no dependence on $\rho(x)$ occurs in Eqs. (83), since $\rho(x)$ is exclusively connected to the second-order effects in $i$:

$$\Delta s_h = iK\left[\int_0^L \frac{\alpha(x)}{k(x)}dx + \frac{1}{T_h}K\,\Delta T\, D_{\alpha,k}\right]$$

$$\Delta s_c = iK\left[\int_0^L \frac{\alpha(x)}{k(x)}dx + \frac{1}{T_c}K\,\Delta T\, D_{\alpha,k}\right]$$

$$s_a = \Delta s_c - \Delta s_h = i\,D_{\alpha,k}K^2\Delta T^2/(T_hT_c). \tag{86}$$

$s_a$ is determined by the sign of $D_{a,k}$ and $i$. For monotonous decreasing $\alpha(x)$, $D_{a,k} > 0$. For increasing $\alpha(x)$, $D_{a,k} < 0$ and for constant $\alpha$, $D_{a,k} = 0$. For nonmonotonously varying $\alpha(x)$, $D_{a,k}$ can accidentally be zero, depending on the $k(x)$ function. If the TE device is in the generator mode, $i\alpha > 0$, i.e., if $\alpha < 0$ for $n$-doped semiconducting material, then also $i < 0$. In order to find the bounds of the $\Delta s_j$ in Eq. (86), the bounds of $KD_{\alpha,k}$ can be obtained by representing $KD_{\alpha,k}$ in the form

$$KD_{\alpha,k} = \int_0^L \frac{\alpha(x)}{k(x)}dx - 2\int_0^L \frac{K}{K(x)}\frac{\alpha(x)}{k(x)}dx.$$

The factor $K/K(x)$ can take on the extreme values 0 or 1, depending on the form of the $k(x)$ profile. Thus, for $\alpha > 0$,

$$-\int_0^L \frac{\alpha(x)}{k(x)}dx < KD_{\alpha,k} < \int_0^L \frac{\alpha(x)}{k(x)}dx.$$

With this, the bounds of $\Delta s_j$ in Eq. (86) for $i\alpha > 0$ are

$$0 < iK\left(1 - \frac{\Delta T}{T_h}\right)\int_0^L \frac{\alpha(x)}{k(x)}dx < \Delta s_h < iK\left(1 + \frac{\Delta T}{T_h}\right)\int_0^L \frac{\alpha(x)}{k(x)}dx,$$

$$iK\left(1 - \frac{\Delta T}{T_c}\right)\int_0^L \frac{\alpha(x)}{k(x)}dx < \Delta s_c < iK\left(1 + \frac{\Delta T}{T_c}\right)\int_0^L \frac{\alpha(x)}{k(x)}dx. \tag{87}$$

Thus, it turns out that $\Delta s_h$ for $i\alpha > 0$ is always >0. $\Delta s_c$ can be smaller than 0, depending on the sign of $1{-}\Delta T/T_c$. For the generated power $P_{el}$ up to first-order $P_1 = (q_{h,1} + q_{c,1})$, the result is obtained from Eq. (86):

$$\mu P_1 = \Delta s_hT_h - \Delta s_cT_c = iK\,\Delta T\int_0^L \frac{\alpha(x)}{k(x)}dx, \tag{88}$$

which is independent of $D_{a,k}$. The *open-circuit voltage* of the TE device can be defined by $P_{el}/i$ for $i \to 0$ and thus is obtained by dividing $\mu P_1$ in Eq. (88) by $i$. It may be interesting to note that this open-circuit voltage is independent from any overall factor of the heat conductivity $k(x)$, but can depend critically on the shape of $k(x)$ for inhomogeneous $\alpha(x)$.

The second-order effects in $i$ are given by the $r_j$ coefficients of Eqs.(84), which are determined by the $g_2(x)$ function (80). By Eq. (66) with $B_1(x) = t_1(x)d\alpha(x)/dx$, it reads

$$g_2(x) = \frac{1}{k(x)}\int_0^x \left[u\alpha'(\tilde{x})t_1(\tilde{x}) - \rho(\tilde{x})u^2\right] d\tilde{x} = \frac{u}{k(x)}\int_0^x [(\alpha(x) - \alpha(\tilde{x}))\,t_1'(\tilde{x}) - \rho(\tilde{x})u]\, d\tilde{x}.$$

$t_1'(x)$ following Eq.(81) can be expressed by the $g_1(x)$ function in Eq. (85), which leads to

$$g_2(x) = \frac{u}{k(x)} \int_0^x [\alpha(x) - \alpha(\tilde{x})] \times \left( g_1(\tilde{x}) - \frac{K}{k(\tilde{x})} \int_0^L g_1(\tilde{\tilde{x}})\, d\,\tilde{\tilde{x}} \right) d\,\tilde{x} - \frac{u^2}{k(x)} \int_0^x \rho(\tilde{x}) d\,\tilde{x}$$

and

$$\int_0^L g_2(x)dx = u \int_0^L \int_0^x \frac{\alpha(x) - \alpha(\tilde{x})}{k(x)}\, g_1(\tilde{x})\, d\,\tilde{x}\, dx + uK\, D_{\alpha,k} \int_0^L g_1(\tilde{x})\, d\,\tilde{x} - u^2 \int_0^L \frac{1}{k(x)} \int_0^x \rho(\tilde{x}) d\,\tilde{x}\, dx.$$

With these expressions for $g_2(x)$ and its integral, a complete analytical representation is obtained for the $r_h$ and $r_c$ in Eq. (84), and in particular for $r = r_h + r_c$:

$$r = r_1 + r_2 = \frac{-k(L) g_2(L)}{A\, u^2}, \quad r_1 = \frac{1}{A} \int_0^L \rho(\tilde{x}) d\,\tilde{x}\,,$$
$$r_2 = \frac{1}{Au} \int_0^L [\alpha(\tilde{x}) - \alpha(L)] \times \left( g_1(\tilde{x}) - \frac{K}{k(\tilde{x})} \int_0^L g_1(\tilde{\tilde{x}})\, d\,\tilde{\tilde{x}} \right) d\,\tilde{x}\,. \quad (89)$$

The first term $r_1$ of $r$ is the usual definition of the internal electrical resistance of the TE device. The second term $r_2$ only differs from zero for nonconstant $\alpha$. By the definition of the function $g_1(x)$ and $K$, it is obvious that $r_2$ scales inversely proportional with an overall factor of the function $k(x)$ and quadratically with an overall factor of $\alpha(x)$. Is it possible to achieve negative values for $r_2$? It is difficult to come to conclusions for the general form of $r_2$ in Eq. (89); however, for the simplifying case that $k(x) = k_c$ is constant and $\alpha(x) = \alpha(0) + \alpha' x$ is linear, the surprisingly simple result can be inferred from (89):

$$r_2 = \frac{\alpha'^{\,2} L^3 (T_h + T_c)}{24A\, k_c}. \quad (90)$$

This is valid for positive as well as for negative $\alpha(x)$ and $\alpha'$ values. From Eq. (90), the hypothesis is established that $r_2 \geqslant 0$ is always valid and $r$ generally is equal or larger than the pure internal electric resistance $r_1$.

From Eq. (84) $r_h$ is obtained by the integral over $g_2(x)$ and thus $r_h$ splits into the terms $r_h = r_{h1} + r_{h2}$, with

$$r_{h1} = \frac{K}{A} \int_0^L \frac{1}{k(x)} \int_0^x \rho(\tilde{x}) d\,\tilde{x}\, dx,$$
$$r_{h2} = -\frac{K}{Au} \left( \int_0^L \int_0^x \frac{\alpha(x) - \alpha(\tilde{x})}{k(x)}\, g_1(\tilde{x})\, d\,\tilde{x}\, dx + K\, D_{\alpha,k} \times \int_0^L g_1(\tilde{x})\, d\,\tilde{x} \right). \quad (91)$$

The index 2 on $r$ here and in the following again denotes the contribution for nonconstant $\alpha$. The question arises whether $r_{h2}$ can become negative. Once more, for constant $k(x)$ and linear $\alpha(x)$, a positive result is obtained:

$$r_{h2} = \frac{\alpha'^{\,2} L^3 (8T_h + 7T_c)}{360A\, k_c}. \quad (92)$$

By Eq. (84), $r_c$ is obtained as $r_c = r - r_h = (r_1 - r_{h1}) + (r_2 - r_{h2}) = r_{c1} + r_{c2}$. So, for the approximation used above for $k(x)$ and $\alpha(x)$, the second term of $r_c$ is also positive:

$$r_{c2} = r_2 - r_{h2} = \frac{\alpha'^{\,2} L^3 (7T_h + 8T_c)}{360A\, k_c}, \quad (93)$$

and the first term is always positive, since it can be written in the form

$$\begin{aligned} r_{c1} &= r_1 - r_{h1} \\ &= \frac{1}{A} \int_0^L \rho(\tilde{x}) d\,\tilde{x} - \frac{K}{A} \int_0^L \frac{1}{k(x)} \int_0^x \rho(\tilde{x}) d\,\tilde{x}\, dx \\ &= \frac{1}{A} \int_0^L \rho(\tilde{x}) d\,\tilde{x} - \frac{K}{A} \int_0^L \int_{\tilde{x}}^L \frac{dx}{k(x)} \rho(\tilde{x})\, d\,\tilde{x} \\ &= \frac{1}{A} \int_0^L \rho(\tilde{x}) d\,\tilde{x} - \frac{K}{A} \int_0^L \left( \frac{1}{K(L)} - \frac{1}{K(\tilde{x})} \right) \rho(\tilde{x})\, d\,\tilde{x} \\ &= \frac{K}{A} \int_0^L \frac{\rho(\tilde{x})}{K(\tilde{x})} d\,\tilde{x} > 0. \end{aligned} \quad (94)$$

Therefore, it can be supposed that $r_2$, $r_{h2}$,and $r_{c2}$ are positive for general $k(x)$ and $\alpha(x)$ functions. It is easily verified that if $k(x)$ *and* $\rho(x)$ are constants, $r_1/2 = r_{h1} = r_{c1}$. Together with $r_2$, $r_{h2}$, and $r_{c2} = 0$ for $\alpha(x) = \text{const}$, this leads to the well-known result $r/2 = r_h = r_c$ for the CMP [40,41].

The generated electric power is given up to second order in current $i$ by utilizing Eqs. (74) and (88):

$$P_{el} = i\, K\, \Delta T \int_0^L \frac{\alpha(x)}{k(x)} dx - r\, i^2,$$

with $r$ from Eq. (89). $P_{el}$ thus is decreased by an additional positive $r_2 i^2$ contribution to the Joule losses in the case of inhomogeneous $\alpha(x)$. Since $r_2$ generally scales inversely proportional with an overall factor of $k(x)$, any positive TE performance is destroyed by $r_2$ in the limit $k(x) \to 0$, although the losses of the heat leakage current $q_{h,0}$ [Eq.(78)] are eliminated. The singularity with respect to $k$ is also revealed in Eq. (90).

### 2. Results for temperature-dependent Seebeck coefficient

In the case of merely temperature-dependent $\alpha(T)$, again electrical and thermal series resistances at the device contact areas can be included by forming the $\rho(x)$ and $k(x)$ functions appropriately. The mathematical description to some extent becomes simpler and more transparent than for spatially dependent $\alpha(x)$; however, it should be noted that the physical description of the TE performance with $\alpha(T)$ is not always reliable. For example, in the case of extremely thin TE-material layers (e.g., for superlattices) the temperature drop along the parasitic thermal series resistances becomes appreciable and, as described in Sec. III for general heat engines, the temperature drop between $T_{fh}$ and $T_{fc}$ along the internal engine (i.e., the TE material) becomes much smaller than $\Delta T = T_h – T_c$. Then, the performance deteriorates accordingly. With only one material function $\alpha(T)$, this effect cannot be described, since the true Seebeck $\alpha$ in the contact intervals $(T_{fj}, T_j)$ is nearly zero and not $\approx a(T_j)$.

Equation (56) applied to the 1D case with $\alpha(T)$ leads to

$$P_{el} = \int_0^L \left(-i\,\alpha(T(x))\frac{dT(x)}{dx} - i^2\rho(x)/A\right) dx$$
$$= i\int_{Tc}^{Th} \alpha(T)\,dT - i^2\int_0^L \frac{\rho(x)}{A}\,dx. \quad (95)$$

The substitution of the integration variable $x$ by $T$ in the first term is valid also for nonmonotonous temperature profile $T(x)$ and is independent of the detailed $T$ function. Equation (95) corresponds to Eq. (69) in the 3D case and both results are valid to all orders in $i$, i.e., the power series of $P_{el}$ is complete with the second order, since $P_n = q_{h,n} + q_{c,n} = 0$ for $n > 2$, as elucidated following (69). However, the series of the individual contact heat flows $q_{j,n}$ in (60) does not stop, except for constant $\alpha$, which leads to $t_n(x) = 0$ for $n > 2$.

By use of Eqs. (83) and (84), the $q_{j,n}$ up to order $n = 2$ can be calculated. From Eq. (80), $g_1(x)$ is obtained with the help of Eq. (66), $B_0(x) = t_0(x)d\alpha(t_0(x))/dx$. Partial integration and change of the integration variable from $x$ to $t_0$ leads to

$$g_1(x) = \frac{u}{k(x)}\left[-\int_{T_h}^{t_0(x)} \alpha(t)\,dt + \alpha[t_0(x)]\,t_0(x) - \alpha(T_h)T_h\right]. \quad (96)$$

Integration over $g_1(x)$ is performed again by substituting $t_0$ as integration variable with the help of $dx/dt_0 = –k(x)/(K\Delta T)$. Since by Eq. (78), $t_0(x)$ is a strictly monotonous function, the inverse $x(t_0)$ exists and $k(x)$ can be replaced by $k(t_0)$:

$$\int_0^x g_1(\tilde{x})d\tilde{x} = \frac{u}{K\Delta T}\int_{T_h}^{t_0(x)}\int_{T_h}^{\tilde{t}_0} \alpha(t)\,dt\,d\tilde{t}_0$$
$$- \frac{u}{K\Delta T}\int_{T_h}^{t_0(x)} \alpha(t)t\,dt - \frac{u}{K(x)}\alpha(T_h)T_h.$$

The first double integral can be evaluated by adjusting integration bounds to be equal by a step function $\theta(t)$ in the integrand and by interchanging the integration sequence:

$$\int_{t_0(x)}^{T_h}\int_{t_0(x)}^{T_h} \theta(t-\tilde{t}_0)\,d\tilde{t}_0\,\alpha(t)dt$$
$$= \int_{t_0(x)}^{T_h} \alpha(t)t\,dt - t_0(x)\int_{t_0(x)}^{T_h} \alpha(t)\,dt,$$

and thus

$$\int_0^x g_1(\tilde{x})d\tilde{x} = \frac{2u}{K\Delta T}\int_{t_0(x)}^{T_h} \alpha(t)t\,dt$$
$$- \frac{u\,t_0(x)}{K\Delta T}\int_{t_0(x)}^{T_h} \alpha(t)\,dt - \frac{u}{K(x)}\alpha(T_h)T_h. \quad (97)$$

With Eqs. (96) and (97), the reversible entropies $\Delta s_j$ according to Eq. (83) are

$$\Delta s_h = \frac{i}{T_h\Delta T}\left(2\int_{T_c}^{T_h} \alpha(t)t\,dt - T_c\int_{T_c}^{T_h} \alpha(t)\,dt\right)$$
$$\Delta s_c = \frac{i}{T_c\Delta T}\left(2\int_{T_c}^{T_h} \alpha(t)t\,dt - T_h\int_{T_c}^{T_h} \alpha(t)\,dt\right) \quad (98)$$

and

$$s_a = \Delta s_c - \Delta s_h = \frac{2i}{T_cT_h}\left(\int_{T_c}^{T_h} \alpha(t)t\,dt - \frac{T_h+T_c}{2}\int_{T_c}^{T_h} \alpha(t)\,dt\right).$$

Again, as for the $\alpha(x)$ result in Eqs. (86) and (87), $\Delta s_h$ for $i\alpha > 0$ is always positive and $\Delta s_c$ can be smaller than zero, when $T_h > 2T_c$. Furthermore, similar to Eq. (88),

$$\mu P_1 = \Delta s_h T_h - \Delta s_c T_c = i\int_{Tc}^{Th} \alpha(T)\,dT,$$

which confirms (95) in first order.

The $r_j$ coefficients of Eqs. (83) for the $\alpha(T)$ case are determined by the $g_2(x)$ function (80) with $B_1(x) = \nabla[t_0(x)t_1(x)\partial\alpha(t_0(x))/\partial T]$ from Eq. (66). With $t_1(0) = t_1(L) = 0$,

$$g_2(x) = \frac{u}{k(x)}t_0(x)t_1(x)\alpha'(t_0(x)) - \frac{u^2}{k(x)}\int_0^x \rho(\tilde{x})\,d\tilde{x},$$
$$g_2(L) = -\frac{u^2}{k(L)}\int_0^L \rho(\tilde{x})d\tilde{x},$$

and the integral of $g_2(x)$ is obtained by changing integration again to $t_0$ by use of $dx/dt_0 = –k(x)/(K\Delta T)$:

$$\int_0^L g_2(x)dx = \frac{u}{K\Delta T}\int_{T_c}^{T_h} t_0\,t_1[t_0]\alpha'(t_0)\,dt_0$$
$$- u^2\int_0^L \frac{1}{k(x)}\int_0^x \rho(\tilde{x})d\tilde{x}\,dx. \quad (99)$$

The function $t_1(x)$ can be expressed as $t_1[t_0(x)]$ by Eq. (81) with $g_1(x)$ and its integral from (96) and (97), and with (78) leading to $K/K(x) = [T_h – t_0(x)]/\Delta T$:

$$t_1[t_0] = \frac{u}{K\Delta T}\left[\frac{T_c(T_h-t_0)}{\Delta T}\int_{T_c}^{T_h} \alpha(t)\,dt - t_0\int_{t_0}^{T_h} \alpha(t)\,dt + \right.$$
$$\left. +2\int_{t_0}^{T_h} t\alpha(t)\,dt - 2\frac{T_h-t_0}{\Delta T}\int_{T_c}^{T_h} t\alpha(t)\,dt\right].$$

Now, Eq. (84) yields for $r$

$$r = r_1 + r_2 = \frac{-k(L)g_2(L)}{A\,u^2} = \frac{1}{A}\int_0^L \rho(\tilde{x})d\tilde{x}, \quad r_2 = 0, \quad (100)$$

which coincides with the first term of Eq. (89), while the $r_2$ contribution is zero, also for nonconstant $\alpha$. This confirms the second term in Eq. (95). However, nonconstant $\alpha$ matters for the hot- and cold-side coefficients $r_h$ and $r_c$ of the heat flows $q_h$ and $q_c$. From Eq. (84), it follows by use of (99) for $r_h =$

$r_{h1} + r_{h2}$ that

$$r_{h1} = \frac{K}{A}\int_0^L \frac{1}{k(x)}\int_0^x \rho(\tilde{x})d\,\tilde{x}\,dx,$$
$$r_{h2} = \frac{-1}{Au\,\Delta T}\int_{T_c}^{T_h} t_0\,t_1[t_0]\alpha'(t_0)\,d\,t_0, \quad (101)$$

with the same $r_{h1}$ as in Eq. (91) for the $\alpha(x)$ theory. Since $r_c = r_{c1} + r_{c2} = r – r_h$, for $r_{c1} = r_1 – r_{h1}$ the same expression applies as in Eq. (92), and for $r_{c2}$

$$r_{c2} = r_2 - r_{h2} = -r_{h2}$$

is obtained. Thus, one of the $r_{h2}$ and $r_{c2}$ will be negative and the other positive, contrary to the $\alpha(x)$ case, where both values are assumed to be positive. If $\alpha(T)$ is a linear function in $T$ with steepness $\alpha'$ and $k(x) = k_c$ is a constant, it is inferred from (101):

$$r_{c2} = -r_{h2} = \frac{\alpha'^2 L\Delta T\,(4T_h^2 + 7T_hT_c + 4T_c^2)}{180A\,k_c} > 0. \quad (102)$$

One is thus led to presume that $r_{c2}$ is positive for general $\alpha(T)$, $k(x)$, and $r_{h2}$ is negative. Thus, $r_{c2}$ gives rise to a negative contribution to the heat flow $q_c$ while $r_{h2}$ evokes a positive contribution to $q_h$ of equal magnitude. So, these contributions have the character of a heat leakage current similar to $q_{h,0}$ in Eq. (78), which however is independent from current $i$. Generally for $\alpha(T)$, all heat-flow terms $q_{j,m}$, $m > 2$, also have this leakage current character according to Eq. (68).

Following Eqs. (72) and (73), the entropy production rate can be expressed generally up to second order in $i$ as

$$s_{\text{irr}} = q_{h,0}\left(\frac{1}{T_c} - \frac{1}{T_h}\right) + (\Delta s_c - \Delta s_h) + i^2\left(\frac{r_c}{T_c} + \frac{r_h}{T_h}\right). \quad (103)$$

The additions $r_{j2}$ caused by nonconstant $\alpha$ in $r_j$ in Eq. (103) are positive for $\alpha(x)$. Also, for $\alpha(T)$ the additional term $i^2 r_{c2}\,(1/T_c – 1/T_h)$ gives rise to a positive contribution. On the other hand, $s_a = \Delta s_c – \Delta s_h$ can become negative in some cases.

The different behavior for the cases of $\alpha(x)$ and $\alpha(T)$ is surprising but it is not inconsistent, since both theories deviate considerably. Generally, it is not possible in the context of our theory to describe the device behavior for a material function $\alpha(T)$ by *one* adapted function $\alpha(x) = \alpha(T(x))$, because $T(x)$ depends, by Eq. (59), on the current scaling $\mu$, and for each contact current $i$ another function $\alpha_\mu(x) = \alpha(T_\mu(x))$ applies. Then $\alpha_\mu(x)$ also has to be expanded in a power series of $\mu$ [which in fact is done in Eqs. (63) and (64)]. This leads to quite different governing equations compared to Eq. (61) with different functions $t_m(x)$.

Both theories have in common the inverse scaling of $r_{h2}$ and $r_{c2}$ with the heat conductivity $k(x)$. $P_{el}$ in the $\alpha(T)$ theory [Eq. (95)] does not at all depend on $k(x)$. However, the efficiency $\eta = P_{el}/q_h$ is zero for $k(x)\to 0$, since $q_{h,2} \sim r_{h2} \to \infty$, unless simultaneously $i \to 0$, which means $P_{el} = 0$. Optimization of TE devices should take into account that reduction of $k$ may be disadvantageous for this reason, or only applicable for sufficiently small electric currents, although increased material's figure of merit $Z = \alpha^2\,(k\rho)$ arises for decreased $k$. In the traditional CMP model the limit for $k \to 0$ is $\eta_{P\max} = \eta_C/(2 – \eta_C/2)$ and $P_{\max} = \alpha^2\Delta T^2/4r$ as will be shown now.

### C. CMP model extended to linear Seebeck coefficicients

The simple 1D theory with constant material properties in the TE legs (CMP-model) is well known [40,41], but will now be briefly recalled in order to compare the entropy concepts with the general case. In addition an analytical extension for linear Seebeck variation of $\alpha(x)$ or $\alpha(T)$ will be established with new material- and device figure of merit for this case.

In the 1D CMP case, the heat balance Eq. (51) for $T(x)$ reduces to a simple linear differential equation: $–Akd^2T/dx^2 = i^2\rho/A$ with boundary conditions $T(0) = T_h$ and $T(L) = T_c$. Then the heat flows $q_h$ and $q_c$ according to Eqs. (54) and (55) are

$$q_h = \Delta TA\,k/L + i\,\alpha T_h - i^2 r/2,$$
$$q_c = -\Delta TA\,k/L - i\,\alpha T_c - i^2 r/2$$

with $Ak/L = AK$ from Eq. (78) and $r = \rho L/A = r_1$ from Eq. (89). In the generator mode the electrical output power $P_{el}$ and maximized $P_{\max}$ with respect to $i = i_{P\max}$ are

$$P_{el} = q_h + q_c = i\,\alpha\Delta T - \mathrm{i}^2 r,$$
$$i_{P\max} = a\Delta T/(2r),\ P_{\max} = \alpha^2\Delta T^2/(4r). \quad (104)$$

The efficiency reads

$$\eta = \frac{P_{el}}{q_h} = \frac{\Delta T}{T_h}\,\frac{i\alpha - i^2 r/\Delta T}{\Delta T\,A\,k/(T_hL) + i\alpha - i^2 r/T_h}. \quad (105)$$

In the literature, its maximization with respect to $i$ utilizes the ratio of internal TE-leg resistance $r$ and external load resistance. Then optimization with respect to this ratio leads to an expression of $\eta$ including a figure of merit for the device:

$$Z = \alpha^2/(r\,AK) = \alpha^2/(\rho k) \quad (106)$$

which—in the case of a single TE leg (unicouple)—is simultaneously the figure of merit for the TE material with constant material properties. Usually thermocouples are considered with $p$- and $n$-doped TE legs put thermally in parallel and electrically in series. Then, for the Seebeck parameters $\alpha_p > 0$ and $a_n < 0$ with corresponding leg geometries $A_{p,n}$ and $L_{p,n}$, the device figure of merit turns out to be [36,41]

$$Z_D = \alpha^2/(r\,AK), \quad \alpha = \alpha_p - \alpha_n,$$
$$r = \rho_pL_p/A_p + \rho_nL_n/A_n, \quad AK = A_pk_p/L_p + A_nk_n/L_n.$$

Maximization of $\eta$ can be performed without inclusion of an artificial external load resistance by eliminating in $\eta$ the variable $r = \alpha^2/(ZAK)$ by $i^2r = (i\alpha)^2/(ZAK)$. Varying $\eta$ with respect to $i\alpha$ as a single variable [35–37], the optimized $i\alpha_{\text{opt}}$ is

$$i\alpha_{\text{opt}} = AK\ \Delta T\ (\sqrt{1+ZT_{\text{av}}} - 1)/T_{\text{av}}, \quad T_{\text{av}} = (T_h + T_c)/2. \quad (107)$$

Inserting this into Eq. (105), one obtains

$$\eta_{\max} = \frac{\Delta T}{T_h}\,\frac{\sqrt{1+ZT_{\text{av}}} - 1}{\sqrt{1+ZT_{\text{av}}} + T_c/T_h}$$
$$= \frac{\Delta T}{T_h}\,\frac{ZT_h/2 + 1 - \sqrt{1+ZT_{\text{av}}}}{ZT_h/2 + \Delta T/T_h}. \quad (108)$$

Obviously $\eta_{\max} \to \eta_C$ for $Z \to \infty$. A broad literature in thermoelectrics is dedicated to achieving high-$Z$ values by reduction of thermal conductivity $k$. As was shown in the previous subsection, this can only be fully successful for the CMP model, which is never realized exactly in practice. With $k \to 0$ in Eq. (107), $i\alpha_{\rm opt} \to 0$ for finite $\alpha$ and $r > 0$, and thus in Eq. (104), $P_{el}$, $q_h \to 0$. In order that $\eta_{\max} \to \eta_C$ and in addition $P_{el} > 0$, it is either required that $\alpha \to \infty$ with $k$, $r$ finite, or for finite $i\alpha$ that $k$ and $r \to 0$. This can be read off from Eq. (105).

These findings are supported by entropy evaluation according to Eqs. (58) and (103):

$$s_{\rm irr} = AK\,\Delta T\left(\frac{1}{T_c} - \frac{1}{T_h}\right) + i^2\frac{r}{2}\left(\frac{1}{T_c} + \frac{1}{T_h}\right),$$

since following Eq. (75) $\Delta s_h = \Delta s_c = i\alpha$ with $s_a = 0$, and due to Eqs. (91) and (94) $r_h = r_c = r/2$. The losses by $s_{\rm irr}$ cause $\eta_{\max} < \eta_C$, except for $\alpha \to \infty$ with $P_{el} \to \infty$, because the losses by $k$, $r > 0$ then are negligibly small. Regrettably, $\alpha$ is limited to small values by the requirement of positive thermal conductance of the electron gas [42]. Superconductors with $r = 0$ are not thermoelectrics because of $\alpha = 0$ in that case.

The efficiency $\eta_{P\max}$ corresponding to $P_{\max}$ in Eq. (104) is found by inserting $i_{P\max}\alpha = ZAK\Delta T/2$ into Eq. (105):

$$\eta_{P\max} = \frac{\eta_C}{4/(ZT_h) + 2 - \eta_C/2}.$$

$P_{\max}$ itself only depends on the power factor $ZAK = \alpha^2/r$ and is independent of $k$. For $k \to 0$, $\eta_{P\max} \to \eta_C/(2–\eta_C/2)$ and $P_{\max} = a^2\Delta T^2/4r$. It can be shown that $\eta_{P\max} < \eta_{CA}$ is always valid with $\eta_{CA}$ from Eq. (4).

The CMP theory can be extended for linear $\alpha(x)$ or $\alpha(T)$ variation with $\rho$ and $k$ being constants. For $\alpha(x) = \alpha(0) + \alpha x$ by use of Eqs. (72) and (86),

$$q_h = \Delta TAk/L + \Delta s_h T_h - i^2 r_h,$$
$$q_c = -\Delta TAk/L - \Delta s_c T_c - i^2 r_c,$$

with

$$\Delta s_h = i[a(0) + a'L(2 + T_c/T_h)/6] = i\,a_h,$$
$$\Delta s_c = i[a(0) + a'L(4 - T_h/T_c)/6].$$

Here $\alpha_h$ is considered as some sort of average of $\alpha(x)$ in the interval $(0, L)$. Then $P_{el} = q_h + q_c = i\alpha_{av}\Delta T – i^2 r$ with $\alpha_{av} = \alpha(L/2)$ and $r = r_h + r_c$ including the singular $r_{h2}$, $r_{c2}$ parts for $k \to 0$ of Eqs. (92) and (93). Similar to Eq. (104), $P_{\max} = \alpha_{av}^2\Delta T^2/(4r)$ and $i_{P\max} = \alpha_{av}\Delta T/(2r)$. For $\eta = P_{el}/q_h$, one obtains

$$\eta = \frac{\Delta T}{T_h}\,\frac{i\alpha_h c - i^2 r/\Delta T}{\Delta T\,A\,k/(T_h L) + i\alpha_h - i^2 r_h/T_h}, \qquad c = \frac{\alpha_{\rm av}}{\alpha_h}, \tag{109}$$

where $c$ is a correction factor in order to have the same variation variable $i\alpha_h$ in the numerator and denominator. Maximizing $\eta$ with respect to $i\alpha_h$ and introducing $r_h = \beta r$ leads to

$$i\alpha_{h,\rm opt} = AK\,\Delta T\,\frac{\sqrt{1 + (T_h - c\beta\,\Delta T)cZ} - 1}{T_h - c\beta\,\Delta T}, \qquad Z = \frac{\alpha_h^2}{r\,AK},$$

$$\eta_{\max} = \frac{\Delta T}{T_h}\,\frac{\sqrt{1 + (T_h - c\beta\,\Delta T)cZ} - 1}{\sqrt{1 + (T_h - c\beta\,\Delta T)cZ}/c + 1/c - 2\beta\Delta T/T_h}$$
$$= \frac{\Delta T}{T_h}\,\frac{ZT_h c/2 + 1 - \sqrt{1 + (T_h - c\beta\,\Delta T)cZ}}{ZT_h/2 + 2\beta\,\Delta T/T_h} \tag{110}$$

For homogeneous $\alpha$ with $c = 1$ and $\beta = r_h/r = 1/2$, Eqs. (107) and (108) are recovered. A figure of merit $Z$ has been introduced in Eqs. (110), which includes a singular $r$ with respect to $k$ and instead of a homogeneous $\alpha$ an averaged $\alpha_h$ defined above. For $Z \to \infty$, $\eta_{\max} = c\eta_C$. However, $Z \to \infty$ is only possible for $\alpha_h$ or $\alpha(0) \to \infty$. Then, $c = 1$ and $\eta_{\max}$ cannot exceed $\eta_C$. For $k \to 0$, $Z$ is now bounded by Eq. (90):

$$\lim_{k\to 0} Z = \alpha_h^2/(r_2 Ak/L) = 24\alpha_h^2\big/[\alpha(L) - \alpha(0)]^2(T_h + T_c). \tag{111}$$

For the ratio $\beta = r_h/r$, it is obtained from Eqs. (89)–(93) that

$$\lim_{k\to\infty}\beta = \frac{r_1/2}{r_1} = 1/2,\ \lim_{k\to 0}\beta = \frac{r_{h2}}{r_2} = \frac{8T_h + 7T_c}{15\,(T_h + T_c)} > 1/2.$$

For linear $\alpha(T)$, the relation $\alpha(T) = \alpha(0) + \alpha' T$ is used with very similar results. The $\Delta s_h$ and $\Delta s_c$ from Eq. (98) then read

$$\Delta s_h = i[a(0) + a'\big(4T_h + T_c + T_c^2/T_h\big)/6] = i\,a_h,$$
$$\Delta s_c = i[a(0) + a'\big(4T_c + T_h + T_h^2/T_c\big)/6],$$

and $P_{el} = i\alpha_{\rm av}\Delta T – i^2 r$ with $\alpha_{\rm av} = \alpha(T_{\rm av})$. Equations (109) and (110) stay valid, now with

$$c = \frac{\alpha_{\rm av}}{\alpha_h} = \frac{\alpha(0) + \alpha' T_{\rm av}}{\alpha(0) + \alpha'(4T_h + T_c + T_c^2/T_h)/6}.$$

In the $\alpha(T)$ theory, according to Eq. (100), $r = r_1$ and $r_2 = 0$. Thus $Z \to \infty$ for $k \to 0$, as for the CMP model. However, following Eq. (102) for $\beta = r_h/r$, $\lim_{k\to 0}\beta = \frac{r_{h2}}{r_1} = \frac{-r_{c2}}{r_1} = -\infty$ and therefore $\eta \to 0$, because $\beta$ appears in the denominator of Eq. (109) through $r_h = \beta r$. For large $k$,

$$\lim_{k\to\infty}\beta = \frac{r_1/2 + r_{h2}}{r_1} = \frac{r_1/2}{r_1} = 1/2.$$

Again, $\eta_{\max} = \eta_C$ is only obtained for $\alpha(0) \to \infty$ with $Z \to \infty$.

The $Z$ variable used in Eq. (110) for the $\alpha(x)$ theory can be written in the form of a material figure of merit by introducing $\rho = rA/L = \rho_1 + \rho_2$, where $\rho_1$ is the material's electric resistivity and $\rho_2 = r_2 A/L$ with $r_2$ from Eq. (90). Then $Z = \alpha_h^2/(rAK) = \alpha_h^2/(\rho k) = \alpha_h^2/[\rho_1 k + (\alpha(L)–\alpha(0))^2(T_h + T_c)/24]$ with the finite limit for $k \to 0$ from Eq. (111). For the $\alpha(T)$ theory, $\rho_2 = 0$ and $Z \to \infty$ for $k \to 0$ is neutralized by the simultaneous limit $\beta \to -\infty$.

## V. CONCLUSION

The separation of total entropy production in ideal reversible parts and irreversible contributions is analyzed in detail for Carnot-like heat engines. The reversible $\Delta S$ in Eqs. (1), (2), and (16) are considered to be entropies for ideal lossless processes at the hot and cold side with irreversibilities turned off. The reversible entropy parts are important system parameters and useful for an efficient description of the irreversibilities, e.g., in Eq. (6). In Ref. [15], the concern was raised that the $\Delta S$ in Eqs. (1), (2), and (8) are not always independent from the irreversibilities (9) in the case of different initial and final temperatures $T_f(t)$ of the working fluid in the isothermal transitions. The present analysis reveals that in any case the reversible $\Delta S = \Delta S_{\rm rev}$ are unchanged, by using the evolution of $T_f(t)$ optimized with respect to entropy minimization for the transitions and apparent inconsistencies are cleared up. Then, in the limit, the $T_f(t)$ become discontinuous functions, as shown in Fig. 1. If nonisentropic transitions in the adiabatic cycle branches are considered, the hot- and cold-side reversibilities $\Delta S_{j,\text{rev}}$, $j = h, c$, are no longer equal and their difference is equal to the entropy production in the adiabats.

For the refrigerator mode, maximization of cooling power is studied with inclusion of nonisentropic adiabats. Results are shown in Eqs. (25) and (26) with corresponding efficiency CoP (27), for the low-dissipation entropy assumption (3) for cold-side transition. In the case of endoreversible entropy model (6) for the isothermal transitions, and low-dissipation model for the adiabats, Eqs. (28)–(30) are obtained for the cooling power. Also, combined occurrence of different entropy models on either side is discussed.

The theory for steady-state engines is introduced by time averaging over one Carnot cycle, to obtain constant entropy rates $\Delta s_j$, $s_j$, $s_a$ and heat flows $q_j$ at the thermal contacts to the reservoirs. The concept of endoreversibility is generalized to pseudo-endoreversibility, which describes an internal irreversible engine connected by heat conductances to the reservoirs. The internal entropy production rate $s_a = \Delta s_c - \Delta s_h$ is the analog to the adiabatic entropy production for the Carnot cycle, whereas the $s_j$ entropy rates in Eq. (32) correspond to the effect of the heat conductances. Power maximization with respect to the internal engine contact temperatures $T_{fh}$ and $T_{fc}$ can be performed for constant heat conductances and Eq. (44) is obtained, which, also for $s_a = 0$, differs essentially in the denominator from the Curzon-Ahlborn result [1]. For $s_a = 0$, the efficiency at maximum power (EMP) is identical to the CA efficiency. The effect of a heat leakage current of arbitrary form is investigated with EMP given in Eq. (46).

The results obtained are a necessary prerequisite to treat thermoelectric converters as steady-state heat engines in 1D and 3D with arbitrary spatially- and temperature-dependent material parameters. The definition of the reversible entropy parts in that general case has been an unsolved problem up to now. A methodology is presented for solving the TE equation (51) (heat-balance equation) in form of a recursive equation system sorted by powers of electric contact current $i$ [Eqs. (61) and (65)]. The reversible entropy parts can be exactly identified by first-order contributions to heat flows $q_j$ in powers of $i$ [Eq. (70)]. The second-order contributions to $q_j$ are given for the common CMP model by Joule losses $-r_j i^2$, and $r = r_h + r_c$, with $r$ determined by the electrical resistivity $\rho$ and $r_h = r_c = r/2$, which is no longer valid outside of the CMP assumption. Exact analytical expressions are presented for $r_j$ in the general case. As a major result it turns out that for inhomogeneously distributed Seebeck coefficient $\alpha(x, T)$ in the device volume, contributions $r_{j2}$ arise in $r_j$ which only depend on the $\alpha$ and the thermal conductivity $k$. The $r_{j2}$ terms are singular for $k \to 0$. This leads to zero efficiency for the TE device in Eq. (109), in contrast to the CMP description which leads for $k \to 0$ to finite EMP and $P_{\max}$. A broad literature in thermoelectrics is dedicated to achieving high-$Z$ values by reduction of $k$. This concept of improving TE materials is in question, and an adapted figure of merit $Z$ is presented to deal with the situation. The analytical calculation methods presented allow for an improved device analysis also in case of low-$k$ materials.

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