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Modeling thermal behavior and work flux in finite-rate systems with radiation

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Abstract

We apply thermodynamic analysis in modeling, simulation and optimization of radiation engines as non-linear energy converters. We also perform critical analysis of available data for photon flux and photon density that leads to exact numerical value of photon flux constant. Basic thermodynamic principles lead to expressions for converter's efficiency and generated work in terms of driving energy flux in the system. Steady and dynamical processes are investigated. In the latter, associated with an exhaust of radiation resource measured in terms of its temperature decrease, real work is a cumulative effect obtained in a system composed of a radiation fluid, sequence of engines, and an infinite bath. Variational calculus is applied in trajectory optimization of relaxing radiation described by a pseudo-Newtonian model. The principal performance function that expresses optimal work depends on thermal coordinates and a dissipation index, h, in fact a Hamiltonian of the optimization problem for extremum power or minimum entropy production. As an example of work limit in the radiation system under pseudo-Newtonian approximation the generalized exergy of radiation fluid is estimated in terms of finite rates quantified by Hamiltonian h. The primary results are dynamical equations of state for radiation temperature and work output in terms of process control variables. In the second part of this paper these equations and their discrete counterparts will serve to derive efficient algorithms for work optimization in the form of Hamilton–Jacobi–Bellman equations and dynamic programming equations. Significance of non-linear analyses in dynamic optimization of radiation systems is underlined.

1. Introduction

The contemporary theory of work flux in energy systems includes both energy generators (engines) and refrigerators or heat pumps. Locally, work flux is an indirect effect of energy transfer between two reservoirs and a thermal machine producing or consuming power. Energy systems can be described by considering the behavior of efficiency, energy flux, entropy production and mechanical power, in steady and unsteady operations. Quite often, a quantitative description of non-linear energy transfer in various parts of the system assumes that the energy flux is proportional to the difference of temperature in a certain power, T^m. A special importance is the case when $m = 4$, which refers to radiation engines. In our previous paper [1] we analyzed effect of non-linear laws on efficiency of power production and entropy generation in systems composed of a resource, the environment and an imperfect (non-Carnot) thermal machine. Observing that a finite flow of a resource fluid in steady systems is consistent with a finite reservoir in unsteady ones, we suggested that common dynamical equations describing changes of a driving fluid property in time (spatial or chronological) can be obtained. Such equations will be derived here for systems with radiation that produce or consume work. They can serve as differential constraints in problems of dynamical optimization, in particular as constraints in work optimization problems. In the optimal control theory such differential constraints are customarily called the state equations.

In this paper we derive various state equations describing the temperature in power production systems with radiation. These equations can be applied to formulate

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Nomenclature

A	generalized exergy of a continuous process
a	universal coefficient related to Stefan–Boltzmann constant
B	classical available energy (exergy)
C_v	heat capacity at a constant volume
c	light speed
c_{mh}	molar heat capacity defined as the derivative dh/dT
E	internal energy
F	free energy, cross-sectional area
G	molar mass flux, total flow rate
g_1, g	partial and overall conductances
H, h_v	enthalpy and enthalpy of unit volume
H_{TU}	height of transfer unit
J	flux density
k_B	Boltzmann constant
N	number of particles
n	mole number
m	temperature exponent in exchange equation
P	pressure, cumulative power output at a stage
p	local power, constant of the photon flux in Eq. (13)
Q_1	cumulative heat
q_1	driving energy flux
r_1, r_2	resistances, reciprocals of g_1 and g_2
S	entropy, entropy of controlled phase
$\Delta S_{1'}$	entropy change of the circulating fluid along the isotherm $T_{1'}$ in Fig. 1
$\Delta S_{2'}$	entropy change of the circulating fluid along the isotherm $T_{2'}$ in Fig. 1
S_σ	entropy produced in the system
$s_{v_{gen}}$	entropy generated per unit volume
T	temperature of controlled phase
T_1, T_2	bulk temperatures of fluids 1 and 2
$T_{1'}$, T_2	temperatures of circulating fluid (Fig. 1)
T^e	constant equilibrium temperature of environment
T'	Carnot temperature, temperature of controlling phase
t	physical time, contact time
$\dot{T} = dT/d\tau$	rate of temperature change as the control variable
u	hydrodynamic velocity
V	system volume, optimal work function
$W = P/G$	work, power per unit flux
x	transfer area coordinate

Greek symbols

α'	overall heat transfer coefficient
ε	emission coefficient
g	cumulative conductance
μ	chemical potential
$\eta = p/q_1$	first-law efficiency
Φ	factor of internal irreversibility
σ	Stefan–Boltzmann constant
σ_s	rate of entropy production
τ	non-dimensional time, number of the heat transfer units (x/H_{TU})

Subscripts

f	flow quantity
i	ith state variable
m	molar quantity
mp	maximum power point
N	Newtonian
v	per unit volume
0	reference state
1, 2	first and second fluid

Superscripts

e	environment, equilibrium
f	final state
i	initial state
N	total number of stages

optimization algorithms, thus leading to optimal controls, optimal trajectories and optimal performance functions. Each optimal performance function represents a potential. In the second part of this paper we will use a part of our earlier results [1] and new findings obtained here to formulate efficient algorithms for work optimization in non-linear energy systems. With the help of these algorithms work potentials can be found as principal functions of related optimization problems. When suitable boundary conditions are assumed in a non-linear system of interest [3] the work potential becomes a finite-rate generalization of the classical, reversible exergy [2]. This results in enhanced bounds on work delivered from or supplied to the system [3–6] in comparison with those implied by the classical exergy, which is the reversible work potential.

Using in part results of [1] the present paper focuses on radiative energy converters (engines and heat pumps) as systems satisfying suitable balance laws and the second law of thermodynamics. In particular, we focus on thermal behavior and work flux from a sequence of radiation engines (Fig. 1) for which we develop several (exact or approximate) expressions for state equations.

Also with basic formulae of black radiation thermodynamics and the Stefan–Boltzmann law (to describe effects of emission and adsorption of radiation), a general formula for converter's efficiency follows, applicable when estimating an irreversible work limit as extension of the classical work potential. The real work is a cumulative effect obtained from a system composed of: radiation fluid at flow, a set of sequentially arranged engines, and an infinite

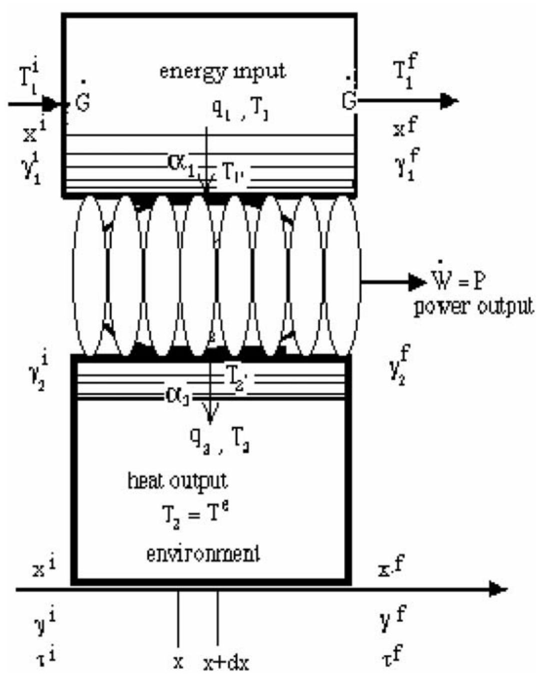

Fig. 1. Sequential power generation in a flow system with radiation, as a resource fluid. The scheme is a tool for evaluation of generalized exergy of radiation fluid.

bath. To set a maximum work problem for this system (Fig. 1) the concept of a multistage process is used in which each elementary stage is the Chambadal–Novikov–Curzon–Ahlborn (CNCA) operation [3,4,7]. Each stage can be illustrated on T–S diagram, and irreversibilities in thermal machines can be considered by using internal irreversibility factor Φ (interpreted in Fig. 1 of our previous paper [1]). In fact, the factor Φ is a synthetic measure of the machine's imperfection. By definition, $\Phi = \Delta S_{2'}/\Delta S_{1'}$ (where $\Delta S_{1'}$ and $\Delta S_{2'}$ are respectively the entropy changes of the circulating fluid along the two isotherms $T_{1'}$ and $T_{2'}$) equals the ratio of the entropy fluxes across the thermal machine, $\Phi = J_{s2'}/J_{s1'}$. The quantity Φ satisfies inequality $\Phi > 1$ for engine mode and $\Phi < 1$ for heat pump mode of the system. The use of an optimization method (e.g. variational calculus) leads to a finite-rate exergy of radiation. This generalized exergy is a function of usual thermal coordinates of radiation and a rate index, h. As every generalized exergy, it implies bounds on the work delivered from (or supplied to) the radiation fluid that are stronger than the classical reversible bounds. In the reversible limit the classical exergy of radiation is recovered.

Black radiation is a specific fluid governed by its characteristic statistical mechanics, thermodynamics and kinetics (Section 2). The mechanism of energy transfer between that fluid and a medium circulating in the engine has the significant influence on the efficiency of power production. In the radiation case the energy transfer is strongly non-linear. Instead of Newton's linear law, the radiative energy transfer obeys the law, $q \propto \Delta(T^m)$, i.e. energy flux is proportional to the difference in T^m for $m = 4$. The performance index or work W delivered in the radiation engine mode is positive by assumption. In the heat-pump mode W is negative, which means that the positive work $(-W)$ must be supplied to the system.

Performance bounds for thermal machines governed by the transfer law $q \propto \Delta(T^m)$ are known from works of De Vos [7], Gordon and Ng [8], Chen and Yan [9], Chen et al. [10,11], Wu [12,13] and coworkers of these researchers. Recent treatments [1,3–6,8] relax the restriction to steady systems (associated with infinite reservoirs), and take into account the effect of internal irreversibilities within energy generators (Carnot engines replaced by more realistic thermal machines). Consequently, a typical contemporary theory is non-linear and treats imperfect processes subject to the assumption of a finite resource (finite hot reservoir).

The problem of a generalized exergy is associated with work production by a finite resource interacting with the environment in a finite time. To find extremum work and associated exergy, optimization problems are considered, for a maximum of work delivery [max W] and for a minimum of the work supply [min$(-W)$]. The generalized exergy is the maximum work that refers to a minimally irreversible, finite-rate process. It is quantified in terms of the states of the resource and environment, a process rate index (hamiltonian h) and an imperfection factor of the thermal machine, Φ. While a number of formulae for generalized exergies were recently proposed [1,3–6], their post-classical terms were evaluated to date under the assumption of the exponential relaxation to equilibrium, consistent with linear dynamics [1,6].

However, in radiation fluids, which are non-linear thermodynamic systems, fluid's properties vary along the path, and the optimal relaxation curve is non-exponential. Still the shape of the optimal curve has to be determined from the condition for the optimum power. In the present paper various differential models of controlled relaxation dynamics are studied, some of them differing with the degree of accuracy of the process description. While simpler models are easier to solve, those more complicated ones may describe the related physics in a more exact way, and this is why they may be preferred. Modifications of relaxation models are also considered, depending on the mode of energy exchange with the environment.

2. Thermodynamics of radiation

A part of this section contains the material familiar to a physicist, yet we shall briefly adduce important formulae to make the paper self-contained. This is, we believe, compensated by the significance of novel information related to the proper adjustment of the so-called photon flux constant essential in consistent description of photon flows.

Free energy of radiation can be derived from Boson statistics [14]. The result is

$$F = E - TS = -\frac{1}{3}aVT^4 = -\frac{4}{3c}\sigma VT^4, \tag{1}$$

where the universal coefficient a is related to the Stefan–Boltzmann constant $\sigma = \Pi^2 k_B^4 (60h^3c^2)^{-1}$ by the direct and inverse formula

$$a = 4\sigma/c \quad \sigma = ac/4. \tag{2}$$

The entropy of homogeneous radiation occupying the volume V is then

$$S = -\frac{\partial F}{\partial T} = \frac{4}{3}aVT^3 = \frac{16}{3c}\sigma VT^3. \tag{3}$$

Whereas the radiation pressure P is

$$P = -\frac{\partial F}{\partial V} = \frac{1}{3}aT^4 = \frac{4}{3c}\sigma T^4 \tag{4}$$

and the energy of radiation is

$$E = F + TS = aVT^4 = \frac{4}{c}\sigma VT^4. \tag{5}$$

This expression corresponds with the heat capacity at the constant volume

$$C_v(T, V) = 4aT^3V = 16c^{-1}\sigma T^3 V. \tag{6}$$

It follows (see below) that the number of photons in a black box is also proportional to the product T^3V. Therefore, the useful conclusion stemming from Eqs. (3) and (6) is that both entropy and heat capacity per one black photon are constant.

Clearly, the following relations are valid

$$PV = \frac{1}{3}aVT^4 = \frac{4}{3c}\sigma VT^4 = \frac{E}{3}. \tag{7}$$

Now we will make use of the fact that the free energy (1) does not contain explicitly the number of particles N. From Eq. (1) and free energy differential the chemical potential of black radiation is

$$\mu = (\partial F/\partial N)_{T,V} = 0. \tag{8}$$

This is consistent with the vanishing Gibbs function for the black radiation

$$G = H - TS = F + PV = -\frac{1}{3}aVT^4 + \frac{1}{3}aVT^4 = 0. \tag{9}$$

Associated with the vanishing chemical potential μ is the equality

$$H = TS = -T\frac{\partial F}{\partial T} = \frac{4}{3}aVT^4 = \frac{16}{3c}\sigma VT^4. \tag{10}$$

When a general formula for the first differential of the pressure (grand) potential

$$d\Omega = -P\,dV - S\,dT - N\,d\mu \tag{11}$$

is applied to the function

$$\Omega \equiv -PV = -\frac{1}{3}aVT^4 = -\frac{4}{3c}\sigma VT^4 = -\frac{E}{3} \tag{12}$$

correct pressure and entropy is obtained by partial differentiation of Ω with respect to the volume and temperature. On the other hand, differentiation of Ω with respect to chemical potential (to get the particle number N) cannot be effective due to the constancy of (vanishing) μ.

Nonetheless, statistical mechanics calculations of quantum theory [14–18] show that N is proportional to VT^3, or $N/(VT^3) = p^0$ is a constant. This also means that the photon flux, $\dot{N}$, the product of the density of photons N/V and their mean flow velocity $c/4$, is proportional to T^3. A numerical value of the related proportionality constant, also called the constant of the photon flux, is approximately

$$p = 1.52 \times 10^{11}\ \text{photons cm}^{-2}\ \text{K}^{-3}\ \text{s}^{-1}. \tag{13}$$

In terms of this quantity, the flux density of photons is $J_N = pT^3$ photons cm^{-2} s^{-1}. Of course, $\dot{N} = pT^3F$, i.e. the flux itself is the product of the quantity J_N and the cross-section area F. The literature values of p fluctuate depending on approximations made in statistical calculations. From Landau and Lifshitz statistical evaluation of photon's number [15]

$$N = 0.244(k_B T\hbar^{-1}c^{-1})^3 V$$

the value of $p = 1.17 \times 10^{11}$ photons cm^{-2} K^{-3} s^{-1} is obtained, which differs from that given by Eq. (13). As we shall show soon, both considered values are approximate, but there is a way to find precise value of p or p^0 based on the requirement that photons must satisfy exactly the state equation for an ideal gas.

Although the numerical value of p in Eq. (13) is not exact we shall use it for a while to show how this approximation influences the form of the state equation and values of some thermodynamic quantities referred to one photon. The proportionality of N to VT^3 means that the entropy per one black photon $S/N =$ constant and that the energy of a single black photon is proportional to the absolute temperature, T. With p of Eq. (13) the entropy per one black photon is

$$\begin{aligned} s_{ph} &= \frac{S}{N} = \frac{J_s}{J_N} = \frac{(4/3)\sigma T^3}{pT^3} = \frac{4\sigma}{3p} \\ &= \left(\frac{4}{3}\right)\frac{5.6696 \times 10^{-5}\ \text{erg cm}^{-2}\ \text{s}^{-1}\ \text{K}^{-4}}{1.52 \times 10^{11}\ \text{cm}^{-2}\ \text{K}^{-3}} \\ &= 4.973 \times 10^{-16}\ \text{erg K}^{-1}. \end{aligned} \tag{14}$$

Comparing this value with the numerical value of the universal Boltzmann constant

$$k_B = 1.3807 \times 10^{-16}\ \text{erg K}^{-1}$$

yields an approximate result

$$s_{ph} = 3.60204 k_B. \tag{15}$$

The energy per one black photon is approximately

$$\begin{aligned} e_{ph} &= \frac{E}{N} = \frac{\sigma T^4}{pT^3} = \frac{\sigma}{p}T \\ &= \frac{5.6696 \times 10^{-5}\ \text{erg cm}^{-2}\ \text{s}^{-1}\ \text{K}^{-4}}{1.52 \times 10^{11}\ \text{cm}^{-2}\ \text{K}^{-3}}T \\ &= 3.73 \times 10^{-16} T\ [\text{erg}] \end{aligned} \tag{16}$$

or as the multiplicity of $k_B T$

$$\frac{e_{ph}}{k_B T} = \frac{3.73 \times 10^{-16}}{1.3807 \times 10^{-16}} = 2.70. \tag{17}$$

As $PV = E/3$, the energy density of photons may be written as

$$E/V = 3P = 2.70 N k_B T/V, \tag{18}$$

whence

$$PV = 0.9 N k_B T. \tag{19}$$

As this is a perfect gas equation with a strange coefficient 0.9 instead of 1, it may be suspected that the coefficient value is caused by approximations in statistical mechanics calculations of $p^0 = N/(VT^3)$. In a newer approach, Massa [16] expresses the average energy of a photon as $3k_B T$ rather than $2.7k_B T$ of Eq. (18). This gives a Wien coefficient that differs from the Planck coefficient by only 6%. This also agrees with Massa's analysis when applied to one photon [18]. His results lead also to reasonable data of gravitational constraints on blackbody radiation and the maximum (Planck) temperature [18].

We observe that, with Massa's adjustment, photons, as they should, are particles satisfying the perfect gas formula exactly

$$PV = N k_B T. \tag{20}$$

Inversion of this formula and use of photons pressure in terms of temperature, $P = (1/3)aT^4 = (4/3c)\sigma T^4$, allows for precise results of the photons number and density flux in terms of their temperature and volume

$$N = \frac{P(T)V}{k_B T} = \frac{a}{3k_B} T^3 V = \frac{4\sigma}{3ck_B} T^3 V, \tag{21}$$

$$J_N = \frac{N}{V}\frac{c}{4} = \frac{ac}{12k_B} T^3 = \frac{\sigma}{3k_B} T^3. \tag{22}$$

This result is the particle counterpart of the Stefan–Boltzmann formula for density of flowing energy

$$\dot{E}/V = \sigma T^4. \tag{23}$$

Applying in formula (16) the readjusted value $3k_B T$ for the energy per one black photon

$$e_{ph} = \frac{E}{N} = \frac{\sigma}{p} T = 3k_B T \tag{24}$$

yields the following value of the photon flux constant

$$p = \frac{\sigma}{3k_B} = \frac{ac}{12k_B}. \tag{25}$$

This yields the exact numerical value of $p = 1.369 \times 10^{11}$ photons $\mathrm{cm^{-2}\,K^{-3}\,s^{-1}}$ (roughly in the middle between two values considered above). This is the value that assures the satisfaction of the state equation of perfect gas in photons world, and sets the value of single photon entropy at the level $s_{ph} = 4k_B$ (see Eq. (27) below)). Eq. (22) thus satisfies the expression $J_N = pT^3$ for the above value of p. The related result for the photon number N, Eq. (21), is in terms of p

$$N = \frac{P(T)V}{k_B T} = \frac{4\sigma}{3ck_B} T^3 V = \frac{4p}{c} T^3 V. \tag{26}$$

The photon density formula involves the constant $p^0 = 4p/c$. The corresponding value of the entropy per one black photon is

$$s_{ph} = \frac{J_s}{J_N} = \frac{(4/3)\sigma T^3}{pT^3} = \frac{4\sigma}{3p} = 4k_B. \tag{27}$$

We can also speak about mass of black photons which is the ratio of their energy E and c^2. In particular, the division of energy (16) by c^2 yields the mass of single black photon as the quantity increasing linearly with the absolute temperature T. With this result and Eq. (14) one thus concludes that the entropy per unit mass of the photon gas is proportional to T^{-1} i.e. it decreases with T. Since the number of photons increases with T^3 and the energy per one photon increases with T, their total mass in the enclosed system, M, increases proportionally to T^4. This is in agreement with Eq. (5) which yields $M = aVT^4/c^2$.

3. Classical exergy of radiation

Work potential of radiation is particularly important in applications. A number of ways to derive exergy of enclosed radiation understood in classical sense can be advocated. First, the exergy of radiation can be derived from a general expression consistent with the exergy definition. As the classical exergy is the maximum reversible work obtained from the system (radiation) and the environment [2,19], the first differential of the radiation exergy satisfies a general relationship

$$\begin{aligned} dB &= dE - T_0\,dS + P_0\,dV - \mu_0\,dN \\ &= (T - T_0)\,dS - (P - P_0)\,dV + (\mu - \mu_0)\,dN \end{aligned} \tag{28}$$

with $\mu = 0$ and $\mu_0 = 0$. The integration of this expression yields the familiar formula

$$B = E - E_0 - T_0(S - S_0) + P_0(V - V_0) + \mu_0(N - N_0), \tag{29}$$

where the last term vanishes for the black radiation. This is the first formula from which the radiation exergy follows in the so-called Petela's form (Eq. (36) below). On the other hand, the formula can easily be transformed to a simpler form after applying the well-known thermodynamic relation

$$E = TS - PV + \mu N \tag{30}$$

for the two states considered, where the first state is the current state and the second one is the zeroth (equilibrium) state

$$E_0 = T_0 S_0 - P_0 V_0 + \mu_0 N_0. \tag{31}$$

The result is

$$B = E - T_0 S + P_0 V + \mu_0 N \tag{32}$$

or equivalently, after repeated use of formula (30)

$$B = (T - T_0)S - (P - P_0)V + (\mu - \mu_0)N. \quad (33)$$

For the black radiation its chemical potentials μ and μ_0 equal zero, hence

$$B = (T - T_0)S - (P - P_0)V \quad (34)$$

and its first differential satisfies Eq. (28) with $\mu = 0$.

Eq. (34) provides probably the simplest way to obtain the radiation exergy enclosed in the volume V. Applying in Eq. (34) the formulae describing entropy S and pressure P in terms of temperature T and volume V, Eqs. (3) and (4), yields familiar Petela's formula for the exergy density

$$b_v \equiv B/V = \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4) \quad (35)$$

[20]. Its alternative form is

$$B = aT^4V\left(1 - \frac{4}{3}\frac{T_0}{T} + \frac{1}{3}\left(\frac{T_0}{T}\right)^4\right). \quad (36)$$

The large bracket of this equation contains Petela's efficiency of the energy conversion, η_P.

Let us transform exergy Eq. (34) using the condition of vanishing Gibbs function, $G = 0$. The condition assures the equalities $TS = H$ and $T_0S_0 = H_0$. Clearly from Eq. (34)

$$B = H - T_0S - (P - P_0)V. \quad (37)$$

But in view of the equality $T_0S_0 = H_0$ one may subtract from this result H_0 and simultaneously add T_0S_0. This yields

$$B = H - H_0 - T_0(S - S_0) - V(P - P_0). \quad (38)$$

This result proves that the exergy of enclosed radiation, satisfying Petela's formula (36), can also be found from the enthalpy counterpart of standard equation (29) subject to the condition $\mu = \mu_0 = 0$, valid for black photons. One can observe a simple connection between Eq. (38) and that describing exergy flux per unit photon flux (see further text). While formula (36) complies with other results [20–22], it is not non-debatable since a number of authors advocated different equations for the exergy of enclosed radiation [19,23]. A through discussion of these issues can be found in papers quoted above and in reviews [24–26]. Our results here confirm that Eq. (36) is valid for the enclosed radiation but, otherwise, they show that its flow counterpart cannot be described by Petela's formula despite of some literature claims (see Section 4). This also means that Petela's efficiency is restricted to enclosed radiation and ceases to be valid for steady photon flux.

A suitable way to evaluate and interpret the classical exergy of radiation is provided by an equation given recently by Ozturk and his coworkers who developed a general scheme of thermodynamic transformations involving availability rather than entropy [27,28]. For a *heat pump mode* of the process (departure from the equilibrium) their equation reads

$$dB = \left(1 - \frac{T_0}{T}\right)C_v(T,V)\,dT + \left[(T - T_0)\left(\frac{\partial P}{\partial T}\right)_V - (P - P_0)\right]dV. \quad (39)$$

Using in this equation the expressions for the pressure

$$P = \frac{1}{3}aT^4 = \frac{4}{3c}\sigma T^4 \quad (4)$$

and heat capacity

$$C_v(T,V) = 4aT^3V = 16c^{-1}\sigma T^3V \quad (6)$$

yields the perfect differential of exergy B in the form

$$dB = 4aVT^3\left(1 - \frac{T_0}{T}\right)dT + \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4)\,dV, \quad (40)$$

where

$$b_v \equiv B/V = \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4)$$

is the exergy of unit volume in Petela's form (35). Eq. (40) in a sense replaces a similar one with particle number N as a variable known in the classical thermodynamics of open systems. In the radiation case the use of the particle number variable simultaneously with T would be inappropriate since N is a function of T rather than an independent coordinate of state. On the other hand, Eq. (40) contains two independent variables T and V that properly characterize the physical state of the system.

An integral form of Eq. (40) for a process starting at (T_0, V_0) and terminating at (T, V) is

$$B = \int_{T_0,V_0}^{T,V}\left(1 - \frac{T_0}{T}\right)4aVT^3dT + \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4)dV. \quad (41)$$

To calculate the integral we start at the point T_0, V_0 and first integrate with respect to temperature along the horizontal line of the constant volume $V = V_0$. After the temperature achieves its upper limit T, the integration is with respect to volume, along a vertical of a constant T, until the upper limit of volume V is attained. The result of integration is

$$B = aV_0(T^4 - T_0^4) - T_0\frac{4}{3}aV_0(T^3 - T_0^3) + \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4)(V - V_0) \quad (42)$$

and the rearrangements yield

$$B = \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4)V_0 + \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4)(V - V_0). \quad (43)$$

Thus finally

$$B = \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4)V \quad (44)$$

in accordance with Petela's formula (35).

For the *engine mode* of the process (approach to the equilibrium) the sign of the right hand side of Eq. (39) is inverted, and for the radiation engine

$$dB = -\left(1 - \frac{T_0}{T}\right)4aVT^3\,dT - \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4)\,dV. \quad (45)$$

Integration of this equation for the inverse reversible process starting at (T, V) and terminating at (T_0, V_0) requires the evaluation of the integral

$$B = \int_{T,V}^{T_0,V_0} -\left(1-\frac{T_0}{T}\right)4aVT^3\,\mathrm{d}T - \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4)\,\mathrm{d}V. \tag{46}$$

Due to absence of derivatives with respect to T and V and the perfect differential property of the integrand, the integration result is the same; i.e. Eqs. (35) and (44) are obtained again. This shows that in reversible processes work produced in a certain process equals to that consumed in its inverse. That property is associated with the potential nature of classical exergy, and does not longer hold when any residual dissipation is admitted in processes with finite rates.

4. Flux of classical exergy

Consider now flow of black photons. The total time derivative of the exergy of enclosed volume

$$\dot{B} = \left(1-\frac{T_0}{T}\right)4aVT^3\dot{T} + \frac{a}{3}(3T^4 - 4T^3T_0 + T_0^4)\dot{V} \tag{47}$$

does not represent the exergy flux. The situation is similar to that for energy at flow when the time derivative of the enclosed energy is not the energy flux because the latter incorporates the work against the pressure forces. As the energy flux is the product of the enthalpy density and the volume flux, the flux of radiation exergy, $\dot{B}_\mathrm{f}$, satisfies the general thermodynamic formula $\dot{B}_\mathrm{f} \equiv \dot{B} + (P - P_0)\dot{V}$. Using this formula and Eq. (38) one obtains for radiation fluid

$$\dot{B}_\mathrm{f} \equiv \dot{B} + (P-P_0)\dot{V} = \{h_v - h_{v0} - T_0(s_v - s_{v0})\}\dot{V}, \tag{48}$$

where subscript v refers to respective quantity per unit volume (density). The same result can be obtained from Eq. (29). Eq. (48) complies with results of general thermodynamics. It is also consistent with an expression for reversible power production associated with exergy flux $\dot{B}_\mathrm{f}$, represented by the integral

$$\dot{B}_\mathrm{f} = -\int_{T,P}^{T_0,P_0} \dot{V}\left(c_v(T)\left(1-\frac{T_0}{T}\right) + \frac{\mathrm{d}P}{\mathrm{d}T}\right)\mathrm{d}T. \tag{49}$$

By applying heat capacity density at the constant volume c_v we omit here familiar difficulties associated with an infinite heat capacity of photons at the constant pressure. As for black radiation $\mathrm{d}P = (4/3)aT^3\,\mathrm{d}T$, we calculate the enthalpy-related power $\dot{B}_\mathrm{f}$ using a *substitutional* heat capacity

$$c_h(T) \equiv c_v(T) + \mathrm{d}P/\mathrm{d}T = (4 + 4/3)aT^3 = (16/3)aT^3. \tag{50}$$

It may be noted that $c_h/c_v = 4/3$ and that the entropy contribution to power is still governed by c_v. We recall that in each black radiation system the value 4/3 is the power coefficient in an equation of isoentropic, adiabatic process, $PV^{4/3} = f(S)$. In fact, equations describing radiation in this process are formally identical with equations of perfect gases in which the ratio c_p/c_v equals 4/3. In the case of black radiation the analogy is only formal because the heat capacity c_p (partial derivative of enthalpy with respect to T at a constant P) is infinite (P is a function of T for the black radiation).

Substitution of Eq. (50) into (49) yields an integral of reversible power produced by black radiation at flow

$$\dot{B}_\mathrm{f} = -4a\dot{V}\int_T^{T_0}\{(4/3)T^3 - T^2T_0\}\,\mathrm{d}T. \tag{51}$$

Its integration between a variable initial temperature T and a constant final temperature T_0 yields

$$\dot{B}_\mathrm{f} = \frac{4}{3}a\dot{V}((T^4 - T_0^4) - T_0(T^3 - T_0^3)). \tag{52}$$

The reader can quickly generalize this result to the power formula applicable when both integration limits are arbitrary, i.e. when the temperature of the environment is not necessarily an integration limit.

Below we verify that Eqs. (49) and (52) describe indeed the enthalpy-based exergy flux of black radiation, i.e. that they satisfy general thermodynamic formula $\dot{B}_\mathrm{f} \equiv \dot{B} + (P - P_0)\dot{V}$. From Eq. (52)

$$\dot{B}_\mathrm{f} = \left(\frac{4}{3}a(T^4 - T_0^4) - T_0\frac{4}{3}a(T^3 - T_0^3)\right)\dot{V} = (h_v - h_{v0} - T_0(s_v - s_{v0}))\dot{V} = \dot{B} + (P - P_0)\dot{V}. \tag{53}$$

Yet, some specific formulae hold for radiation caused by the condition $\mu = 0$ for black photons. The upper line of Eq. (53) yields after simplification

$$\dot{B}_\mathrm{f} = \frac{4}{3}a(T^4 - T^3T_0)\dot{V} = \frac{4}{3}aT^4(1 - T_0/T)\dot{V}. \tag{54}$$

But, since the enthalpy density satisfies the formula

$$h_v = Ts_v = \frac{4}{3}aT^4 = \frac{16}{3c}\sigma T^4, \tag{10}$$

we conclude that the exergy flux of black photons is equal to the product of the enthalpy flux and the Carnot efficiency

$$\dot{B}_\mathrm{f} \equiv \{h_v - h_{v0} - T_0(s_v - s_{v0})\}\dot{V} = \frac{4}{3}aT^4\dot{V}(1 - T_0/T) = h_v(1 - T_0/T)\dot{V}. \tag{55}$$

In brief, the flux of the classical exergy of radiation satisfies the formula

$$\dot{B}_\mathrm{f} = \dot{H}_\mathrm{f}(1 - T_0/T) = \dot{S}_\mathrm{f}(T - T_0). \tag{56}$$

The energy flux is expressed above as in the case of usual substance, i.e. in terms of enthalpy flux, $h_v\dot{V}$, and the entropy flux equals $s_v\dot{V}$.

In conclusion, the calculation of exergy flux of radiation is as exact as that of a substance, and the same general formulae can be applied provided that the constraint $P = P(T)$ is incorporated for radiation.

5. Efficiencies of energy conversion

The enthalpy base of the energy flux is in complete agreement with the energy flux formula obtained as the formal component of the energy momentum tensor for isotropic radiation [17]. The enthalpy-based exergy efficiency is that of Carnot

$$\eta_{\rm J} \equiv \frac{\dot{B}_{\rm f}}{\dot{H}_{\rm f}} = \frac{(4/3)a(T^4 - T^3 T_0)\dot{V}}{(4/3)aT^4\dot{V}} = 1 - \frac{T_0}{T} \tag{57}$$

in agreement with Jeter's result for the radiation conversion [23]. This result can be compared with Petela's efficiency, for which

$$\eta_{\rm P} \equiv \frac{B}{E} = 1 - \frac{4}{3}\frac{T_0}{T} + \frac{1}{3}\left(\frac{T_0}{T}\right)^4. \tag{58}$$

This expression is often called the Landsberg–Petela–Press efficiency as it was derived independently by each of these authors. It predicts efficiencies lower than Carnot. Numerous efficiency formulae are available in Refs. [24–26,29–33], where, in particular, it is explained that efficiency (58) takes into account more irreversibilities than efficiency (57). Spanner's efficiencies can additionally be quoted [19] whose values lie between the values of efficiencies of Carnot and Petela

$$\eta_{\rm Sp} \equiv \frac{B}{E} = 1 - \frac{4T_0}{3T}. \tag{59}$$

The discrepancies between various efficiencies were explained by Bejan [24]. Using his procedure under the framework of endoreversible thermodynamics Badescu [30–32] found relationships generalizing Jeter [23], Spanner [19] and Petela [26] efficiencies. For example, the relation generalizing the last efficiency is

$$\eta_{\rm B} \equiv 1 - \frac{4}{4-n}\left(\frac{T_0}{T}\right)^n + \frac{n}{4-n}\left(\frac{T_0}{T}\right)^4, \tag{60}$$

where n is a parameter characterizing endoreversible thermal engine. For $n = 1$ (the case of Carnot engine) Petela's efficiency is recovered from Eq. (60). As already said, Petela's efficiency is lower then that of Carnot. Badescu [34] argues that this is so because it takes into account two irreversibilities, filling the system with and emptying it of radiation. More irreversibilities – less efficiency is a simple rule stemming from the discussed works. Yet, except [1], these works ignore (factor of) internal irreversibilities Φ, which also contribute to the efficiency decrease in practical systems.

6. Towards a dissipative exergy of radiation at flow

Further analysis is directed towards generalization of the radiation exergy for finite rates. As dissipative components are present in real reservoirs and within energy generators, any finite rates involve an inevitable minimum of dissipation. To define a rate-dependent exergy that extends the classical exergy for processes with dissipation a sequence of Chambadal–Novikov–Curzon–Ahlborn (CNCA) thermal machines is the basic theoretical tool. During the approach to the equilibrium the so-called *engine mode* of the system takes place in which work is released, during the departure – the so-called *heat-pump mode* occurs in which work is supplied. The work W delivered in the engine mode is positive by assumption (engine convention).

It is advisable to recognize the quantities that do not vary along paths of flow processes. In sequential processes with constant cross-sectional area F that are pertinent for exergy evaluation one of the constants is the flux density of the radiation volume, J_v

$$J_v = \frac{\dot{V}}{F} \equiv u. \tag{61}$$

The constancy of $J_v = u$ means that an average macroscopic velocity of the photons mixture in the direction of its flow, u, is the same for each point of the system. (For a special case of photons leaving the black box the constant value of $u = J_v$ equals $c/4$.) For sequential processes, in which cross-sectional area F perpendicular to the photon flow is natural constant quantity, the constancy of the volumetric density of photons, $u = J_v$, implies the constancy of their volume flux through the stages

$$\dot{V} = FJ_V = Fu. \tag{62}$$

In steady macroscopic flows of black photons, the constancy of volume flux $\dot{V}$ may be compared with that of particle flux for traditional particles. In fact, the constancy of $\dot{V}$ in a steady flow system is the counterpart of the condition of constant volume V in the enclosed system. For traditional particles the particle flux is conserved along a flow, for photons this is not a case. As the photon flux satisfies the equality

$$\dot{N} = \frac{N}{V}\dot{V} \tag{63}$$

and the density of black photons N/V is a function of T which varies along the flow, the flux of black photons cannot be constant in systems with a constant $\dot{V}$. Using perfect gas formula (20) associated with Massa's assumption $e_{\rm ph} = 3k_{\rm B}T$ [16] we evaluate the variation of photon flux along the process path in terms of current temperature T and volume flow $\dot{V}$

$$\dot{N} = \frac{a}{3k_{\rm B}}T^3\dot{V} = \frac{4\sigma}{3ck_{\rm B}}T^3\dot{V}. \tag{64}$$

The corresponding flux density of photons is

$$J_{\rm N} = \frac{\dot{N}}{F} = \frac{4\sigma}{3ck_{\rm B}F}T^3\dot{V}. \tag{65}$$

For constant $\dot{V}$ these formulae ensure a decrease of $\dot{N}$ and $J_{\rm N}$ in the engine mode of the process when T decreases along the path and energy is delivered from the radiation engine. On the other hand, the formulae ensure an increase of $\dot{N}$ and J_N when energy is consumed in a radiation-utilizing heat pump mode and radiation temperature T increases along the path. For constant volume flux, $\dot{V}$, both N and $\dot{N}$ depend on T in the same way, and Eq. (63) implies constancy of photons volume along the path of the considered process. This means that the state of flowing photons (T, V) contains one redundant variable, V. Therefore, when describing steady, one-dimensional photon flows, it suffices to use T as the only variable, similarly as in the case of enclosed radiation.

In irreversible finite-rate situations quasistaticity is lost and any extension of exergy to irreversible situations is non-trivial. It is due to finite rates that instantaneous efficiencies η are different from those of Carnot at each time instant. Therefore before any formulation of a work integral prior evaluation of a proper efficiency η should be made. In optimization approaches based on the variational calculus, η has to be evaluated as a function of state T and rate $\mathrm{d}T/\mathrm{d}\tau$, to assure the functional property (path dependence) of related work integral. As any exergy is a limiting work, its evaluation must be associated with the optimization that maximizes work W and assures an optimal path. The optimal work follows in the form of a potential function that depends on the end states and duration. This function is a finite-rate exergy when the final state of engine mode is that of equilibrium with the environment. Another function, also exergy type, is obtained when the initial state of heat-pump mode is that of equilibrium with the environment. While the reversibility property is lost for extended exergies, their kinetic bounds are stronger and hence more useful than classical thermostatic bounds. This substantiates the role of extended exergies for evaluation of energy limits in practical systems.

For the exergy evaluation the finiteness of the resource (radiation fluid) is essential; this makes the power production process unsteady in time. The analysis of a single CNCA unit is insufficient in this case, rather the treatment of complex sequential system with (finite or infinite number of) CNCA units is necessary. The work-production process involves the active energy exchange between two fluids through finite "conductances" (products of the effective transfer coefficient and the area). In the case of the radiation exergy the first fluid in Fig. 1 is the radiation fluid. As it follows from the Stefan–Boltzmann law, the transfer coefficient of radiation fluid α_1 is necessarily temperature dependent, $\alpha_1 = 4\sigma\varepsilon T_1^3$. The second fluid is a low-temperature fluid representing either low temperature radiation or the usual environment composed of the common substances of the Earth, as defined in the exergy theory. In any case the second fluid possesses a boundary layer as its own dissipative component, so that the corresponding exchange coefficient is α_2. (The second coefficient of the energy exchange in the system, α_2, can also be temperature dependent.) In the physical space, the direction of the macroscopic flow of radiation is along a horizontal coordinate x. Depending on the choice of the second fluid, two various exergy-like functions are obtained.

However, the use of transfer coefficients α_i is unnecessary in radiation problems. In fact, functions $\alpha_1 = \alpha_{10}T_1^3$ and $\alpha_2 = \alpha_{20}T_2^3$ are applied only in the so-called pseudo-Newtonian approach when, by assumption, a temperature dependent conductance is attributed to the driving force defined as the simple temperature difference. As we shall see later, the virtue of the pseudo-Newtonian approach is its potential of getting an analytical solution under an approximation of an overall coefficient for energy transfer. While this takes into account the temperature dependence, more exact approaches to the energy flux are preferred that involve differences of temperature T in power $m = 4$, i.e. use the Stefan–Boltzmann law. Then the concept of the effective transport coefficient is abandoned. However, these approaches do not lead to analytical solutions, so that numerical optimization techniques must be developed. They are briefly characterized below, see also [1].

We begin with the considerations of symmetric non-linear case in which the energy transfer rate is proportional to the difference of absolute temperatures in power m The case of $m = 4$ refers to the radiation, $m = -1$ to the Onsagerian kinetics and $m = 1$ to the Fourier law of heat exchange. (In the Onsagerian case quantities g_i are negative in the common formalism.)

Next we adduce the "hybrid non-linear case" in which the kinetics in the lower reservoir is Newtonian. The upper-temperature fluid is still governed by the kinetics proportional to the difference in T^m. Still other cases are possible, as, e.g. the case with the environmental kinetics governed by laws of the natural convection (where $q \propto (\Delta T)^m$), and some "mixed" cases.

Consequently, variety of physical models and related optimization algorithms can be applied, each model leading to its own generalized exergy function.

7. Basic analytical formulae of steady pseudo-Newtonian model

First we focus on a single infinitesimal CNCA engine as a one-stage component of the sequential system shown in Fig. 1. Next, an analysis will be developed to model cumulative power output (input) from (to) an infinite number of infinitesimal steps that model thermal behavior and exergy of the sequential system at the continuous limit. As the theory of elementary CNCA process is well known, we briefly present here its counterpart called Stefan–Boltzmann engine under the pseudo-Newtonian approximation and then pass to main formulae associated with cumulative power and entropy production of the sequential system at its continuous limit.

A single engine in Fig. 1 depicts an infinitesimal stage of the system. The location of this stage in the system is between x and $x + \mathrm{d}x$, where x is the geometric coordinate in the direction of the radiation flow. In a steady situation the state changes of the fluid in the differential engine (two isotherms and two irreversible adiabates) are stationary loops in the space. The radiation fluid (subscript 1) flows as a whole in the direction of the axis x with a finite volume flux, $\dot{V}$. The unknowns $T_{1'}$ and $T_{2'}$ (explicit in Fig. 1) are upper and lower temperatures of the fluid circulating in each engine. Between x and $x + \mathrm{d}x$ located is the circulation loop of each small engine and the differential conductances $g_1 = \mathrm{d}\gamma_1$ and $g_2 = \mathrm{d}\gamma_2$, where $\mathrm{d}\gamma_1 = \alpha_1(T_1)\mathrm{d}A_1$ and $\mathrm{d}\gamma_2 = \alpha_2(T_2)\mathrm{d}A_2$. The differentials $\mathrm{d}A_1$ and $\mathrm{d}A_2$ are two exchange areas at the infinitesimal stage. They are components of the composite area A whose differential satisfies $\mathrm{d}A = \mathrm{d}A_1 + \mathrm{d}A_2$. The *overall* conductance γ is defined in terms of $g_1 = \mathrm{d}\gamma_1$ and $g_2 = \mathrm{d}\gamma_2$ in the traditional way; $(\mathrm{d}\gamma)^{-1} = (\mathrm{d}\gamma_1)^{-1} + (\mathrm{d}\gamma_2)^{-1}$. Consequently, $\mathrm{d}\gamma$ is the product of an overall coefficient of heat transfer, α', and total differential area $\mathrm{d}A$.

The differential flux, $\mathrm{d}\dot{Q}_1$, is the energy flux subtracted from the radiation fluid when its state changes from T_1 to $T_1 + \mathrm{d}T_1$. The radiative energy exchange $\mathrm{d}\dot{Q}_1$ occurs by the emission and adsorption of radiation in the temperature range T_1 and $T_{1'}$. In the pseudo-Newtonian modeling the (non-Newtonian) flux of the exchanged radiation energy is the product of the variable coefficient $g_1 = \mathrm{d}\gamma_1 = \alpha_1(T_1^3)\mathrm{d}A_1$ and the temperature difference $T_1 - T_{1'}$. When the exact Stefan–Boltzmann law is used its energy exchange model takes rigorously into account entropy generation caused by simultaneous emission and absorption of black-body radiation. The entropy generation is the "classical" sum: $\mathrm{d}\dot{Q}_1(T_{1'}^{-1} - T_1^{-1}) + \mathrm{d}\dot{Q}_2(T_2^{-1} - T_{2'}^{-1})$, where $\mathrm{d}\dot{Q}_1$ is given by the Stefan–Boltzmann law.

The low-T part of the engine releases the heat proportional to $T_{2'} - T_0$ to the environment (or fluid 2) through conductance $\mathrm{d}\gamma_2$. This conductance can also be temperature dependent, as discussed below.

Due to the engine imperfection the first-law efficiency of each infinitesimal unit is given by the pseudo-Carnot formula, $\eta = 1 - \Phi T_{2'}/T_{1'}$ [1], where $\Phi = \Delta S_{2'}/\Delta S_{1'} = J_{s2'}/J_{s1'}$ is the parameter of internal irreversibility. Φ is measured in terms of the entropy changes of the circulating fluid along the two isotherms $T_{1'}$ and $T_{2'}$. Yet, $T_{1'}$ and $T_{2'}$ are not independent but connected by the entropy balance

$$\frac{g_2(T_2)(T_{2'} - T_2)}{T_{2'}} - \Phi\frac{g_1(T_1)(T_1 - T_{1'})}{T_{1'}} = 0. \tag{66}$$

We invert pseudo-Carnot formula, $\eta = 1 - \Phi T_{2'}/T_{1'}$, to substitute $T_{2'} = (1-\eta)\Phi^{-1}T_{1'}$ into the above entropy balance. We then obtain an equation for $T_{1'}$

$$T_{1'} = (g_1 + \Phi^{-1}g_2)^{-1}(g_1T_1 + (1-\eta)^{-1}g_2T_2). \tag{67}$$

With this result the flux of the radiation energy,

$$q_1 = \mathrm{d}\dot{Q}_1 \cong g_1(T_1^3)(T_1 - T_{1'}), \tag{68}$$

exchanged by simultaneous emission and adsorption follows in the pseudo-Newtonian formalism as

$$q_1 = g'(T_1 - \Phi T_2/(1-\eta)). \tag{69}$$

In Eq. (69) operational overall conductance was defined *with all g_i as functions of respective bulk temperatures of reservoirs*

$$g' \equiv g_2g_1(\Phi g_1 + g_2)^{-1} = (g_1^{-1} + \Phi g_2^{-1})^{-1}. \tag{70}$$

This, in fact, is the overall conductance of an inactive heat transfer that is suitably modified due to the presence of coefficient of internal dissipation. The work flux (power) follows in the form

$$p = \eta q_1 = \eta g'(\Phi, T_1, T_2)\left(T_1 - \frac{\Phi T_2}{1-\eta}\right). \tag{71}$$

The expression

$$T' = \Phi T_2(1-\eta)^{-1} \tag{72}$$

appearing in Eqs. (69) and (71) describes the so-called Carnot temperature in terms of the efficiency. The thermodynamic definition of Carnot temperature is $T' \equiv T_2T_{1'}/T_{2'}$ [1]. Despite temperature dependent conductances g_1 and g_2, Eq. (71) yields the same maximum power efficiency $\eta_{\mathrm{mp}} = 1 - \sqrt{\Phi T_2/T_1}$ as for engines driven by usual fluids whose heat flux is governed by (linear) Newtonian law of cooling. However, the non-linearity of radiation conductance g_1 becomes essential in dynamical problems, when the temperature of photons changes along the path.

Quite generally, i.e. regardless the form of kinetics involved, the differential of total entropy produced is obtained [1]

$$\begin{aligned}\mathrm{d}S_\sigma &= \frac{\mathrm{d}Q_1}{T_2}\left(\Phi\frac{T_{2'}}{T_{1'}} - \frac{T_2}{T_1}\right) \\ &= \mathrm{d}Q_1\left(\frac{(\Phi-1)}{T'} + \left(\frac{1}{T'} - \frac{1}{T_1}\right)\right).\end{aligned} \tag{73}$$

Yet, generality of Eq. (73) is limited to forms not involving time t. In fact, the time derivative of this equation, i.e. power of entropy production contains energy flux q_1 that is certainly influenced by the form of a respective kinetic formula, e.g. Eq. (77) below.

In pseudo-Newtonian description of power yield driven by non-linear exchange processes conductances g_i are only functions of temperatures of respective reservoirs. This is an approximation because, in fact, they are also influenced by temperatures of fluid circulating in the engine. A way to improve this situation is described below.

8. Steady non-linear models applying Stefan–Boltzmann equation

In a more exact modeling of radiation engines we abandon the concept of transfer coefficients and related conductances and exploit the Stefan–Boltzmann equation for energy transfer in its exact form.

In the *symmetric non-linear case* [1] we assume that the energy flux exchanged in each reservoir depends on the difference of temperatures in the same power m

$$q_1 = g_1(T_1^m - T_{1'}^m). \tag{74}$$

($m = 4$ for radiative energy exchange and 1 for Newtonian one.) Conductances g_i are now constants, different that those of previous section, yet, as usual, they are proportional to the respective areas; $g_i = \sigma_i A_i$, where each σ_i is the product of Stefan–Boltzmann constant σ and emission coefficient ε_i. We can still use the notion of Carnot temperature $T' \equiv T_{1'}T_2/T_{2'}$ as a suitable control variable in engine modeling [1]. From this definition temperature $T_{2'}$ satisfies the inverse expression $T_{2'} \equiv T_{1'}T_2/T'$. Substituting this expression into internal balance equation for entropy

$$\Phi g_1(T_1^m - T_{1'}^m)/T_{1'} = g_2(T_{2'}^m - T_2^m)/T_{2'} \tag{75}$$

and solving the result obtained with respect to $T_{1'}$ yields

$$T_{1'} = \left(T_1^m - g_2\frac{T_1^m - T'^m}{\Phi g_1(T'/T_2)^{m-1} + g_2}\right)^{1/m}. \tag{76}$$

From Eq. (76) and Eq. (74) written in the form

$$T_{1'} = (T_1^m - q_1/g_1)^{1/m} \tag{74'}$$

energy flux $q_1(T')$ follows

$$q_1 = g_1 g_2 \frac{T_1^m - T'^m}{\Phi g_1(T'/T_2)^{m-1} + g_2}. \tag{77}$$

This formula represents "thermal characteristics" of the system. An expression for $T_{2'}$ corresponding with (76) follows from the thermodynamic definition of Carnot temperature, $T_{2'} \equiv T_{1'}T_2/T'$. Also, one may calculate heat flux $q_2 = q_1(1-\eta) = \Phi T_2 q_1/T'$. The power yield related to Eq. (77) is

$$p = g_1 g_2 \frac{T_1^m - T'^m}{\Phi g_1(T'/T_2)^{m-1} + g_2}\left(1 - \Phi\frac{T_2}{T'}\right). \tag{78}$$

The maximization of p can be performed analytically or graphically, using Carnot temperature T' as the free control.

The entropy generation caused by simultaneous emission and absorption of black body radiation is the external part of the total entropy production that follows as the "classical" sum:

$$\sigma_s^{\text{ext}} = q_1(T_{1'}^{-1} - T_1^{-1}) + q_2(T_2^{-1} - T_{2'}^{-1}), \tag{79}$$

where each q_i incorporates the Stefan–Boltzmann law. Yet, this is only a part of the entropy production in the system. For the "symmetric" kinetics governed by the differences in T^m the T'-representation of the total entropy production in the system follows from Eqs. (73) and (77)

$$\sigma_s = g_1 g_2 \frac{T_1^m - T'^m}{\Phi g_1(T'/T_2)^{m-1} + g_2}\left(\frac{(\Phi-1)}{T'} + \left(\frac{1}{T'} - \frac{1}{T_1}\right)\right). \tag{80}$$

In this model no explicit formula exists for mechanical power or entropy production in terms of driving energy flux, q_1. A hybrid model, considered below, offers such opportunity.

In the *non-symmetric or hybrid non-linear case* [1] the radiation law ($m = 4$) governs the energy flow in the upper reservoir only, whereas the energy exchange in the lower one is Newtonian

$$q_2 = g_2(T_{2'} - T_2). \tag{81}$$

As before, to get $T_{1'}$ in terms of T' we substitute the expression $T_{2'} \equiv T_{1'}T_2/T'$ into the suitable (internal) balance equation for the entropy

$$\Phi g_1(T_1^m - T_{1'}^m)/T_{1'} = g_2(T_{2'} - T_2)/T_{2'}. \tag{82}$$

Yet, the procedure leads now to T' explicit in terms of $T_{1'}$ rather than $T_{1'}$ in terms of T'

$$T' = T_{1'} - \Phi g_1(T_1^m - T_{1'}^m)/g_2. \tag{83}$$

The mechanical power p in terms of $T_{1'}$ is

$$\begin{aligned} p &= q_1\eta \\ &= g_1(T_1^m - T_{1'}^m)\left(1 - \frac{\Phi T_2}{T_{1'} - \Phi g_1(T_1^m - T_{1'}^m)/g_2}\right). \end{aligned} \tag{84}$$

The large bracket of this formula contains the pseudo-Carnot efficiency expressed in terms of temperature $T_{1'}$ rather than in T'. With Eq. (74), the energy flux representation of power (84) is readily obtained

$$p = q_1\eta = q_1\left(1 - \frac{\Phi T_2}{(T_1^m - q_1/g_1)^{1/m} - \Phi q_1/g_2}\right). \tag{85}$$

The corresponding entropy production satisfies Eq. (73) with T' defined by (83). Hence the power of entropy generation in terms of temperature $T_{1'}$ is

$$\sigma_s = g_1(T_1^m - T_{1'}^m)\left(\frac{\Phi}{T_{1'} - \Phi g_1(T_1^m - T_{1'}^m)/g_2} - \frac{1}{T_1}\right). \tag{86}$$

For the upper reservoir $T_{1'} = (T_1^m - q_1/g_1)^{1/m}$, and Eq. (83) yields the following expression for Carnot temperature T' in terms of q_1

$$\begin{aligned} T' &= T_{1'} - \Phi g_1(T_1^m - T_{1'}^m)/g_2 \\ &= (T_1^m - q_1/g_1)^{1/m} - \Phi q_1/g_2. \end{aligned} \tag{87}$$

Eqs. (86) and (87) now lead to the representation of the entropy source in terms of q_1

$$\sigma_s = q_1\left(\frac{\Phi}{(T_1^a - q_1/g_1)^{1/m} - \Phi q_1/g_2} - \frac{1}{T_1}\right). \tag{88}$$

Eqs. (78), (84) or (85) allow analytical or graphical maximization of power with respect to a single control variable, T', $T_{1'}$ or q_1. Due to reversible component of power that persist for vanishing rates these equations have non-trivial optimal solutions even in absence of constraints on the rates. Optimization leads to the steady limits on power production in imperfect units. On the other hand Eqs. (80), (86) and (88) for entropy source have non-trivial optimization solutions only when their control variables are constrained. Otherwise they imply vanishing σ_s at the reversible Carnot point as an unconstrained minimum for σ_s. In dynamical problems considered below the constraints are those resulting from balances of energy and matter.

9. Dynamical theory for pseudo-Newtonian models

In dynamical problems temperature of at least one of the reservoirs changes (decreases in engine mode of the sequential process) due to the reservoir's finite capacity. This is the case involving a finite resource, appropriate to define an exergy. By integration of power expressions of previous section, functionals of cumulative power generation (consumption) and related exergies are obtained.

Our exergy-directed analysis extends those previous ones by considering the sequential operation with internal irreversibilities (within thermal machines of each stage). The factor of internal irreversibilities, Φ, satisfies inequality $\Phi > 1$ for engine mode and $\Phi < 1$ for heat pump mode of the system. In terms of Φ suitable formulae follow for generalized work and exergy in finite resource systems. Use of the substitutional quantity $c_h(T)$, Eq. (50), leads to the enthalpy density of black photons and allows to overcome known difficulties resulting form infinite value of c_p of photon gas.

As already remarked several physical models can be applied, each leading to its own generalized exergy. Below we shall consider these models in an order. First we focus on the pseudo-Newtonian model and corresponding exergies for two modes considered.

We begin with the energy exchange formula (69) written in terms of quantities cumulative along the process path

$$\mathrm{d}\dot{Q}_1 \equiv \mathrm{d}\gamma'(T_1 - \Phi T_2/(1-\eta)). \tag{89}$$

Its inversion yields the first-law efficiency of the imperfect process in the form

$$\eta = 1 - \Phi\frac{T_0}{T - \mathrm{d}\dot{Q}_1/\mathrm{d}\gamma'} = 1 - \Phi\frac{T_0}{T - \mathrm{d}\dot{Q}_1/(\alpha'\,\mathrm{d}A)}, \tag{90}$$

where T designates any value of T_1 on the path. The derivative term $\upsilon = -\mathrm{d}\dot{Q}_1/\mathrm{d}\gamma'$ is a control with units of temperature itself. It may be written in the form of several alternative expressions

$$\begin{aligned}\mathrm{d}\dot{Q}/\mathrm{d}\gamma' &\equiv -\upsilon = -\dot{V}c_h(T)\,\mathrm{d}T/(\alpha'(T)a_v F\,\mathrm{d}x)\\ &= -c_h(T)\,\mathrm{d}T/(\alpha'(T)a_v\,\mathrm{d}t) = -\chi\mathrm{d}T/\mathrm{d}t\\ &= -\mathrm{d}T/\mathrm{d}\tau\end{aligned} \tag{91}$$

of which the two last ones are the most suitable. In Eq. (91) $\chi = c_h/(\alpha' a_v)$ is a time constant for the energy exchange process. Two other useful quantities can also be selected in Eq. (91). The first one is a spatial scale for the overall transfer, H_{TU},

$$\frac{\dot{V}c_v}{\alpha' a_v F} = H_{\mathrm{TU}},$$

whereas the second is a non-dimensional time, τ,

$$\tau \equiv \frac{x}{H_{\mathrm{TU}}} = \frac{\alpha' a_v F}{\dot{V}c_v}x.$$

H_{TU} has the units of length and is known as the 'height of the heat transfer unit'. By definition the H_{TU} introduced above is referred to the radiation fluid at state 1. The independent variable τ is a non-dimensional length, $\tau = x/H_{\mathrm{TU}}$ called the 'number of transfer units'. Clearly τ measures the system extent, and it is a measure of the fluid's residence time t. Due to the similar type of dependence of α' and c_h on T, the time constant $\chi \equiv c_s/(\alpha' a_v)$ linking t and τ is practically temperature independent. This substantiates the usefulness of τ.

For ignored thermal resistance of environmental fluid (entropy production only due to the emission and adsorption of radiation), the overall coefficient of radiation energy transfer, α', varies proportionally to T^3, and so does c_h. In this limiting case χ is constant exactly, in other cases its constancy is only an approximation. Assuming a non-dissipative environment one can accept the constancy of χ in the last two expressions of Eq. (91) as a suitable property. With Eq. (91) the efficiency formula (90) becomes a simple modification of the Carnot formula

$$\eta = 1 - \Phi\frac{T_0}{T + \chi\mathrm{d}T/\mathrm{d}t} = 1 - \Phi\frac{T_0}{T + \mathrm{d}T/\mathrm{d}\tau}. \tag{92}$$

Yet, this result is not as universal as its quasistatic (zero rate) limit; in fact its denominator contains the Carnot temperature operator $T'(T, \dot{T})$ in the form restricted to pseudo-Newtonian models. Primarily classical fluids satisfy Eq. (92), see, e.g. [6,45,46]; its applicability to radiation is due to the approximate constancy of χ, discussed above.

The process is the passage of the vector $\mathbf{T} = (T, \tau)$ from its initial state $\mathbf{T}^{\mathrm{i}}$ to its final state $\mathbf{T}^{\mathrm{f}}$. In absence of frictional effects the power functional corresponding to efficiency (92) is the following generalization of reversible functional (49)

$$\begin{aligned}\dot{W}_{\mathrm{f}} &= -\dot{V}\int_T^{T_0}\left(c_v(T)\left(1 - \Phi\frac{T_0}{T + \chi\mathrm{d}T/\mathrm{d}t}\right) + P_T\right)\mathrm{d}T\\ &= -\dot{V}\int_T^{T_0}\left(c_h(T) - c_v(T)\Phi\frac{T_0}{T + \chi\mathrm{d}T/\mathrm{d}t}\right)\mathrm{d}T,\end{aligned} \tag{93}$$

where $P_T \equiv \mathrm{d}P/\mathrm{d}T = (4/3)aT^3$ and $c_h(T) \equiv c_v(T) + P_T = (16/3)aT^3$. A more transparent form of the above power integral is obtained after transforming it so as to extract from it the effect of the reversible power (49) and the associated efficiency term. For the pseudo-Newtonian model we obtain

$$\begin{aligned}\dot{W}_{\mathrm{f}} &= -\dot{V}\int_T^{T_0}\left(c_h(T) - c_v(T)\frac{T_0}{T}\right)\mathrm{d}T\\ &\quad - T_0\dot{V}\int_T^{T_0}\left(c_v(T)\left(\frac{\chi(\mathrm{d}T/\mathrm{d}t)^2}{T(T + \chi\mathrm{d}T/\mathrm{d}t)}\right.\right.\\ &\quad \left.\left. + (1-\Phi)\frac{\mathrm{d}T/\mathrm{d}t}{T + \chi\mathrm{d}T/\mathrm{d}t}\right)\right)\mathrm{d}t.\end{aligned} \tag{94}$$

Associated entropy production per unit flowing volume can be evaluated as the difference between the outlet and inlet entropy fluxes. In terms of the Carnot temperature $T' = T_1 + \chi\mathrm{d}T_1/\mathrm{d}t$ and after using $q_2 = q_1\Phi T_0/T'$ we find for the pseudo-Newtonian model

$$\sigma_s = \frac{q_2}{T_2} - \frac{q_1}{T_1} = \frac{g'(T_1 - T')^2}{T_1 T'} + q_1 \frac{(\Phi - 1)}{T'}. \quad (95)$$

This is consistent with general equation (73) and the model-related equation (89). Comparison of Eqs. (94) and (95) shows that the term multiplied by T_0 in the power expression (94) is the entropy production of the pseudo-Newtonian model. It is here split into the sum of two non-negative terms. The first term, related to the approximate description of the effect of emission and adsorption of radiation, is obviously positive. The second term, or the product $q_1(\Phi - 1)/T'$, is always non-negative as the signs of q_1 and $\Phi - 1$ are the same (positive for engine and negative for heat pump). A concise form of power functional (94)

$$\dot{W}_{\mathrm{f}} = -\dot{V}\int_T^{T_0}\left(c_h(T) - c_v(T)\frac{T_0}{T}\right)\mathrm{d}T - T_0\dot{V}\int_T^{T_0}\sigma_v\,\mathrm{d}t \quad (96)$$

(where, for photons $c_v(T) = 4aT^3$) is in agreement with the Gouy–Stodola law. This form is quite general and not restricted to the pseudo-Newtonian model. However, the (first) reversible term of this equation apparently shows the disagreement between the resulting, reversible efficiency and the Carnot efficiency. Therefore we stress that the reversible *thermal* efficiency of the radiation conversion is always Carnot. Indeed, comparison of Eqs. (48) and (49) shows that the apparent disagreement is caused by the additive, work-related term $P_T \equiv \mathrm{d}P/\mathrm{d}T$ in the exergy formulae, Eqs. (49), (93) and a like. For radiation fluids, the pressure contribution to the exergy in the form of the term $P_T \equiv \mathrm{d}P/\mathrm{d}T$ is masked by the dependence of P on T.

Integration of the first (reversible) part of integral (96) and calculation of $\dot{W}_{\mathrm{f}}^{\mathrm{rev}}/\dot{V}$ yields the classical exergy of flowing radiation fluid per unit volume, Eqs. (48)–(53). When the environment temperature is not necessarily a limit of the integration, the specific work of flowing radiation between two arbitrary states is obtained as the exergy difference. From Eq. (51)

$$\begin{aligned}\dot{W}_{\mathrm{f}}^{\mathrm{rev}}/\dot{V} &= -\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}}\{(16/3)aT^3 - 4aT^2T_0\}\,\mathrm{d}T \\ &= (h_v^{\mathrm{i}} - h_v^{\mathrm{f}}) - T_0(s_v^{\mathrm{i}} - s_v^{\mathrm{f}}) = \Delta b_v. \quad (97)\end{aligned}$$

These results are in agreement with general thermodynamics. They confirm that the first term of power functional (94) is path independent. Thus, whenever an extremum of the functional is sought, only the second, irreversible term contributes to the optimization solution.

In terms of non-dimensional time $\tau = t/\chi$ and per unit system volume entropy production functional of the pseudo-Newtonian model, Eq. (94), is

$$\begin{aligned}s_{v_{\mathrm{gen}}} &\equiv \dot{S}_{\mathrm{gen}}/\dot{V} \\ &= \int_T^{T_0}\left(c_v(T)\left(\frac{\dot{T}^2}{T(T+\dot{T})} + (1-\Phi)\frac{\dot{T}}{T+\dot{T}}\right)\right)\mathrm{d}\tau. \quad (98)\end{aligned}$$

The additive structure of two parts in Eq. (94) is an important property that causes that the two problems of extremum work (94) and the associated problem of minimum entropy generation (98) have the same solutions whenever end states are fixed. The optimization problem can thus be stated as the variational problem for either functional of work or of entropy production. When work W is an optimization criterion, the problem is that of maximum W for engine mode and that of minimum of $(-W)$ for heat-pump mode. When optimization of the entropy production is considered, a minimum is sought for each process mode. The generalized exergy is the extremum of W with appropriate integration limits ($T^{\mathrm{i}} = T$ and $T^{\mathrm{f}} = T_0$ for the engine mode and $T^{\mathrm{i}} = T_0$ and $T^{\mathrm{f}} = T$ for the heat-pump mode. In the quasistatic limit (zero rates, $\dot{T} = 0$), Eq. (94), leads always to *classical exergy*. Moreover, it leads to the same classical exergy for each mode when proper integration limits, stated above, are used. The absolute value of work (94) describes a change of generalized exergy of radiation in operations with imperfect thermal machines and when dissipative phenomena due to the radiation emission and adsorption are essential.

We focus here on the minimum entropy production formulation for functional (98). An equation for the optimal temperature follows from the condition $\varepsilon = h$, where $\varepsilon = (\partial L/\partial\dot{T})\dot{T} - L$ is the energy-like integral for Lagrangian L contained in equations of power or entropy production, and h is a constant value of ε determined from the boundary conditions for T and τ. The present h has units of entropy density or specific heat per unit volume, and should be distinguished from other Hamiltonians used occasionally with respect to the energy, $E = h$. Our $h = H/VT_0$, where H is the Hamiltonian expressed in the energy units and V is the volume. For any rate independent Φ the first integral for L of Eq. (98) is

$$\varepsilon(T,\dot{T}) = \frac{\partial L}{\partial\dot{T}}\dot{T} - L = \Phi c_v(T)\frac{\dot{T}^2}{(T+\dot{T})^2} = h. \quad (99)$$

We obtain an optimal trajectory from Eq. (99). After introducing the function

$$\begin{aligned}\xi\left(\frac{h}{\Phi c_v(T)}\right) &\equiv \pm\sqrt{\frac{h}{\Phi c_v(T)}}\left(1 - \pm\sqrt{\frac{h}{\Phi c_v(T)}}\right)^{-1} \\ &= \left(\pm\sqrt{\frac{\Phi c_v(T)}{h}} - 1\right)^{-1} \quad (100)\end{aligned}$$

(upper sign refers to the heat-pump mode, lower one to the engine mode) a pseudo-exponential extremal follows in the form

$$\dot{T} = \xi(h, \Phi, T)T. \quad (101)$$

In this equation the slope of the logarithmic rate $\xi = \mathrm{d}\ln T/\mathrm{d}\tau$ is a state dependent quantity. The slope ξ is the rate indicator, positive for the fluid's heating and negative for fluid's cooling.

Application of extremal (101) in Eq. (98) leads to the minimum entropy production in the form

$$s_{v_{\rm gen}} = \int_{T^{\rm i}}^{T^{\rm f}} \frac{c_v(T)}{T}\left(\pm\sqrt{\frac{h}{\Phi c_v(T)}} + (1-\Phi)\left(1 - \pm\sqrt{\frac{h}{\Phi c_v(T)}}\right)\right){\rm d}T. \quad (102)$$

With this result and the Gouy–Stodola law we obtain the density of generalized exergy for the fluid at flow

$$a_v(T,T_0,h) = b_v(T,T_0,0) \pm T_0 s_{v_{\rm gen}} = \frac{4}{3}aT^4(1-T_0/T) \pm T_0\int_{T}^{T_0} \frac{c_v(T)}{T}\left(\pm\sqrt{\frac{h}{\Phi c_v(T)}} + (1-\Phi)\left(1 - \pm\sqrt{\frac{h}{\Phi c_v(T)}}\right)\right){\rm d}T, \quad (103)$$

where the second-line term is non-classical. For radiation $c_v = 4aT^3$ and the expression $h = (4/3)aT^4$ is the enthalpy of the radiation fluid. The classical term in the above exergy equation is the reversible flow exergy of black radiation per unit volume which is recovered at the reversible limit when Hamiltonian $h = 0$. This classical exergy satisfies the formula

$$b_v \equiv \dot{B}_{\rm f}/\dot{V} = h_v - h_{v0} - T_0(s_v - s_{v0}) \quad (104)$$

consistent with Eq. (55) for the radiation fluid. For that fluid the optimal trajectory which solves Eqs. (100) and (101) is

$$\pm(4/3)a^{1/2}\Phi^{1/2}h^{-1/2}(T^{3/2} - T^{{\rm i}3/2}) - \ln(T/T^{\rm i}) = \tau - \tau^{\rm i}. \quad (105)$$

The integration limits refer to initial (i) and current state (no index) of the radiation fluid, i.e. to temperatures $T^{\rm i}$ and T, corresponding with $\tau^{\rm i}$ and τ. Fig. 2 shows an example of optimal paths for radiation in both process modes. Relaxation to the equilibrium occurs in engine mode whereas utilization or escape from the equilibrium – in heat-pump mode. Clearly, radiation does not relax exponentially. Qualitative difference of relaxation curve from those describing exponential relaxation in linear processes is observed.

Eq. (105) also allows to draw curves describing non-dimensional durations $t^{\rm f} - \tau^{\rm i}$ in terms of Hamiltonian h for various internal irreversibilities ϕ and at fixed end temperatures $T^{\rm i}$ and $T = T^{\rm f}$. This is illustrated in Fig. 3, for $T^{\rm i} = 300$ K and $T^{\rm f} = 5800$ K.

After inverting these data to obtain curves for which duration $\tau^{\rm f} - \tau^{\rm i}$ is an independent variable one can solve the problem of numerical value of Hamiltonian needed for a prescribed duration, as shown in Fig. 4.

Eqs. (104) and (105) are associated with the entropy production (98) and the generalized availability of radiation

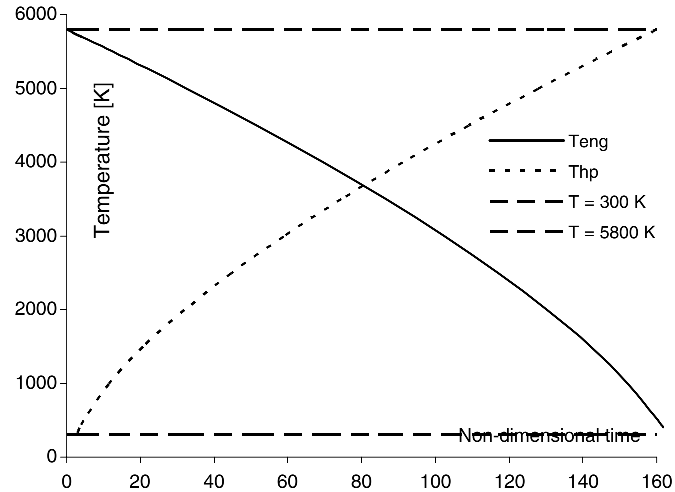

Fig. 2. Decreasing temperature of radiation relaxing in engine mode and increasing temperature of radiation utilized in heat pump mode in terms of non-dimensional time, for a constant value of Hamiltonian $h = 1 \times 10^{-8}$ [J K^{-1} m^{-3}], and the same coefficient $\phi = 1.0$ in both modes ("endoreversible" relaxation and utilization of radiation).

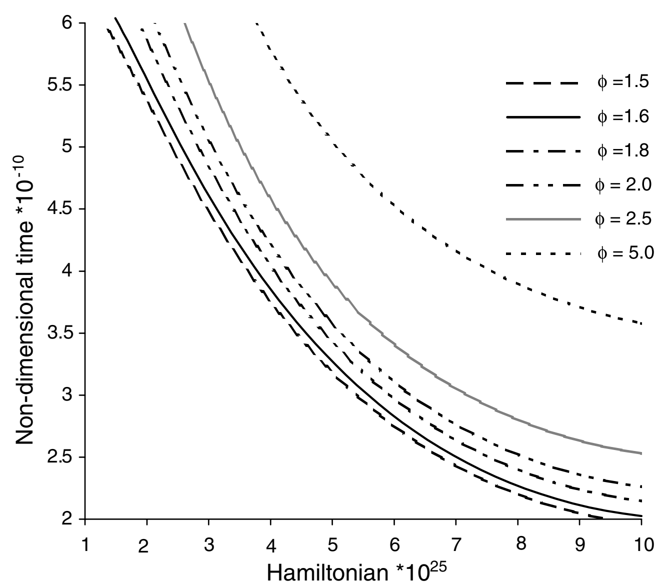

Fig. 3. Non-dimensional duration of engine mode in terms of Hamiltonian h [J K^{-1} m^{-3}] as an intensity index for various values of coefficient of internal irreversibilities ϕ, at prescribed boundary temperatures, $T^{\rm i} = 300$ K and $T^{\rm f} = 5800$ K.

$$a_v(T,T_0,h) = b_v(T,T_0,0) \pm (4/3)a^{1/2}h^{1/2}\Phi^{1/2}T_0(T^{3/2} - T_0^{3/2}) + (4/3)aT_0(1-\Phi)(T^3 - T_0^3). \quad (106)$$

The classical availability of *radiation at flow* resides in the above equation in Jeter's form

$$b_v(T,T_0,0) = h_v - h_{v0} - T_0(s_v - s_{v0}) = h_v(1 - T/T_0) = (4/3)aT^4(1 - T/T_0) \quad (107)$$

(see Eq. (55) and Ref. [23]).

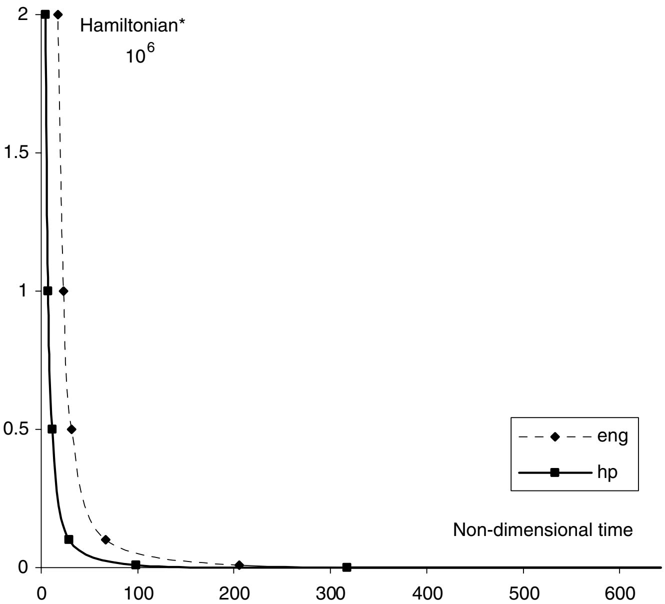

Fig. 4. Hamiltonian h [J K^{-1} m^{-3}] as a function of non-dimensional duration for engine mode (eng) and heat-pump mode (hp) at prescribed boundary temperatures, $T^{\mathrm{i}} = 300$ K and $T^{\mathrm{f}} = 5800$ K.

As two modes are included, in generalized availability (106) the common symbol T refers to the initial temperature of engine mode or the final temperature of heat-pump mode of the process. The qualitative properties of this availability function are similar to those described in Fig. 2 of our earlier paper [1]. The variable non-dimensional duration in engine or heat-pump modes is denoted in Fig. 2 of [1] by the common symbol $\Delta\tau$.

The slope ξ is constant in traditional Newtonian fluids with a constant c_v. ξ is positive for fluid's heating process (heat pump mode) and negative for a fluid's cooling process (engine mode). The numerical value of Newtonian ξ characterizes a constant logarithmic intensity satisfying the relation $\mathrm{d}\ln T = \xi\,\mathrm{d}\tau$. Its integration for the fixed-end boundary conditions leads to familiar equation

$$T(\tau) = T^{\mathrm{i}}\exp(\xi(\tau - \tau^{\mathrm{i}})). \tag{108}$$

The associated Carnot temperature control ensuring extremum work is

$$\begin{aligned} T'(\tau) &= T(\tau)(1 + \xi(\Phi)) \\ &= T^{\mathrm{i}}(T^{\mathrm{f}}/T^{\mathrm{i}})^{(\tau-\tau^{\mathrm{i}})/(\tau^{\mathrm{f}}-\tau^{\mathrm{i}})}(1 + \ln(T^{\mathrm{f}}/T^{\mathrm{i}})/(\tau^{\mathrm{f}} - \tau^{\mathrm{i}})). \end{aligned} \tag{109}$$

It corresponds with the power formula (85) in the case $m = 1$. The exponential decay of T, implied by Eq. (108) in Newtonian engine mode (negative ξ), can be compared with temperature decrease in radiation relaxation process described by Eq. (105). The value of ξ can be determined from the boundary conditions of the fixed-end problem

$$\xi = (\tau^{\mathrm{f}} - \tau^{\mathrm{i}})^{-1}\ln(T^{\mathrm{f}}/T^{\mathrm{i}}). \tag{110}$$

In the Newtonian process the density of entropy generated is described by the formula

$$s_{v_{\mathrm{gen}}} = c_v\left(\left(\pm\sqrt{\frac{h}{\Phi c_v}}\right) + (1-\Phi)\left(1 - \pm\sqrt{\frac{h}{\Phi c_v}}\right)\right)\ln\frac{T^{\mathrm{f}}}{T^{\mathrm{i}}}. \tag{111}$$

For endoreversible processes ($\Phi = 1$), we recover from above equation the special formula

$$s_{v_{\mathrm{gen}}} = \pm c_v\int_{T^{\mathrm{i}}}^{T^{\mathrm{f}}}\sqrt{\frac{h}{c_v}}\mathrm{d}\ln T = \pm c_v\sqrt{\frac{h}{c_v}}\ln\frac{T^{\mathrm{f}}}{T^{\mathrm{i}}}. \tag{111'}$$

This result is exploited to obtain the generalized exergy of a compressible Newtonian fluid in which viscous friction is ignored

$$\begin{aligned} b_v(T,T_0,h) &= b_v(T,T_0,0) + c_{p_v}T_0\left(\frac{\xi}{1+\xi}\right)\ln(T/T_0) \\ &= c_{p_v}T_0\left[(T/T_0-1) - \ln(T/T_0) + \ln(P/P_0)^{\frac{k-1}{k}}\right] \\ &\quad + c_{p_v}T_0\left(\left(\pm\sqrt{\frac{h}{\Phi c_{p_v}}}\right) + (1-\Phi)\left(1 - \pm\sqrt{\frac{h}{\Phi c_{p_v}}}\right)\right)\ln\frac{T}{T_0}. \end{aligned} \tag{112}$$

The last line describes the rate-related term. In the classical case the pressure contributes to the exergy with a separate term. This is not a surprise because in this case T and P are two independent variables, whereas in the case of radiation the specification of T already defines the pressure P. It may be shown that for a linear fluid the logarithmic mean of temperatures T and T_0 plays the role of a substitutional temperature on which the Carnot efficiency is based, and that the classical thermal exergy of the linear fluid is equal to the product of enthalpy change $c_p(T - T_0)$ and this particular efficiency.

10. Dynamical models using Stefan–Boltzmann equation

Again, the optimization task is to find an optimal profile of the driving temperature T' along the radiation resource path (path of fluid 1) that assures the minimum of the integral entropy production and – simultaneously – the extremum of the work consumed or delivered. However the non-dimensional time τ of the previous section related to *overall* number of transfer units cannot be now used as it is no longer an effective variable. Rather a suitably defined time variable τ_1 (associated solely with the properties resource fluid; Eq. (120) below), will be applied.

Exact modeling of mechanical power yield from radiation, that uses the Stefan–Boltzmann equation, involves several difficulties. As in each rigorous model non-linearities are irreducible. They may be attributed to the temperature dependence of quantity $G_c \equiv GC_{\mathrm{m}}$ or the product of the molar fluid's flow and its molar heat capacity. From Eq. (6) capacities per unit volume are $c_v(T) \equiv 4aT^3$ and $c_h(T) \equiv c_v(T) + \mathrm{d}P/\mathrm{d}T = (16/3)aT^3$. Whereas, from Eq. (26), the ratio of photons volume to their number or a single photon volume (the reciprocal of the number density) is

$$v_{\mathrm{ph}} \equiv \frac{V}{N} = \frac{k_{\mathrm{B}}T}{P(T)} = \frac{3k_{\mathrm{B}}}{a}T^{-3} = \frac{c}{4p}T^{-3}. \tag{113}$$

The molar volume, V_m, is the product of this quantity and Avogadro number, A_v. This leads to evaluation of products $c_{v_{ph}} \equiv vc_v(T) = 12k_B$ and $c_{h_{ph}} \equiv vc_h(T) = 16k_B$. This also means that molar heat capacities of black photons are, respectively, $C_{mv} = 12R$ and $C_{mh} = 16R$, where R is the universal gas constant.

As shown by the state equation (26), products $\dot{V}c_v(T)$ and $\dot{V}c_h(T)$ in power functionals (49), (93) and (94) vary in time. For a constant $\dot{V}$, Eq. (26) implies that both particle and molar flows, $\dot{N}$ and $\dot{G}_m = \dot{N}/A_v$, are proportional to T^3.

$$\dot{G}_m = \frac{4p}{cA_v}T^3\dot{V} = \frac{\dot{V}}{V_m} \tag{114}$$

(Note that in our previous work [1] we used the bare symbol G for the molar flux.) Eq. (114) is, in fact, a simple transformation of Eq. (26). For a constant $\dot{V}$ Eq. (114) proves the decrease of the photons flux in the engine mode and the increase of this flux in the heat pump mode. These effects are associated with corresponding decrease and increase of T along the process path. The products $G{\cdot}_m C_{mv}$ and $G{\cdot}_m C_{mh}$ are respectively

$$GC_{mv} = \frac{48k_Bp}{c}T^3\dot{V} \quad GC_{mh} = \frac{64k_Bp}{c}T^3\dot{V}. \tag{115}$$

These formulae serve to accomplish effective calculations of the work integrals.

However, there are also non-linearities associated with analytical structure of differential constraints, different from those in pseudo-Newtonian model of Section 9. In fact, the differential constraint of that model was contained in Eq. (91) linking the local heat control υ with the temperature change, $\upsilon = -\chi\,dT/dt = -dT/d\tau$. Simplicity of that constraint caused its easy imbedding in the power functional. Yet, in non-linear models of the present section constrains are non-linear counterparts of Eq. (91), thus they are more involved, an example is Eq. (129) below. Their imbedding into power functionals (to express these in terms of T and dT/dt) is not always possible, so they reside in the mathematical model as separate entities. Therefore typical control schemes are those of Pontryagin's maximum principle where controls are more complex than the simple derivatives of state coordinates with respect to time.

Based on local power expression $p_1 = \eta q_1$ the cumulative power is the integral over $\eta\,d\dot{Q}_1$ or

$$\dot{W} = \int_0^{\dot{Q}_1}\left(1 - \Phi\frac{T_2}{T'}\right)d\dot{Q}_1. \tag{116}$$

From the energy balance the differential energy flux q_1 corresponding with infinitesimal changes of dT_1, dx and dt equals $d\,\dot{Q}_1 = -\dot{G}_m(T_1)C_m\,dT_1$. The related functional of cumulative power is

$$\dot{W} = -\int_{t^i}^{t^f}\dot{G}_m(T_1)C_m\left(1 - \frac{\Phi T_2}{T'}\right)\dot{T}_1\,dt. \tag{117}$$

In hybrid models it is possible to express T' in the form $T' = T'(T_1, \dot{T}_1)$, as we shall see soon. In power formulas like the above, the dots over symbols refer either to flow quantities (e.g. $G{\cdot}_m(T_1)$) or to time derivatives of thermal potentials (e.g. T_1) with respect to physical time, t, which is the contact time of the driving fluid with the power generator. However, it should be noted that, due to the invariance $\dot{T}_1^{(t)}\,dt = \dot{T}_1^{(\xi)}\,d\xi$, the product $\dot{T}_1\,dt$ in the above functional describes the same differential dT_1 for any definition of time variable. Such definition can involve non-dimensional times τ and τ_1, cumulative area A, or fluid's contact time t. In effect, dots over the temperature symbol in formulas like (117) may be referred to an arbitrary independent variable, whereas dots over the symbols of flow quantities (e.g. $\dot{G}_m(T_1)$) must be reserved to flows in physical time, t.

With Eq. (80) the cumulative power of the entropy production describing lost work in equations of extended availabilities is an integral

$$\sigma_s = -\int_{t^i}^{t^f}\dot{G}_m(T)C_m\left(\frac{\Phi}{T'} - \frac{1}{T_1}\right)\dot{T}_1\,dt. \tag{118}$$

For fixed end states the limiting production or consumption of mechanical energy is associated with extremum work (117) or minimum of entropy production (118). Whenever an operator describing Carnot temperature T' in terms of radiation temperature T_1 and its time derivative can be found, variational calculus can be applied to solve the optimization problem of extremum work. In the opposite case Eq. (118) and the related work functionals must be written in the form in which T' and T_1 are two distinct variables in an algorithm of the optimal control. This is Pontryagin's algorithm in which a differential equation constraints changes of T_1, dT_1/dt, and T' (see Eq. (129) below).

We shall now specialize with the *symmetric non-linear case*. It involves the radiative heat transfer ($m = 4$) in both reservoirs and corresponds with form (80) of the local entropy production. We exploit both the variable heat-capacity flux $\dot{G}_{ch}(T)$ and the effective heat coefficient $\alpha_1(T_1)$ to define the non-dimensional time τ_1 by the equality

$$\begin{aligned} q_1/g_{1N} &= g_1(T_1^m - T_{1'}^m)/g_{1N} \\ &= -\dot{G}_{ch}(T_1)\,dT_1/(\alpha_1(T_1)a_vF_1\,dx) \\ &\equiv -dT_1/d\tau_1 = \sigma(T_1^m - T_{1'}^m)/\alpha_1(T_1) \\ &\cong T_1 - T_{1'}, \end{aligned} \tag{119}$$

where the ratio g_1/g_{1N} above equals $\sigma/\alpha_1 = T^{-3}$ and $\dot{G}_{ch} \equiv \dot{G}_m c_{mh}$ is the product of the fluid's molar flow and its molar heat capacity, the second expression in Eq. (115). The non-dimensional time τ_1 is defined by the equality

$$d\tau_1 = \frac{\alpha_1(T_1)a_vF_1}{\dot{G}_{ch}(T_1)}\,dx. \tag{120}$$

Since both quantities $\dot{G}_{ch}$ and $\alpha_1(T_1)$ vary as T^3, the effect of T cancels out and non-dimensional time τ_1 is a suitable quantity proportional to physical residence time t. Eq. (119) describes the energy balance for the radiation fluid.

The non-dimensional time τ_1 is simultaneously the number of energy transfer units related to the fluid in state 1. Eq. (119) shows that the driving energy flux can be measured in terms of the temperature drop of radiation fluid per unit of non-dimensional time τ_1. Eq. (119) is, in fact, a mixed structure: while it uses Stefan–Boltzmann law, it also bears some properties of pseudo-Newtonian systems due to the presence the transfer coefficient $\alpha_1(T_1)$ in the definition of non-dimensional time τ_1. After using Eq. (76) for $T_{1'}$,

$$T_{1'} = \left(T_1^m - g_2\frac{T_1^m - T'^m}{\Phi g_1(T'/T_2)^{m-1} + g_2}\right)^{1/m} \tag{76}$$

in Eq. (119) we obtain the state equation

$$-\mathrm{d}T_1/\mathrm{d}\tau_1 = T_1 - \left(T_1^m - g_2\frac{T_1^m - T'^m}{\Phi g_1(T'/T_2)^{m-1} + g_2}\right)^{1/m}. \tag{121}$$

We may also proceed in another way. We exploit energy exchange formula (77)

$$q_1 = g_1 g_2\frac{T_1^m - T'^m}{\Phi g_1(T'/T_2)^{m-1} + g_2} \tag{77}$$

with conductances $g_i = \sigma A_i$ based on universal Stefan–Boltzmann constant, σ. Comparing two boundary expressions of formula (119) with Eq. (77) we obtain a differential equation

$$\mathrm{d}T_1/\mathrm{d}\tau_1 = -\frac{g_1 g_2}{g_{1\mathrm{N}}}\frac{T_1^m - T'^m}{\Phi g_1(T'/T_2)^{m-1} + g_2}, \tag{122}$$

which corrects Eq. (35) of our previous work [1] by inclusion of ratio $g_2/g_{1\mathrm{N}}$. For radiation the ratios $g_2/g_{1\mathrm{N}}$ and $g_1/g_{1\mathrm{N}}$ appearing in formula (122) equal respectively $\sigma/\alpha_1 = T_1^{-(m-1)} = T_1^{-3}$ and $\sigma/\alpha_2 = T_2^{-3}$.

While each of Eqs. (121) and (122) can be used as a constraint in the optimization of work (117) their transfer-coefficient base lead us to a further search towards an exact equation containing only universal (Stefan–Boltzmann) constants. This exact equation can be obtained from an alternative form of energy balance (119) which is

$$\begin{aligned}-G_{ch}(T_1)\,\mathrm{d}T_1 &= \sigma_1(T_1^m - T_{1'}^m)a_v F_1 u\,\mathrm{d}t\\ &= \sigma_1(T_1^m - T_{1'}^m)a_v\dot{V}\,\mathrm{d}t.\end{aligned} \tag{123}$$

Note that the time variable used is the contact time of the radiation fluid with the energy generator, i.e. $t = t_1$, but, for simplicity, we shall further neglect index 1 when designating any property of the fluid. This will also serve to point out that such properties can be variable quantities rather than constants. Expressing in Eq. (123) molar flux $\dot{G}_\mathrm{m}$ as a function of volume flux $\dot{V}$ and molar volume V_m

$$\dot{G}_\mathrm{m} = \frac{\dot{V}}{V_\mathrm{m}} = \frac{4p}{cA_v}T^3\dot{V} = p_\mathrm{m}^0 T^3\dot{V}, \tag{124}$$

where $p_\mathrm{m}^0 \equiv 4p/(cA_v)$ is the molar constant of photon's density we obtain

$$-c_{\mathrm{m}h}\frac{\mathrm{d}T_1}{\mathrm{d}t} = \sigma_1(T_1^m - T_{1'}^m)a_v V_\mathrm{m}. \tag{125}$$

This simple result describes, in fact, heating of one mole of photons with volume V_m and effective heat capacity $c_{\mathrm{m}h}$ in an energy exchange process governed by the Stefan–Boltzmann law. Writing molar volume V_m in terms of the universal constant, $V_\mathrm{m} = T^{-(m-1)}/p_\mathrm{m}^0$, we obtain

$$\frac{\mathrm{d}T_1}{\mathrm{d}t} = -\beta\frac{T_1^m - T_{1'}^m}{T_1^{m-1}}, \tag{126}$$

where

$$\beta \equiv \frac{\sigma_1 a_v}{c_{h\mathrm{m}}p_\mathrm{m}^0}. \tag{127}$$

As $T_{1'}$ is not an independent control variable, it is suitable to express this equation in terms of variables such as T' or η that are independent controls. In terms of Carnot temperature the differential constraint is obtained by using Eq. (76) in (126); the result is

$$\frac{\mathrm{d}T_1}{\mathrm{d}t} = -\left(\frac{\sigma_1 a_v}{c_{h\mathrm{m}}p_\mathrm{m}^0}\right)\frac{T_1^m - T'^m}{(\Phi(g_1/g_2)(T'/T_2)^{m-1} + 1)T_1^{m-1}}. \tag{128}$$

Now we can ignore subscript 1 in the variable temperature of the radiation fluid and lump coefficients into a single constant β. In terms of the fluid's variable temperature $T = T_1(t)$ and Carnot temperature T' the state equation (128) is

$$\frac{\mathrm{d}T}{\mathrm{d}t} = -\beta\frac{T^m - T'^m}{(\Phi'(T'/T_2)^{m-1} + 1)T^{m-1}}, \tag{129}$$

where coefficient β is defined by Eq. (127) and

$$\Phi' \equiv \Phi g_1/g_2 \tag{130}$$

and time variable t is the contact time of the radiation fluid with the engine.

We shall now consider the *hybrid non-linear case* in which the radiative energy transfer ($m = 4$) occurs only in the first (upper) reservoir. Whereas, in the second reservoir, the energy exchange is governed by mechanism of convective heat exchange described by Newton's law (81)

$$q_2 = g_2(T_{2'} - T_2). \tag{81}$$

In order to obtain a power functional in this case we use the particular representation of power p in terms of $T_{1'}$

$$\begin{aligned}p &= q_1\eta\\ &= g_1(T_1^m - T_{1'}^m)\left(1 - \frac{\Phi T_2}{T_{1'} - \Phi g_1(T_1^m - T_{1'}^m)/g_2}\right).\end{aligned} \tag{84}$$

From the energy balance the differential energy flux q_1 corresponding with changes of $\mathrm{d}T_1$, $\mathrm{d}x$ and $\mathrm{d}t$ equals $\mathrm{d}\dot{Q}_1 = -\dot{G}_\mathrm{m}(T_1)C_{h\mathrm{m}}\,\mathrm{d}T_1$. Calculating cumulative power as the integral over $\eta\,\mathrm{d}\dot{Q}_1$ with the help of Eqs. (83), (84) and (117) yields

$$\dot{W} = -\int_{t^\mathrm{i}}^{t^\mathrm{f}}\dot{G}_\mathrm{m}(T_1)C_{h\mathrm{m}}\left(1 - \frac{\Phi T_2}{T_{1'} - \Phi g_1(T_1^m - T_{1'}^m)/g_2}\right)\dot{T}_1\,\mathrm{d}t. \tag{131}$$

With Eq. (126), temperature $T_{1'}$ of Eq. (131) can be expressed in terms of variables T and $\mathrm{d}T_1/\mathrm{d}t$. Consequently, the production (consumption) of mechanical energy is described by the following power integral

$$\dot{W} = -\int_{\tau^i}^{t^f} G_c(T_1)\left(1 - \frac{\Phi T_2}{(T_1^m + \dot{T}_1^m)^{1/m} + \Phi \dot{T}_1^m g_1/g_2}\right)\dot{T}_1\,\mathrm{d}\tau_1. \tag{132}$$

The temperature function $\dot{G}_{ch}(T)$ in Eq. (132) and in power equations below is defined as

$$\dot{G}_{ch}(T) \equiv \dot{G}_{\mathrm{m}} C_{h\mathrm{m}} = \frac{64 k_{\mathrm{B}} p}{c} T^3 \dot{V} C_{h\mathrm{m}} = p^0_{\mathrm{m}} T^3 \dot{V} C_{h\mathrm{m}}. \tag{133}$$

This formula follows from the second expression in Eqs. (115) and (124). Eq. (132) uses operator representation of the temperature of upper circulating fluid

$$T^m_{1'} = T^m_1 + \frac{\mathrm{d}T^m_1}{a\beta \mathrm{d}t} \equiv T^m_1 + \frac{\mathrm{d}T^m_1}{\mathrm{d}\tau_1} \equiv T^m_1 + \dot{T}^m_1, \tag{134}$$

which results from Eq. (126). This operator representation also defines the dimensionless time of the problem, $\tau_1 \equiv \beta a t$.

The related expression for the total entropy production is

$$\sigma_s = -\int_{\tau^i}^{\tau^f} \dot{G}_{ch}(T_1)\left(\frac{\Phi}{(T_1^m + \dot{T}_1^m)^{\frac{1}{m}} + \dot{T}_1^m \Phi g_1/g_2} - \frac{1}{T_1}\right)\dot{T}_1\,\mathrm{d}\tau_1. \tag{135}$$

While an equation of this form was suggested earlier [1], only the present work defines the relation between dimensionless time and physical or contact time: $\tau_1 \equiv \beta m t$. As it is our policy here to prefer formulae using physical time t, we write down below power formula (132) in terms of t rather than τ

$$\dot{W} = -\int_{\tau^i}^{t^f} \dot{G}_{ch}(T_1)\left(1 - \frac{\Phi T_2}{(T_1^a + \chi \dot{T}_1^m)^{1/m} + \Phi \chi \dot{T}_1^m g_1/g_2}\right)\dot{T}_1\,\mathrm{d}t, \tag{136}$$

where $\chi = (m\beta)^{-1}$ and $\dot{T}_1^m \equiv \mathrm{d}T_1^m/\mathrm{d}t = mT_1^{m-1}\mathrm{d}T/\mathrm{d}t$. Hence, after the omission of undue subscript 1 at T_1

$$\dot{W} = -\int_{\tau^i}^{t^f} \dot{G}_{ch}(T)\left(1 - \frac{\Phi T_2}{(T^a + \beta^{-1}T^{m-1}\dot{T})^{1/m} + \Phi\beta^{-1}T^{m-1}\dot{T} g_1/g_2}\right)\dot{T}\,\mathrm{d}t. \tag{137}$$

Eqs. (132) and (135)–(137) contain Carnot temperature operator T' expressed in terms of temperature of upper reservoir and its appropriate time derivative. As these equations are the Lagrange functionals, the classical method of calculus of variations can be applied for their optimization. Yet, this property only refers to the hybrid model, because the Lagrange structures do not appear in the symmetric model (with the radiative exchange on both sides of the engine).

Optimal control approaches are also possible for hybrid models. After identifying the temperature derivative as the possible control $\dot{T} = u$ we obtain

$$\dot{W} = -\int_{\tau^i}^{t^f} \dot{G}_{ch}(T)\left(1 - \frac{\Phi T_2}{(T^m + \beta^{-1}T^{m-1}u)^{1/m} + \Phi\beta^{-1}T^{m-1}u g_1/g_2}\right)u\,\mathrm{d}t. \tag{138}$$

The differential constraint for the above integral has a trivial form resembling the one in Eq. (91)

$$\mathrm{d}T/\mathrm{d}t = u. \tag{139}$$

Analogously one can treat integral of the entropy production, Eq. (135). In terms of u the procedure yields the functional

$$\sigma_s = -\int_{t^i}^{t^f} \dot{G}_{ch}(T)\left(\frac{\Phi}{(T^m + \beta^{-1}T^{m-1}u)^{1/m} + \Phi\beta^{-1}T^{m-1}u g_1/g_2} - \frac{1}{T}\right)u\,\mathrm{d}t. \tag{140}$$

Again, it should be minimized subject to Eq. (139).

As in the case of symmetric problem, integrals of power and entropy production of the hybrid problem can always be treated by the algorithm of Pontryagin's maximum principle. In that case Eq. (138) or (140) are optimized subject to constraint (139). However, the most suitable way in optimization of hybrid models is to write down and then solve the Euler–Lagrange equation of the variational problem. For this purpose functionals of T and $\dot{T}$ are relevant, such as Eqs. (135) or (136). Analytical solutions are seldom, thus one has to rest on numerical techniques.

11. Hamilton–Jacobi–Bellman approaches

We shall now describe some benefits resulting from the derived differential models. Eqs. (121), (122), (126), (128), (129) and (139) are differential constraints in problems extremizing power or total entropy production treated by Pontryagin's maximum principle. This extremization leads to optimal profiles $T'(\tau_1)$ and $T_1(\tau_1)$ that assure extremum work produced in a sequential engine system (Fig. 1) or consumed in a sequential heat pump system. Both systems are multistage arrangements with an infinite number of infinitesimal stages. The extremum work obtained refers to a finite-time exergy of the resource fluid working in a continuous system. An example is the extended exergy referred to Eq. (106). Its discrete counterparts for finite stages are also of interest (see our next paper [49]). Both kind of functionals (those for work and those for the entropy production) yield the same optimal paths whenever boundary states and times are assumed fixed at the beginning and end of the operation.

With power functionals at disposal we can formulate the Hamilton–Jacobi–Bellman theory (HJB theory) for extremum work and related extended exergy. Hamiltonian and Lagrangian formalisms associated with extremum work can also be developed. The latter are most suitable settings for optimal paths although the principal function (optimum work function) is not explicit in them. In these formalisms the principal function is found after finding an optimal path and by the evaluation of the work integral along this path.

The HJB theory of the principal function is the basic ingredient in variational calculus and optimal control [35–42]. HJB equations can be continuous or discrete. The former are associated with ordinary differential equations (such as those in this paper), the latter – with difference equations. Bellman's recurrence equation can be regarded as a discrete HJB equation, yet there are also discrete equations that are structurally closer to HJB equations of continuous systems [42]. A HJB equation generalizes the classical Hamilton–Jacobi equation [37,39] by inclusion of extremum conditions for control variables.

In a future paper along this line we shall formulate and solve HJB equations for some continuous models of this work. We shall also develop discrete counterparts of these models for genuine cascade processes with stages of finite size. It will be essential to develop numerical methods in complex cases with state dependent coefficients, when a HJB equation cannot be solved analytically. Due to the direct link between the HJB theory and the method of dynamic programming associated numerical approaches will make use Bellman's recurrence equation [41,42].

Work optimization in discrete systems (cascades) applies directly the one-stage model of energy production or consumption i.e. the Chambadal–Novikov–Curzon–Ahlborn (CNCA) engine [43]. Its non-linear extension called Stefan–Boltzmann engine [7] is, in fact, the subject matter of Section 8 of the present paper, although we use in its description a non-standard control, Carnot temperature T'. Our future analysis will extend this model to multistage processes (for applications of single-stage models to endoreversible conversion of radiation, see [7,12,13,32,33,44]). This extension will also lead to generalized exergies of genuine discrete processes with radiation.

12. Final remarks

In this research dynamical state equations are obtained for continuous processes with radiation. These are ordinary differential equations that describe the response of a radiation system to an external control. Also generalized exergies are found under pseudo-Newtonian approximation. Examples of these exergies are shown in Eqs. (106) and (112) of this paper. In a future paper along this line [49] optimization algorithms (HJB equations, dynamic programming equations and Hamilton's canonical sets) will be obtained and solved for these continuous processes as well as for their genuine discrete counterparts, describing cascades with finite stages.

Generalized exergy of a continuous process, A^{∞}, prohibits processes from operating below the heat-pump mode line (for a fractional value of Φ) thus yielding a lower bound for work supplied. It also prohibits processes from operating above the engine mode line (for a value of Φ larger than unity) which defines an upper bound for work produced. Diagrams of generalized exergy mark regions of possible improvements when imperfect thermal machines are replaced by those with better performance coefficients, terminating at endoreversible limits for Carnot machines.

Generalized exergies are irreversible extensions of the classical exergy by including minimally irreversible processes. Limiting work estimates made with the help of classical exergies are too weak and often insufficient; generalized exergies, whose examples are given here, assure stronger work limits [45–49].

A generalized exergy of processes departing from the equilibrium (fluid's utilization) is larger than the one in processes approaching the equilibrium (fluid's relaxation). This is because one respectively adds or subtracts the product of T_0 and entropy production in a formula describing the generalized exergy. By taking into account the entropy production, limits for mechanical energy yield or consumption provided by generalized exergies are stronger than those defined by the classical exergy. It follows that finite rates in real processes increase a minimum work that must be supplied to the system and decrease a maximum work that can be produced by the system. These conclusions help an engineer in better evaluation of energy limits in practical processes with radiation, especially in those undergoing in solar engines, solar driven heat pumps and solar cells.

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