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Thermal Radiation and the Second Law of Thermodynamics

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Abstract *Thermal radiation is an important phenomenon in many engineering systems. However, up to now, radiation thermodynamic effects are generally neglected or evaluated incorrectly by the engineering community. Therefore, we dedicate this note to radiation thermodynamics:*

- *misconceptions surrounding radiation thermodynamics are discussed;*
- *the second law of thermodynamics is defined to explicitly account for radiation thermodynamic effects.*
- *and the reversible and irreversible sources of radiation entropy are discussed.*

Keywords*: Second law of thermodynamics; Thermal radiation; Entropy generation,*

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Nomenclature

A	Area
c	Speed of light
h	Planck's constant, or enthalpy
I_λ	Spectral radiation intensity
$I_{b\lambda}$	Spectral blackbody intensity
$\mathbf{j}_Q$	Heat current density
k_b	Boltzmann's constant
L_λ	Spectral radiation entropy intensity
$\dot{m}$	Mass flow rate
$\mathbf{n}_A$	Unit normal vector of boundary
$\mathbf{r}$	Unit position vector
$\dot{S}'''_{gen}$	Rate of entropy generation density
$\mathbf{s},\mathbf{s}'$	Unit direction vectors
s	Mass-specific entropy
T	Temperature
T_λ	Spectral radiation temperature
t	Time
V	volume
	Greek Symbols
$\kappa_{a\lambda}$	Spectral absorption coefficient
$\kappa_{s\lambda}$	Spectral scattering coefficient
λ	Wavelength
Φ	Scattering phase function
Ω	Solid angle

I. Introduction

In the engineering community, several misconceptions surround the role and calculus of radiation entropy generation [1]. In fact, these misconceptions are built up step-by-step in undergraduate classes during the introduction of the second law of thermodynamics. In standard textbooks [2, 3], the second law is formulated first in terms of the Clausius inequality:

$$\oint \frac{\delta Q}{T} \leq 0 \tag{1}$$

which, when applied to a closed system that interacts with the environment (Fig. 1a), shows the degree of irreversibility of different paths going from an initial state to a final state, i.e.:

$$S_{gen} = S_2 - S_1 - \int_1^2 \frac{\delta Q}{T} \geq 0 \tag{2}$$

Eq. (2) is easily extended to open systems by noting that, in addition to heat, entropy is also transported with mass flow (Fig. 1b). The rate of entropy generation in an open system is thus given by the second law in the form

$$\dot{S}_{gen} = \frac{\partial S}{\partial t} - \frac{\dot{Q}}{T} + \sum_{out} \dot{m}s - \sum_{in} \dot{m}s \geq 0 \tag{3}$$

Eq. (3) is supposed to govern entropy generation in all type of systems [2, 3].
By expressing the heat transfer term in vector form, several authors show that radiation thermodynamic effects are accounted for as follows [1]:

$$\dot{S}_{gen,heat} = \mathbf{j}_Q \cdot \nabla \frac{1}{T} = -\mathbf{j}_Q \cdot \left(\nabla T / T^2 \right) = -\left(\mathbf{j}_Q^C + \mathbf{j}_Q^R \right) \cdot \nabla T / T^2 \tag{4}$$

This equation is in general *not* correct, and it actually points to a fundamental weakness in the setup of the energy equation in which thermal radiation is treated as a source term. Such an approach may not correctly describe the behavior of thermal radiation. Correct extension of the second law of thermodynamics is discussed herein.

II. Fundamental Radiation Thermodynamics

2.1 Planck's equation of non-equilibrium radiation thermodynamics

Planck [5] derived the spectral radiative entropy intensity of an incoherent unpolarized radiation beam:

$$L_\lambda = \frac{2k_b c}{\lambda^4} \left\{ \left(1 + \frac{I_\lambda}{2hc^2\lambda^{-5}} \right) \ln \left(1 + \frac{I_\lambda}{2hc^2\lambda^{-5}} \right) - \frac{I_\lambda}{2hc^2\lambda^{-5}} \ln \frac{I_\lambda}{2hc^2\lambda^{-5}} \right\} \tag{5}$$

Eq. (5) is considered the most fundamental equation in non-equilibrium radiation thermodynamics [6]. In the special case of an equilibrium radiation field, the spectral intensity is given by Planck's law [5]:

$$I_{b\lambda} = \frac{2hc^2}{\lambda^5} \frac{1}{\exp\left[hc / \lambda k_b T \right] - 1} \tag{6}$$

2.2 Thermal radiation and the second law

With Planck's definition for the spectral radiation entropy intensity, the second law of thermodynamics can readily be extended to account for thermal radiation effects. Consider the open thermodynamic system shown in Fig. 2. In its most general form, the second law states that the total change of entropy in the system is caused by the reversible entropy change (transferred entropy) and the irreversible entropy change (entropy generation) [7]. The rate at which the total entropy in the system changes is thus [7]:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{d_e S_{rev}}{\mathrm{d}t} + \frac{d_i S_{irr}}{\mathrm{d}t} \tag{7}$$

Now, consider these terms separately:

(a) The total entropy change

If we neglect thermal radiation, then the total entropy change in the system occurs in matter, and is given by [7]:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}S_M}{\mathrm{d}t} = \int_V \frac{\partial (\rho s)}{\partial t} \mathrm{d}V \tag{8}$$

However, when a radiation field is present, then the total entropy change in the system consists of the entropy change in matter plus the entropy change in the radiation field. The entropy change in the radiation field is [8]:

$$\frac{\mathrm{d}S_R}{\mathrm{d}t} = \int_V \int_\lambda \int_{4\pi} \frac{1}{c} \frac{\partial L_\lambda (\mathbf{r}, \mathbf{s}, t)}{\partial t} \mathrm{d}\Omega \mathrm{d}\lambda \mathrm{d}V \tag{9}$$

which is negligible for most systems because of the factor 1/c. Hence, in the presence of thermal radiation, the total entropy change is

$$\frac{\mathrm{d}S}{\mathrm{d}t}=\frac{\mathrm{d}S_M}{\mathrm{d}t}+\frac{\mathrm{d}S_R}{\mathrm{d}t}\cong\int_V\frac{\partial(\rho s)}{\partial t}\mathrm{d}V \tag{10}$$

(b) The reversible entropy change

Again, neglecting thermal radiation, and taken into account entropy transfer into the system with heat conduction at the boundary and with the mass flow, then

$$\frac{d_eS_{rev}}{\mathrm{d}t}=\frac{\mathrm{d}\dot{S}_c}{\mathrm{d}t}+\frac{\mathrm{d}\dot{S}_m}{\mathrm{d}t}=\sum_{boundary}\frac{\dot{Q}}{T}+\sum_{in}\dot{m}s-\sum_{out}\dot{m}s \tag{11}$$

When a radiation field is also present, we need to consider that there is a radiative entropy flow in the radiative field, and a radiative entropy flow associated with the absorption-emission of radiation heat by matter [9, 10]. Hence, in the medium, the total reversible radiative entropy change is

$$\left.\frac{\mathrm{d}\dot{S}_r}{\mathrm{d}t}\right)_{(medium)}=\left(\frac{\mathrm{d}\dot{S}_r^R}{\mathrm{d}t}\right)_m+\left(\frac{\mathrm{d}\dot{S}_r^M}{\mathrm{d}t}\right)_m \tag{12}$$

where,

$$\begin{aligned}\left(\frac{\mathrm{d}\dot{S}_r^R}{\mathrm{d}t}\right)_m&=\int_{\mathrm{d}A}\int_\lambda\int_{4\pi}(\mathbf{n}_A\cdot\mathbf{s})L_\lambda(\mathbf{r},\mathbf{s})\mathrm{d}\Omega\mathrm{d}\lambda\mathrm{d}A\\&=\int_V\int_\lambda\int_{4\pi}\mathbf{s}\cdot\nabla L_\lambda(\mathbf{r},\mathbf{s})\mathrm{d}\Omega\mathrm{d}\lambda\mathrm{d}V\end{aligned} \tag{13}$$

and

$$\left(\frac{\mathrm{d}\dot{S}_r^M}{\mathrm{d}t}\right)_m=-\frac{\int_V\int_\lambda Q_\lambda\mathrm{d}\lambda\mathrm{d}V}{T}=\int_V\int_\lambda\frac{\kappa_{a\lambda}}{T}\int_{4\pi}\left[I_\lambda(\mathbf{r},\mathbf{s})-I_{b\lambda}(T)\right]\mathrm{d}\Omega\mathrm{d}\lambda\mathrm{d}V \tag{14}$$

In the medium at solid walls, the total reversible radiative entropy change is given by

$$\left.\frac{\mathrm{d}\dot{S}_r}{\mathrm{d}t}\right)_{(wall)}=\left(\frac{\mathrm{d}\dot{S}_r^R}{\mathrm{d}t}\right)_w+\left(\frac{\mathrm{d}\dot{S}_r^M}{\mathrm{d}t}\right)_w \tag{15}$$

where, for an opaque wall surface,

$$\left(\frac{\mathrm{d}\dot{S}_r^R}{\mathrm{d}t}\right)_w=-\int_A\int_\lambda\int_{4\pi}L_\lambda(\mathbf{r}_w,\mathbf{s})(\mathbf{n}_w\cdot\mathbf{s})\mathrm{d}\Omega\mathrm{d}\lambda\mathrm{d}A \tag{16}$$

and

$$\begin{aligned}\left(\frac{\mathrm{d}\dot{S}_r^M}{\mathrm{d}t}\right)_w&=-\frac{\int_A\int_\lambda Q_\lambda(\mathbf{r}_w)\mathrm{d}\lambda\mathrm{d}A}{T(\mathbf{r}_w)}\\&=\frac{1}{T(\mathbf{r}_w)}\int_A\int_\lambda\int_{4\pi}I_\lambda(\mathbf{r}_w,\mathbf{s})(\mathbf{n}_w\cdot\mathbf{s})\mathrm{d}\Omega\mathrm{d}\lambda\mathrm{d}A\end{aligned} \tag{17}$$

Hence, in the presence of thermal radiation, the reversible entropy change relation takes on the form

$$\frac{d_eS_{rev}}{\mathrm{d}t}=\frac{\mathrm{d}\dot{S}_c}{\mathrm{d}t}+\frac{\mathrm{d}\dot{S}_m}{\mathrm{d}t}+\frac{\mathrm{d}\dot{S}_r}{\mathrm{d}t} \tag{18}$$

(c) The irreversible entropy change

When radiation is neglected, the total entropy generation is

$$\frac{d_i S_{irr}}{\mathrm{d}t} = \int_V \dot{S}'''_{gen} \mathrm{d}V \tag{19}$$

In the presence or radiation, Eq.(17) must also be considered. In this case,

$$\frac{d_i S_{irr}}{\mathrm{d}t} = \int_V \dot{S}'''_{gen} \mathrm{d}V + \int_A \dot{S}'''^{wall}_{gen,r} \mathrm{d}A \tag{20}$$

Hence, the second law of thermodynamics, restated to account for thermal radiation, assumes the following form:

$$\dot{S}_{gen} = \frac{\mathrm{d}S}{\mathrm{d}t} - \frac{\dot{Q}^C}{T} - \left(L + \frac{\dot{Q}^R}{T} \right) + \sum_{out} \dot{m}s - \sum_{in} \dot{m}s \geq 0 \tag{21}$$

The first term in the bracket is for the radiative entropy flow in the radiative field, while second one is for the radiative entropy flow in matter, as shown in Fig. 2.

2.3 The reversible and irreversible sources of radiation entropy

The extended second law of thermodynamics derived in the previous section can in principle be separated into three parts, i.e. one part for each of the carriers of entropy:

$$\begin{pmatrix} \dot{S}_{gen,m} \\ \dot{S}_{gen,c} \\ \dot{S}_{gen,r} \end{pmatrix} = \frac{\mathrm{d}S}{\mathrm{d}t} - \begin{pmatrix} \sum_{in} \dot{m}s - \sum_{out} \dot{m}s \\ \dfrac{\dot{Q}^C}{T} \\ \dfrac{\dot{Q}^R}{T} + L \end{pmatrix} \geq 0 \tag{22}$$

The generation terms on the LHS of above expression are the irreversible sources of entropy, while the RHS bracket contains the reversible (transferred) entropy sources. The radiation irreversible source term accounts for radiation entropy generation in the medium and at the solid walls. The following relations holds:

$$\left(\dot{S}_{gen,r} \right) = \begin{pmatrix} \dot{S}^{medium}_{gen,r} \\ \\ \dot{S}^{wall}_{gen,r} \end{pmatrix} \geq 0 \tag{23}$$

with

$$\dot{S}^{medium}_{gen,r} = L_{medium} + \left. \frac{Q^R}{T} \right)_{medium} \geq 0 \tag{24}$$

and

$$\dot{S}^{wall}_{gen,r} = L_{wall} + \left. \frac{Q^R}{T} \right)_{wall} \geq 0 \tag{25}$$

The RHS expressions in these equations are the reversible (transferred) radiation entropy sources. They can be determined from the relations derived in the previous sections:

(a) Reversible radiative entropy sources in medium:

$$L_{medium} = \left(\frac{\mathrm{d}\dot{S}^R_r}{\mathrm{d}t} \right)_m = \int_V \int_\lambda \int_{4\pi} \mathbf{s} \cdot \nabla L_\lambda \left(\mathbf{r}, \mathbf{s} \right) \mathrm{d}\Omega \mathrm{d}\lambda \mathrm{d}V \tag{26}$$

$$\left. \frac{Q^R}{T} \right)_{medium} = \left(\frac{\mathrm{d}\dot{S}^M_r}{\mathrm{d}t} \right)_m = \int_V \int_\lambda \frac{\kappa_{a\lambda}}{T} \int_{4\pi} \left[I_\lambda \left(\mathbf{r}, \mathbf{s} \right) - I_{b\lambda} \left(T \right) \right] \mathrm{d}\Omega \mathrm{d}\lambda \mathrm{d}V \tag{27}$$

(b) Reversible radiative entropy sources at solid walls:

$$L_{wall} = \left(\frac{\mathrm{d}\dot{S}_r^R}{\mathrm{d}t}\right)_w = -\int_A \int_\lambda \int_{4\pi} L_\lambda\left(\mathbf{r}_w, \mathbf{s}\right)\left(\mathbf{n}_w \cdot \mathbf{s}\right) \mathrm{d}\Omega \mathrm{d}\lambda \mathrm{d}A \tag{28}$$

$$\left.\frac{Q^R}{T}\right)_{wall} = \left(\frac{\mathrm{d}\dot{S}_r^M}{\mathrm{d}t}\right)_w = \frac{1}{T\left(\mathbf{r}_w\right)} \int_A \int_\lambda \int_{4\pi} I_\lambda\left(\mathbf{r}_w, \mathbf{s}\right)\left(\mathbf{n}_w \cdot \mathbf{s}\right) \mathrm{d}\Omega \mathrm{d}\lambda \mathrm{d}A \tag{29}$$

With eq. (5), and using the radiative energy transfer equation (RETE) [11]:

$$\begin{aligned} \mathbf{s} \cdot \nabla I_\lambda\left(\mathbf{r}, \mathbf{s}\right) &= -(\kappa_{a\lambda} + \kappa_{s\lambda}) I_\lambda\left(\mathbf{r}, \mathbf{s}\right) + \kappa_{a\lambda} I_{b\lambda}\left(T\left(\mathbf{r}\right)\right) \\ &+ \frac{\kappa_{s\lambda}}{4\pi} \int_{4\pi} I_\lambda\left(\mathbf{r}, \mathbf{s}'\right) \Phi_\lambda\left(\mathbf{s}, \mathbf{s}'\right) \mathrm{d}\Omega' \end{aligned} \tag{30}$$

to derive the radiative entropy transfer equation (REnTE):

$$\begin{aligned} \mathbf{s} \cdot \nabla L_\lambda\left(\mathbf{r}, \mathbf{s}\right) &= \left(\partial L_\lambda\left(\mathbf{r}, \mathbf{s}\right) / \partial I_\lambda\right)\left(\mathbf{s} \cdot \nabla I_\lambda\left(\mathbf{r}, \mathbf{s}\right)\right) \\ &= -(\kappa_{a\lambda} + \kappa_{s\lambda}) \frac{I_\lambda\left(\mathbf{r}, \mathbf{s}\right)}{T_\lambda\left(\mathbf{r}, \mathbf{s}\right)} + \kappa_{a\lambda} \frac{I_{b\lambda}\left(T\left(\mathbf{r}\right)\right)}{T_\lambda\left(\mathbf{r}, \mathbf{s}\right)} \\ &+ \frac{\kappa_{s\lambda}}{4\pi} \int_{4\pi} \frac{I_\lambda\left(\mathbf{r}, \mathbf{s}'\right)}{T_\lambda\left(\mathbf{r}, \mathbf{s}\right)} \Phi_\lambda\left(\mathbf{s}, \mathbf{s}'\right) \mathrm{d}\Omega' \end{aligned} \tag{31}$$

we can restate the reversible radiative entropy sources in their local forms, which can be solved numerically by the procedures given in [10], and employ them to evaluate the local irreversible radiative entropy sources:

(c) Local irreversible and reversible radiative entropy sources in medium:

$$\begin{aligned} \dot{S}_{gen,r}'''^{medium} &= L_{medium}''' + \left.\frac{Q^R}{T}\right)_{medium}''' \\ &= \int_\lambda \int_{4\pi} \left[-(\kappa_{a\lambda} + \kappa_{s\lambda}) \frac{I_\lambda\left(\mathbf{r}, \mathbf{s}\right)}{T_\lambda\left(\mathbf{r}, \mathbf{s}\right)} + \kappa_{a\lambda} \frac{I_{b\lambda}\left(T_{\mathrm{M}}\left(\mathbf{r}\right)\right)}{T_\lambda\left(\mathbf{r}, \mathbf{s}\right)} \right. \\ &\left. + \frac{\kappa_{s\lambda}}{4\pi} \int_{4\pi} \frac{I_\lambda\left(\mathbf{r}, \mathbf{s}'\right)}{T_\lambda\left(\mathbf{r}, \mathbf{s}\right)} \Phi_\lambda\left(\mathbf{s}, \mathbf{s}'\right) \mathrm{d}\Omega' \right] \mathrm{d}\lambda \\ &+ \int_\lambda \frac{\kappa_{a\lambda}}{T_{\mathrm{M}}\left(\mathbf{r}\right)} \int_{4\pi} \left[I_\lambda\left(\mathbf{r}, \mathbf{s}\right) - I_{b\lambda}\left(T_{\mathrm{M}}\left(\mathbf{r}\right)\right) \right] \mathrm{d}\Omega \mathrm{d}\lambda \end{aligned} \tag{32}$$

(d) Local irreversible and reversible radiative entropy sources at walls:

$$\dot{S}_{gen,r}''^{wall} = L_{wall}'' + \left.\frac{Q^R}{T}\right)_{wall}'' = \int_\lambda \int_{4\pi} \left[\frac{I_\lambda\left(\mathbf{r}_w, \mathbf{s}\right)}{T\left(\mathbf{r}_w\right)} - L_\lambda\left(\mathbf{r}_w, \mathbf{s}\right) \right] \left(\mathbf{n}_w \cdot \mathbf{s}\right) \mathrm{d}\Omega \mathrm{d}\lambda \tag{33}$$

The spectral radiative entropy intensity at solid boundaries can be written in terms of wall emissivity using Planck's law:

$$L_\lambda\left(\mathbf{r}_w, \mathbf{s}\right) = \frac{2k_b c}{\lambda^4} \left\{ \left(\mathrm{X} + 1\right) \ln\left(\mathrm{X} + 1\right) - \mathrm{X} \ln \mathrm{X} \right\} \tag{34}$$

where,

$$\mathrm{X} = \frac{\varepsilon\left(\mathbf{r}_w\right)}{\exp\left(hc / k\lambda T_w\right) - 1} \tag{35}$$

III. Conclusion

Radiation thermodynamics has significant implications for engineering systems. It is however not part of standard university curriculum, neither is it correctly treated in any textbooks. As long as radiation thermodynamics is neglected, engineering students will be insufficiently educated in the limitations of Clausius inequality and the second law of thermodynamics. In addition, by neglecting radiation thermodynamics we fail to address the flaw in the first law of thermodynamics. In the setup of the first law, all phenomena that are difficult to treat at first instance, including radiation, are considered to be sources. This approach does not correctly describe the behavior of thermal radiation. For this reason, the heat current density in the energy equation does not give an accurate account for radiation heat transfer. This is also why the conventional extension of the second law is incorrect. The implementation of radiation thermodynamic effects in the second law is an still initial step in treating the thermodynamics of electromagnetic phenomena. It is important to implement all the physics described by Maxwell equation in the second law. The interdisciplinary field of thermodynamics, fluid dynamics, and electromagnetism has important engineering application such as magneto hydrodynamic casting, and plasma flow.

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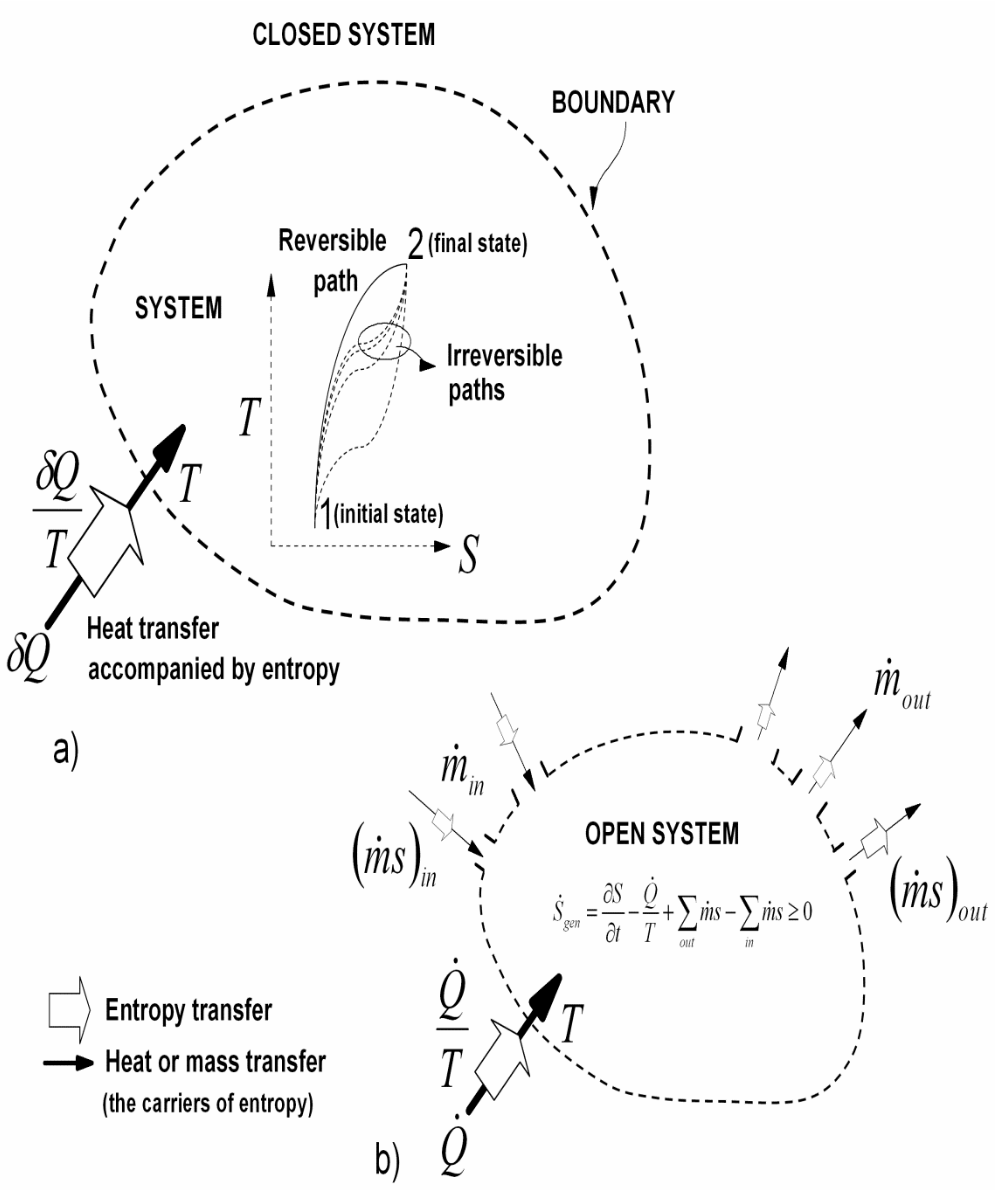

Fig. 1 Entropy transfer in closed and open thermodynamic systems

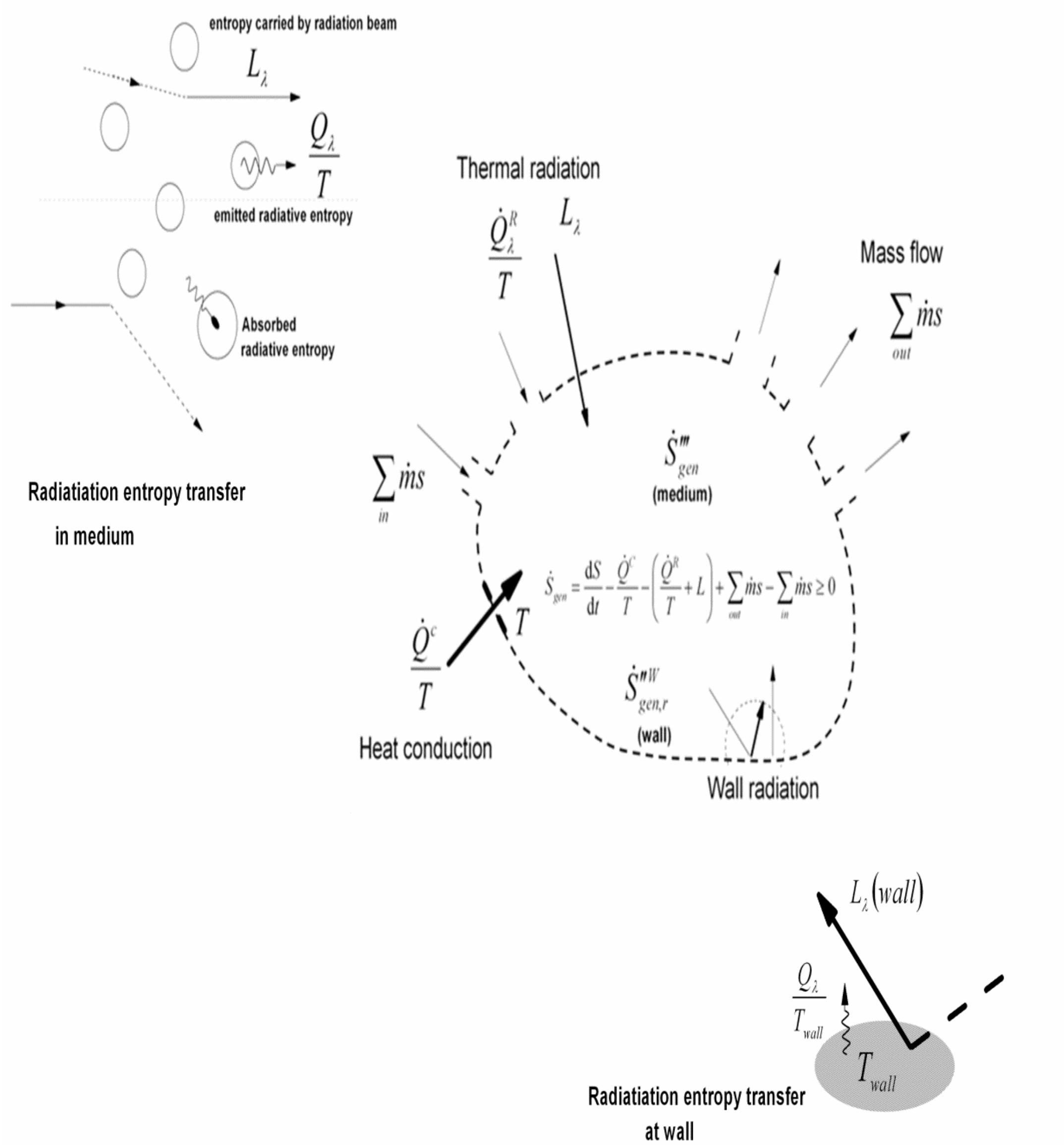

Fig. 2 Open thermodynamic system with radiation entropy transfer

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