Thermo-charged capacitors and the Second Law of Thermodynamics

Germano D’Abramo

IASF - Istituto Nazionale di Astrofisica,
Via Fosso del Cavaliere 100,
00133, Roma, Italy.
E–mail: Germano.Dabramo@iasf-roma.inaf.it
Fax number: +39 06 49934188

Physics Letters A, accepted.

Abstract

In this paper we describe a vacuum spherical capacitor that generates a macroscopic voltage between its spheres harnessing the heat from a single thermal reservoir at room temperature. The basic idea is trivial and it makes use of two concentric spherical electrodes with different work functions. We provide a mathematical analysis of the underlying physical process and discuss its connections with the Second Law of Thermodynamics.

PACS (2010): 79.40.+z, 67.30.ef, 65.40.gd, 84.32.Tt
Keywords: thermionic emission · capacitors · second law of thermodynamics

1 Introduction

The Second Law of Thermodynamics, explicitly in the form of Kelvin-Planck postulate, puts a fundamental limit to the way in which usable work can be extracted from heat reservoirs, and to the maximum amount of work extractable (Carnot’s principle). In particular, Kelvin-Planck postulate states that it is not possible to cyclically extract work from a single heat reservoir. Clausius postulate of the Second Law, which is notoriously equivalent to the
Kelvin-Planck one, makes the impossibility more striking and understandable: heat can not spontaneously flow from sources at absolute temperature \(T_1\) to sources at absolute temperature \(T_2\) when \(T_2 \geq T_1\).

Although in the macroscopic physical world the Second Law seems authoritatively to make the difference between what is allowed and what is forbidden (to date, no experimental violation of the Second Law has been claimed), in the microscopic realm it seems to be continuously violated: let us take into account the Brownian motion or every fluctuation phenomena, for example.

About Brownian motion, Poincaré wrote [1]:

“[..]we see under our eyes now motion transformed into heat by friction, now heat changed inversely into motion, and that without loss since the movement lasts forever. This is contrary to the principle of Carnot.”

Almost every past attempt to understand and exploit such microscopic violation relies on the approach of fluctuations rectification. Even the famous thought experiment of Maxwell’s Demon is actually an idealized version of fluctuations rectification. The main difficulties which seem to afflict all these past approaches (sentient and non-sentient) are that every macroscopic/microscopic rectifier device seems either to suffer fluctuations itself, which neutralize every usable net effect, or its functioning seems to increase the total entropy of the system (at least of the same amount of the alleged reduction) mainly because of energy dissipation and/or entropy cost in the acquisition of information needed to run the device (for sentient devices).

For an interesting historical account of Second Law classical challenges (starting from Maxwell, and passing through Smoluchowski, Szilard, Brillouin, till Landauer) and their attempted resolutions, see Earman and Norton [2].

Nonetheless, over the last 10-15 years an unparalleled number of challenges has been proposed against the status of the Second Law of Thermodynamics. During this period, more than 50 papers have appeared in the refereed scientific literature (see, for example, references [6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 24, 25]), together with a monograph entirely devoted to this subject [4]. Moreover, during the same period of time two international conferences on the limit of the Second Law were also held [3, 5].

The general class of recent challenges [4, 21, 25] spans from plasma [20], chemical [24], gravitational [13] and solid-state [22, 23, 25]. Currently, all these approaches appear immune to standard Second Law defenses (for a
compendium of classical defenses, see [2] again) and several of them account
laboratory corroboration of their underlying physical processes.

The present paper aims to describe another approach to microscopic recti-
fication that poses interesting theoretical questions along the aforementioned
recent line of research: we are referring to an equivalent of the photo-electric
effect with materials emitting electrons at room temperature. If we succeed
in collecting all the electrons emitted by these materials in consequence of
the absorption of black-body radiation from the uniformly heated environ-
ment, then we would be able to create a macroscopic voltage out of a single
heat reservoir. Although this voltage appears to be prima facie an innocuous
consequence of some well established physical laws, the whole process of
thermo-charging presents quite interesting and paradoxical features which,
analyzed with the tools of classical Thermodynamics, appear to violate the
Second Law and seem to provide support to the recent results presented in
the above cited literature.

The paper is organized as follows: in the next Section we describe our
thermo-charged capacitor, which bears interesting similarities with some re-
cent challenges presented in [20, 21], and provide a thorough mathematical
analysis of its functioning. In the last Section we discuss the paradoxical
features of the physical process and show quantitatively why it seems to be
at odds with the Second Law of Thermodynamics.

2 Thermo-charged spherical capacitor

In Fig. [1] a sketched section of our vacuum spherical capacitor is shown.
The outer sphere has radius $b$ and it is made of (conductive) material with
high work function ($\phi_{ext.} \gg 1\text{eV}$). High work function means relatively low
thermionic emission. The inner sphere, instead, has radius $a$ and it is made of
a thermionic (conductive) material with relatively low work function ($\phi_{in.} \lesssim
1\text{eV}$). It should be clear that in such case the two thermionic fluxes are
different, being the latter greater than the former and the former negligible.
Actually, this is true only at the beginning of the thermo-charging process;
as a matter of fact, to reach our goal it suffices to concentrate on the initial
phase of the process.

Let us describe how our device works. All the electrons emitted by the
inner sphere, due to thermionic emission at room temperature, is collected
by the outer (very low emitting) sphere creating a macroscopic difference of
potential $V$. Such process lasts until $V$ is too high to be overcome by the
kinetic energy $K_e$ of the main fraction of emitted electrons (namely, when
$K_e < eV$, where $e$ is the charge of electron).
Opaque case (with $\phi \gg 1$ eV)

Environment $T \simeq 298$ K

Figure 1: Scheme of the thermo-charged spherical capacitor with inner electrode made of Ag–O–Cs (with $\phi_{in.} \lesssim 0.7$ eV).

Being the work function of the outer sphere greater than that of the inner one, $\phi_{ext.} \gg \phi_{in}$, the reverse process, namely the electronic flux from the outer sphere to the inner one, may be neglected without sensibly modifying our results. As said before, this is true only at the beginning of the charging process. At equilibrium, both fluxes are equal to that of the outer sphere and they balance each other exactly. Anyhow, our analysis concerns exclusively the initial phase of the process and the validity of our results remains unaffected by the establishment of the final equilibrium.

It could be interesting to provide an estimate of the value of $V$ obtainable and an estimate of the time needed to reach such value, given the physical characteristics of the capacitor and the quantum efficiency curve $\eta(\nu)$ of thermionic material of the inner sphere.

The capacitor is placed in a heat bath at room temperature (environment) and it is subject to black-body radiation. Both spheres, at thermal equilibrium, emit and absorb an equal amount of radiation (Kirchhoff’s law of thermal radiation), thus the amount of radiation absorbed by the inner sphere is the same as that emitted by that sphere according to the black-body radiation formula (Planck equation). Given the room temperature $T$, Planck equation provides us with the number distribution of photons absorbed as a function of their frequency.

According to the law of thermionic emission, the kinetic energy $K_e$ of the emitted electron is given by the following equation,

$$K_e = h\nu - \phi.$$  \hspace{1cm} (1)

where $h\nu$ is the energy of the photon with frequency $\nu$ ($h$ is the Planck constant) and $\phi$ is the work function of the material. Thus, only the tail of the Planck distribution of the absorbed photons, with frequency $\nu > \nu_0 = \phi/h$, can contribute to the thermionic emission.

The voltage $V$ reachable with frequency $\nu_1$ is given by the following formula,
\[ eV = h\nu_1 - \phi, \]  

where \( eV \) is the inter-spheres potential energy, and thus, 

\[ \nu_1 = \frac{eV + \phi}{h}. \]  

The total number of photons per unit time \( F_p \) with energy greater than or equal to \( h\nu_1 \), emitted and absorbed in thermal equilibrium by the inner sphere, is given by the Planck equation, 

\[ F_p = \frac{2\pi S}{c^2} \int_{\nu_1}^{\infty} \frac{\nu^2 d\nu}{e^{h\nu/kT} - 1}, \]  

where \( S \) is the inner sphere surface area, \( c \) is the speed of light, \( k \) is the Boltzmann constant and \( T \) the room temperature.

If \( \eta(\nu) \) is the quantum efficiency (or quantum yield) curve of thermionic material of the inner sphere, then the number of electrons per unit time \( F_e \) thermionically emitted by the inner sphere towards the outer sphere with kinetic energy greater than or equal to \( h\nu_1 - \phi \), is given by, 

\[ F_e = \frac{2\pi \cdot 4\pi a^2}{c^2} \int_{\nu_1}^{\infty} \frac{\eta(\nu)\nu^2 d\nu}{e^{h\nu/kT} - 1}, \]  

where \( 4\pi a^2 \) is the surface area of the inner sphere.

For a vacuum spherical capacitor, the voltage \( V \) between the spheres and the charge \( Q \) on each sphere are linked by the following equation, 

\[ V = \frac{Q}{4\pi \varepsilon_0} \frac{b - a}{ab}. \]  

Now, we derive the differential equation which governs the process of thermo-charging. In the interval of time \( dt \) the charge collected by the outer sphere is given by, 

\[ dQ = eF_e dt = \frac{2\pi e \cdot 4\pi a^2}{c^2} \left( \int_{eV(t)+\phi}^{\infty} \frac{\eta(\nu)\nu^2 d\nu}{e^{h\nu/kT} - 1} \right) dt, \]  

where we make use of eq. (3) for \( \nu_1 \) and \( V(t) \) is the voltage at time \( t \). Thus, through the differential form of eq. (6), we have, 

\[ dV(t) = \frac{2\pi e a(b - a)}{\varepsilon_0 c^2 b} \left( \int_{eV(t)+\phi}^{\infty} \frac{\eta(\nu)\nu^2 d\nu}{e^{h\nu/kT} - 1} \right) dt, \]  

or
\[ \frac{dV}{dt} = \frac{2\pi e a(b-a)}{\epsilon_0 c^2} \int_0^\infty \frac{\eta(\nu)\nu^2 d\nu}{e^{\frac{h\nu}{kT}} - 1}. \] (9)

Since our aim is to maximize the production of voltage \( V \), we have to choose \( a \) and \( b \) such that they maximize the geometrical factor \( a(b-a)/b \). It is not difficult to see that the maximum is reached when \( a = b/2 \). So we have,

\[ \frac{dV}{dt} = \frac{\pi eb}{2\epsilon_0 c^2} \int_0^\infty \frac{\eta(\nu)\nu^2 d\nu}{e^{\frac{h\nu}{kT}} - 1}. \] (10)

Unfortunately, provided that an analytical approximation of a real quantum efficiency curve \( \eta(\nu) \) exists, the previous differential equation appears to have no general, simple analytical solution.

However, a close look at the Planckian integral of eq. (10) suggests to us the asymptotic behavior of \( V(t) \). Even if we do not know \textit{a priori} how \( \eta(\nu) \) is, we know it to be a bounded function of frequency, with values between 0 and 1; usually, the higher is \( \nu \), the closer to 1 is \( \eta(\nu) \). Thus, independently of \( \eta(\nu) \), a slight increase of \( V(t) \) makes the value of the Planckian integral to be smaller and smaller very fast. Heuristically, this suggests that \( V(t) \) should tend quite rapidly to an ‘asymptotic’ value (since \( \frac{dV}{dt} \) tends to 0).

In the rest of this section we provide a numerical solution of the above differential equation for the practical case of inner sphere made of Ag–O–Cs [26, 27, 28] (see Fig. 1). To do that we need to adopt an approximation, however: the approximation consists in the adoption of a constant value for \( \eta \), a sort of suitable mean value \( \overline{\eta} \).

The differential equation (10) thus becomes,

\[ \frac{dV(t)}{dt} = \frac{\pi eb}{2\epsilon_0 c^2} \int_0^\infty \frac{\nu^2 d\nu}{e^{\frac{h\nu}{kT}} - 1}. \] (11)

A straightforward variable substitution in the integral of eq. (11) allows to write it in its final, simplified form,

\[ \frac{dV(t)}{dt} = \frac{\pi eb\overline{\eta}}{2\epsilon_0 c^2} \left( \frac{kT}{\hbar} \right)^3 \int_0^\infty \frac{x^2 dx}{e^{\frac{x}{kT}} - 1}. \] (12)

Here we provide an exemplificative numerical solution of eq. (12), adopting the following nominal values for \( \phi, b, T \) and \( \overline{\eta} \): \( \phi = 0.7 \text{ eV}, b = 0.20 \text{ m}, T = 298 \text{ K}, \) and \( \overline{\eta} = 10^{-5} \). In order to make a conservative choice for the value of \( \overline{\eta} \) we note that only black-body radiation with frequency greater than \( \nu_0 = \phi/\hbar \) can contribute to thermionic emission. This means that for
Figure 2: Thermo-charging process of the spherical capacitor described in the text \( (\phi = 0.7 \text{ eV}, b = 0.20 \text{ m}, T = 298 \text{ K}, \text{ and } \eta = 10^{-5}). \) These two plots show with different ranges in time-scale the behavior of \( V(t) \). Plot (a) shows how only after 60 seconds the voltage of the capacitor becomes more than 0.15 volts. Instead, plot (b) tells us that the voltage of the capacitor requires some hours to approach 0.3 volts.

In Fig. 2 the numerical solution of the above test it is shown. In plot (a) we could easily see how only after 60 seconds the voltage of the capacitor exceeds the value of 0.15 volts. Indeed, this is a macroscopic voltage. Instead, plot (b) tells us that the voltage of the capacitor requires some hours to approach 0.3 volts. Even in the more pessimistic scenario where \( \eta = 10^{-8} \) we see that a macroscopic voltage should arise quite rapidly between the plates, see Fig. 3.

3 Discussion and conclusions

At first sight, the charging process is a quite straightforward physical mechanism and it appears almost unproblematic. However, one feature of the thermo-charging should catch our attention. During the charging of the device the inner thermionic sphere substantially absorbs heat from the environment and releases this energy to the thermionic electrons. Such electrons fly to the outer sphere and impinge on it with non-zero velocity (since a non-zero fraction of them gathers their kinetic energy from the high energetic tail of the Planck distribution of black-body radiation). When they impinge on

the Ag–O–Cs photo-cathode only radiation with wavelength smaller than \( \lambda_0 = h c / \phi \simeq 1700 \text{ nm} \) contributes to the emission. According to Fig. 1 in Bates [28], the quantum yield of Ag–O–Cs for wavelengths smaller than \( \lambda_0 \) (and thus, for frequency greater than \( \nu_0 \)) is always greater than \( 10^{-5} \). Anyway, a laboratory realization of the capacitor, together with the experimental measurement of \( V(t) \), should provide us with a realistic estimate of \( \eta \) for the Ag–O–Cs photo-cathode.

In Fig. 2 the numerical solution of the above test it is shown. In plot (a) we could easily see how only after 60 seconds the voltage of the capacitor exceeds the value of 0.15 volts. Indeed, this is a macroscopic voltage. Instead, plot (b) tells us that the voltage of the capacitor requires some hours to approach 0.3 volts. Even in the more pessimistic scenario where \( \eta = 10^{-8} \) we see that a macroscopic voltage should arise quite rapidly between the plates, see Fig. 3.

3 Discussion and conclusions

At first sight, the charging process is a quite straightforward physical mechanism and it appears almost unproblematic. However, one feature of the thermo-charging should catch our attention. During the charging of the device the inner thermionic sphere substantially absorbs heat from the environment and releases this energy to the thermionic electrons. Such electrons fly to the outer sphere and impinge on it with non-zero velocity (since a non-zero fraction of them gathers their kinetic energy from the high energetic tail of the Planck distribution of black-body radiation). When they impinge on
the outer sphere, they release their kinetic energy substantially heating the outer sphere. Thus, we are facing a spontaneous process involving an isolated system at uniform temperature (capacitor + environment), in which a part of the system (the inner sphere of the capacitor) absorbs heat at temperature \( T \) and transfers a fraction of this heat to the other part of the system (the outer sphere) at the same temperature. This seems to macroscopically violate the Second Law of Thermodynamics in the Clausius formulation. As a matter of fact, if \( Q_i \) is the energy absorbed by the inner sphere from the environment, \( U \) is the energy stored in the electric field between the spheres (\( U = \frac{1}{2} C V^2 \), where \( C = \frac{4 \pi \varepsilon_0 ab}{b-a} \) is the capacitance of the spherical capacitor), and \( Q_f \) is the energy transferred through the flying electrons to the outer sphere as heat (according to the First Law of Thermodynamics \( Q_f + U = Q_i \), thus \( Q_i > Q_f \)), then the Clausius entropy variation of the whole system, as rough estimate, amounts to:

\[
\Delta S_{\text{tot}} \simeq -\frac{Q_i}{T} + \frac{Q_f}{T} < 0. \quad (13)
\]

In order to make the above result more striking, let us consider the following analogue in classical Thermodynamics/Mechanics: a boulder of mass \( m \) rests at the bottom of a valley, below a hill of height \( h \), all the system at constant temperature \( T \). Suddenly, the boulder spontaneously absorbs an amount \( Q_1 \) of heat (energy) from the environment and spontaneously starts to climb the hill at decreasing velocity (since the initial kinetic energy is being transformed into gravitational potential energy). Near the top of the hill the boulder hits a sort of wall and then stops. The friction experienced
during the hit against the wall lets the boulder release to the environment an amount $Q_2$ of heat, obviously smaller than $Q_1$. According to the First Law of Thermodynamics we have: $Q_1 - Q_2 = mgh$, where $mgh$ is the gravitational potential energy variation of the boulder from the valley to the top of the hill.

Now, the total Clausius entropy variation is:

$$\Delta S_{tot} = -\frac{Q_1}{T} + \frac{Q_2}{T} = -\frac{mgh}{T} < 0.$$  \hspace{1cm} (14)

The behavior of the boulder-environment system is practically the same as that of our electrons-environment system, and it is undoubtedly puzzling from the point of view of the Second Law of Thermodynamics.

Since the thermo-charging process is a spontaneous process, the variation of the Gibbs free energy of the system $\Delta G = \Delta H - T\Delta S$ should be negative. The enthalpy variation for constant pressure systems is given by $\Delta H = \Delta E + \Delta W$, where $\Delta E$ is the system internal energy variation and $\Delta W$ is the work produced. $\Delta H$ is equal to 0 since, from the First Law of Thermodynamics, $\Delta H = \Delta Q = 0$ (after all, we are dealing with an isolated system -capacitor plus environment-, then the total $\Delta Q$ is equal to zero), and thus we have $\Delta G = -T\Delta S > 0$. This is another way to see the paradoxical behavior of our system.

One possible objection could be that some other physical changes take place in the system during the process that may cancel out the apparent entropy decrease. Surely, during the charging process an electric field, and thus an electric potential, is created inside the capacitor where none existed before. Thus, one could attribute to the creation of the electric field an entropy increase greater than the entropy decrease due to the cooling and warming of the spheres.

A problem with this explanation could follows directly from the logic of the entropy variation analysis done for the ideal Carnot engine: the electric field represents a sort of work produced and stored in potential form by our capacitor, as could happen with a standard mechanical Carnot engine whose work is stored in a lifted weight. Hence, we are not able to see why for classical Carnot engine (and for classical Thermodynamics) the work $W$ is not taken into account in the evaluation of the total entropy variation (unless it is transformed into heat, but it is not the case here), while for our thermo-charged capacitor the macroscopic stored energy (work) $U$ should be taken into account for the evaluation of the total $\Delta S$. In order to save the validity of the Second Law of Thermodynamics we need to find other sources of positive entropy during the charging process.

The above results do not seem to depend on the particular value of the
work function of the outer sphere, provided that $\phi_{\text{ext.}} \gg 1 \text{ eV}$. One may suppose that when the electrons fly into the outer sphere with higher work function, they diminish their potential energy and release a kinetic energy greater than that they had before impinging on the sphere, thus producing $Q_f > Q_i$ in eq. (13), and eventually giving $\Delta S > 0$. But, what about the conservation of energy? As a matter of fact, if at some point of the charging process we try to neutralize both spheres putting them into contact at the same time with two distinct huge (infinite) chunks of neutral (conductive) materials, respectively of the same composition of the two spheres (in order to avoid problems with junction potentials) and at the same temperature $T$, then this process will release further energy through the Joule effect of the discharge (as a matter of fact, each sphere disperses its charge into the huge chunk of neutral material). This energy is equal to $U$, the energy of the thermo-generated electric field. The energy balance $\Delta E_{\text{tot}}$ of the entire process, thermo-charging and neutralization, thus gives: the total subtracted energy amounts to $Q_i$, the released energy amounts to $Q_f + U$, but according to the above attempted solution of the entropy paradox $Q_f > Q_i$, and thus $\Delta E_{\text{tot}} = Q_f + U - Q_i > U > 0$, namely we would have a spontaneous energy production inside an isolated system. So, the above argument cannot be an acceptable explanation of the paradox.

This last incongruity sounds familiar, since it is not the first time that the Second Law is put against to the First Law in scientific literature, see [23], p. 473.

Moreover, Sommerfeld in 1952 [29], trying to show how a quasi-static process does not always mean a reversible one, described the slow discharge of a charged capacitor through a very large resistance submerged in a heat reservoir: the discharge will take place by an arbitrarily small current, and negligible disturbance of electrostatic equilibrium, thus, such a process is quasi-static, but not reversible. In fact, the reverse process, he said, is not allowed by the Second Law [30].

To the author knowledge, our result represents an easily understandable and not so trivially refutable challenge to the Clausius formulation of the Second Law (see eq. (13)). In its current incarnation, however, it is not completely clear how this alleged challenge could be made exploitable, namely how our capacitor could be transformed into a device able to cyclically produce usable work\(^1\) out of a single heat bath (e.g. challenging the Kelvin-Planck formulation of the Second Law).

\(^1\)E.g., as DC current, or as electro-mechanical work like in [22, 23, 25]. We can not reasonably rely on the inter-sphere heat flux alone, since it is microscopic and hence it can hardly be exploited thermodynamically/mechanically.
As a matter of fact, if our result will resist the deep scrutiny of the scientific community in the years to come, then we are reasonably confident that, for our approach, an efficient path from “Clausius violation” to the “Kelvin-Planck violation” of the Second Law can be found, being the two formulation notoriously equivalent. This last subject is currently under investigation by the author.

Acknowledgments

This work was partially supported by an Italian Space Agency (ASI) grant. The author acknowledges the instructive and supportive attitude of the Editor and the two anonymous referees. The author wishes also gratefully acknowledge stimulating and encouraging discussions with Prof. Daniel P. Sheehan (University of San Diego) during the preparation of an early draft of the manuscript.

References

[1] H. Poincaré, in: Sopka, K.R.(ed.) Physics for a New Century: Papers Presented at the 1904 St. Louis Congress. Tomash, Los Angeles, 1986, pp. 281–299.

[2] J. Earman, J. Norton, Stud. Hist. Phil. Mod. Phys. 29 (1998) 435; J. Earman, J. Norton, Stud. Hist. Phil. Mod. Phys. 30 (1999) 1.

[3] D. P. Sheehan (Ed.), First International Conference on Quantum Limits to the Second Law, AIP Conference Proceedings, Vol. 643, AIP Press, Melville, NY, 2002.

[4] V. Čapek, D. P. Sheehan, Challenges to the Second Law of Thermodynamics–Theory and Experiments, Fundamental Theories of Physics, Vol. 146, Springer, Dordrecht, Netherlands, 2005.

[5] D. P. Sheehan (Ed.), The Second Law of Thermodynamics: Foundation and Status, Proceedings of Symposium at 87th Annual Meeting of the Pacific Division of AAAS, University of San Diego, June 19–22, 2006; Special Issue of Found. Phys. 37 (2007).

[6] L.G.M. Gordon, Found. Phys. 11 (1981) 103; L.G.M. Gordon, Found. Phys. 13 (1983) 989; L.G.M. Gordon, J. Coll. Interf. Sci. 162 (1994) 512; L.G.M. Gordon, Entropy 6 (2004) 38, 87, 86.
[7] J. Denur, Am. J. Phys. 49 (1981) 352;  
J. Denur, Phys. Rev. A 40 (1989) 5390;  
J. Denur, Entropy 6 (2004) 76.

[8] V. Čápek, J. Phys. A 30 (1997) 5245;  
V. Čápek, Czech. J. Phys. 48 (1998) 993;  
V. Čápek, Czech. J. Phys. 47 (1997) 845;  
V. Čápek, Czech. J. Phys. 48 (1998) 879;  
V. Čápek, Mol. Cryst. Liq. Cryst. 335 (2001) 24;  
V. Čápek, J. Bok, J. Phys. A 31 (1998) 8745;  
V. Čápek, Physica A 290 (2001) 379;  
V. Čápek, T. Mančal, Europhys. Lett. 48 (1999) 365;  
V. Čápek, T. Mančal, J. Phys. A 35 (2002) 2111;  
V. Čápek, D. P. Sheehan, Physica A 304 (2002) 461.

[9] J. Bok, V. Čápek, Entropy 6 (2004) 57.

[10] A. E. Allahverdyan, Th. M. Nieuwenhuizen, Phys. Rev. Lett. 85 (2000) 1799;  
A. E. Allahverdyan, Th. M. Nieuwenhuizen, Phys. Rev. E 64 (2001) 056117;  
A. E. Allahverdyan, Th. M. Nieuwenhuizen, Phys. Rev. B 66 (2003) 115309;  
A. E. Allahverdyan, Th. M. Nieuwenhuizen, J. Phys. A 36 (2004) 875.

[11] Th. M. Nieuwenhuizen, A. E. Allahverdyan, Phys. Rev. E 66 (2002) 036102.

[12] B. Crosignani, P. Di Porto, Am. J. Phys. 64 (1996) 610;  
B. Crosignani, P. Di Porto, Europhys. Lett. 53 (2001) 290;  
B. Crosignani, P. Di Porto, C. Conti, in: Quantum Limits to the Second Law, p. 267  
B. Crosignani, P. Di Porto, C. Conti, Entropy 6 (2004) 50.

[13] D. P. Sheehan, J. Glick, J. D. Means, Found. Phys. 30 (2000) 1227;  
D. P. Sheehan, J. Glick, Phys. Scr. 61 (2000) 635;  
D. P. Sheehan, J. Glick, T. Duncan, J. A. Langton, M. J. Gagliardi, R. Tobe, Found. Phys. 32 (2002) 441;  
D. P. Sheehan, J. Glick, T. Duncan, J. A. Langton, M. J. Gagliardi, R. Tobe, Phys. Scr. 65 (2002) 430.

[14] A. Trupp, in: Quantum Limits to the Second Law, p. 201, 231.
[15] P. Keefe, J. Appl. Opt. 50 (2003) 2443; P. Keefe, Entropy 6 (2004) 116.
[16] J. Berger, Phys. Rev. B 70 (2004) 024524.
    J. Berger, Physica E 29 (2005) 100.
    J. Berger, Found. Phys. 37 (2007) 1738.
[17] S. V. Dubonos, V. I. Kuznetsov, I. N. Zhilyaev, A. V. Nikulov, A. A. Firsov, JETP Lett. 77 (2003) 371.
[18] A. V. Nikulov, Phys. Rev. B 64 (2001) 012505;
    A. V. Nikulov, I. N. Zhilyaev, J. Low Temp. Phys. 112 (1998) 227.
[19] C. Pombo, A. E. Allahverdyan, Th. M. Nieuwenhuizen, in: Quantum Limits to the Second Law, p. 254.
[20] D. P. Sheehan, Phys. Plamas 2 (1995) 1893;
    D. P. Sheehan, Phys. Plamas 3 (1996) 104;
    D. P. Sheehan, J. D. Means, Phys. Plamas 5 (1998) 2469.
[21] D. P. Sheehan, J. Sci. Expl. 12 (1998) 303.
[22] D. P. Sheehan, J. H. Wright, A. R. Putnam, Found. Phys. 32 (2002) 1557;
    D. P. Sheehan, J. H. Wright, A. R. Putnam, A. K. Pertuu, Physica E 29 (2005) 87.
[23] D. P. Sheehan, D. H. E. Gross, Physica A 370 (2006) 461.
[24] D. P. Sheehan, Phys. Rev. E 57 (1998) 6660.
    D. P. Sheehan, Physica A 280 (2001) 185.
[25] D. P. Sheehan, J. Sci. Expl. 22 (2008) 459.
[26] A.H. Sommer, Photoemissive materials: preparation, properties, and uses, John Wiley & Sons, New York, 1936.
[27] A.H. Sommer, IRE Transactions on Nuclear Science (1956) 8.
[28] C.W. Bates Jr., Phys Rev Lett 47-3 (1981) 204.
[29] A. Sommerfeld, Vorlesungen über Theoretische Physik, Band 5, Thermodynamik and Statistik, 1952 (Wiesbaden: Dieterichsche Verlagsbuchhandlung).
[30] J. Uffink, Stud. Hist. Phil. Mod. Phys. 32 (2001) 305.