“Closed-loop” analysis of a thermo-charged capacitor

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Abstract

In this Letter, an explicit application of conservation of energy and zero net work principle around a closed path (“closed-loop” analysis) is carried out on a thermo-charged capacitor at equilibrium with ambient heat at uniform temperature. This analysis corroborates the results of previous studies [Phys. Lett. A 374 (2010) 1801, Physica A 390 (2011) 481] that a potential drop $\Delta V$ does actually occur at capacitor terminals.

Keywords second law of thermodynamics · thermionic emission · contact potential · diffusion · capacitors · vacuum tube

1 Introduction

In a series of papers, the first one of which dates back to 2010, I theoretically investigated the possibility of harnessing energy from ambient heat at uniform temperature. I introduced what I have then called “thermo-charge capacitor” along with a mathematical model of its alleged functioning. Let me briefly review its design to set the stage for what is going to be the topic of the present paper. For those interested in further details, refer to [1 2 3 4 5].

A thermo-charged capacitor (TCC) is vacuum capacitor (spherical or flat) spontaneously charged harnessing the heat absorbed from a single thermal reservoir at room temperature.

In Figure 1 a sketch with the essential features of a TCC is given. Electrode $A$ is made of metallic material with relatively high work function ($\phi_A = \phi_{3-4} > 1\text{eV}$). Electrode $B$ is made of the same conductive material as $A$, but it is coated with a layer (2) of semiconductor Ag–O–Cs, which
Figure 1: Sketch of a vacuum thermo-charged capacitor: electrode $A$ is made of a high work function metal ($3 - 4$), electrode $B$ is made of a high work function metal ($1 - 5$) coated with a layer of semiconductor Ag–O–Cs with low work function (2). Work functions are such that $\phi_{1-5} = \phi_{3-4} > \phi_2$. 

is known to have a relatively low work function ($\phi_2 \lesssim 0.7$ eV, but $\phi_{1-5} = \phi_A$). When TCC is properly shielded from light or other electromagnetic disturbance (natural and man-made e.m. waves, cosmic rays and so on), only the energetic tail of black body radiation originating from ambient heat is responsible for the thermionic (actually, “thermo-voltaic”) emission at electrodes $A$ and $B$. In such a design, the thermionic fluxes from $A$ to $B$ and from $B$ to $A$ are different, the latter being greater than the former, at least at the beginning of the charging process.

A fraction of the electrons thermionically emitted from electrode $B$ are definitely collected by (very low emitting) electrode $A$, creating a macroscopic difference of potential $\Delta V$ between $A$ and $B$ (for the equations governing the thermionic emission charging process, see [1, 2]). At first, such a process is unbalanced, the flux from electrode $B$ being greater than that from $A$, but later, with the increase of potential $\Delta V$, the two-way effective fluxes tend to balance each other exactly. A dynamical equilibrium of charges (space charge) between the electrodes is eventually attained. Remind that in vacuum the thermionic emission can be seen as a ballistic ejection process.

In paper [2] I also showed that the experimental measurement of $\Delta V$ between 4 and 5 is not an easy task: an electrometer with extremely high input impedance (several TΩ) is needed since output currents are expected
to be of the order of $10^{-14}$ A.

Legitimate doubts may arise that even if the mathematical treatment made in those papers were unexceptionable, it might be incomplete: for some hidden reasons there might be no potential drop at capacitor terminals (4 and 5), leaving out the measurement problem.

Since the publication of the cited papers no one seems to have put forward any criticism. This notwithstanding, I myself devoted some time and energy to address at least two possible objections to the above design and functioning.

The first one is related to the presence of a Schottky rectifying junction inside electrode $B$ (between metal and Ag–O–Cs layer), which appears to prevent any charge displacement from metal to semiconductor, and thus to prevent any current flow across the whole capacitor when terminals 4 and 5 are shorted (or, equivalently, zero voltage drop between 4 and 5 when they are left open). Actually, this objection has already been addressed in the second paper on TCC, and the interested reader could easily go through the original source [2].

The second objection has been the topic of an Addendum to the second paper on TCC [2]. Since it is important for what we shall see in the following Section, let me resume below its key aspects.

As already noted, the contact surface between the metallic part 1 of electrode $B$ and its semiconductor layer 2 (Ag–O–Cs) is a metal/n-type semiconductor junction (Fig. 1, region 1–2). Across such a junction a contact potential builds up, equal to the differences between the two work functions divided by the electronic charge, $\Delta V = \frac{\phi_1 - \phi_2}{e}$. This potential is the result of charge diffusion across the junction 1–2 as soon as the two materials are physically joined. The junction is thus the region where, at equilibrium, a balance between electrostatic and diffusive (thermally driven) forces is attained.

In almost all textbooks it is said that a voltage drop builds up not only across the contact surface 1–2, but instantaneously also between the surfaces at the free ends of the joined materials (free surface of semiconductor 2 on one side and free surface 5 of the metal on the other, but also free surface of semiconductor 2 and free surface 3 of electrode $A$, when terminals 4 and 5 are shorted, see Fig 1).

Note that this voltage drop is not intended to be that generated by thermionic emission of electrons from $B$ to $A$. It is intended to originate from an overall charge displacement in the bulk of electrode $B$ across the junction as soon as the materials 1 and 2 are physically joined. To my knowledge, no textbook or published paper on the subject clearly explains how and why these charges collectively and macroscopically move inside the
bulk of electrode $B$ across the junction so as to charge the metal (1$-$5, or
1$-$5$-$4$-$3 when terminals 4 and 5 are shorted) negatively and semicon-
ductor 2 positively. This voltage drop is of the same magnitude of the contact
potential.

All this is usually explained appealing to a supposed straightforward ap-
plication of the Kirchhoff’s second (loop) rule. If this were true, then it
would prevent any net current flow across the whole capacitor when the two
electrodes are electrically shorted at their free ends (terminals 4 and 5), so as
to establish a closed circuit. As a matter of fact, in order to reach electrode
$A$, any electron escaping electrode $B$ would need the same energy needed
by an electron escaping electrode $A$ to reach electrode $B$. $B$-electrons need
an energy equal to $\phi_2 + e\Delta V$, since they must be ejected (required energy
$\phi_2$) and then they have to overcome the potential drop $\Delta V$ instantaneously
generated between 2 and 3 due to the contact between 1 and 2, (energy equal
to $e\Delta V$). $A$-electrons need $\phi_3$ (only the energy to be ejected). But, since
$e\Delta V = \phi_1 - \phi_2 = \phi_3 - \phi_2$, $B$-electrons need $\phi_2 + e\Delta V = \phi_3$.

I have explicitly shown in another paper [3] that no electric field, and
thus no voltage drop, builds up between the surfaces at the free ends of
two materials with different work functions (namely, between 2 and 5, or
equivalently between 2 and 3, when terminals 4 and 5 are shorted) when the
materials are physically joined at one end (region 1$-$2).

In that paper I performed the following “closed-loop” analysis, namely I
made an explicit application of the path-independence law and/or Kirchhoff’s
loop rule. The physical principle at the basis of these two laws is the more
fundamental law of conservation of energy.

At equilibrium, conservation of energy demands that a test electronic
charge $e$ conveyed around a closed path $\gamma$ in the device bulk of Fig. 2 (which
equivalently represents either the sole electrode $B$ of Fig. 1 or the whole
TCC of Fig. 1 if terminals 4 and 5 are shorted), through physical junction
J-I (1$-$2) and gap J-II between 2 and 5, if Fig. 2 is intended to be the sole
electrode $B$, or between 2 and 3 if Fig. 2 is intended to be the whole TCC
of Fig. 1 with terminals 4 and 5 shorted, must undergo zero net work from
all the forces present along the path. Mathematically, we must have,

$$\oint_{\gamma} dW_{tot} = 0. \quad (1)$$

Note that for this analysis I completely neglect the thermionic emis-
sions of all the materials. I am focusing only on the physical process across
the contact junction 1$-$2 at equilibrium.

At equilibrium, the only two regions where forces are allowed to be non-
null are the J-I and J-II regions. An electric field elsewhere in the device
Figure 2: This figure equivalently represents either the sole electrode $B$ of Fig. [1] or the whole TCC of Fig. [1] if terminals 4 and 5 are shorted. J-I is the physical junction 1 – 2 and J-II is the gap between 2 and 5, if this figure is intended to be the sole electrode $B$, or between 2 and 3 it is intended to be the whole TCC of Fig. [1] with terminals 4 and 5 shorted. Work functions are such that $\phi_1 > \phi_2$.

bulk (other than in the contact region) would generate a current, which contradicts the assumption of equilibrium. When the test charge $e$ crosses J-I, it is subject to the built-in electric field force $eE_{bi}$ and to the diffusion force $F_{diff}$. This “force” is the thermally driven force responsible for the establishment of the contact potential at J-I. We know that at equilibrium $eE_{bi} = -F_{diff}$ and that $F_{diff}$ is different from zero and constantly present, otherwise $E_{bi}$ would soon drop to zero, thus,

$$0 = \oint_{\gamma} dW_{tot} = \int_{J-I} (eE_{bi} + F_{diff}) \cdot d\vec{\gamma} + \int_{J-II} dW_{ext} = 0 + \int_{J-II} dW_{ext}. \quad (2)$$

In the J-II gap there are no diffusion forces, since it is a vacuum gap, and eventually we have,

$$0 = \int_{J-II} dW_{ext} = \int_{J-II} eE_{J-II} \cdot d\vec{\gamma} = e|E_{J-II}|x_g \quad \rightarrow \quad |E_{J-II}| = 0, \quad (3)$$

where $x_g$ is the gap width.
In the following Section, I perform the same “closed-loop” analysis across the whole TCC by taking into account the thermionic (thermo-voltaic) emission between 2 and 3, and by considering the capacitor thermionically charged and at equilibrium (with terminals 4 and 5 not shorted). The outcome gives further support to the results of the cited studies that a potential drop $\Delta V$ does actually occur at the free ends (4 and 5) of a TCC.

## 2 Closed-loop analysis across a thermionically charged TCC

I apply the energy conservation analysis made in [2, 3] across the whole thermionically charged capacitor at equilibrium. In what follows reference is made to Figure 3.

Figure 3 shows a charged TCC at equilibrium (with non shorted terminal leads). As in Fig. 1 region 1−2 is the depletion region at the metal/Ag–O–Cs junction. Dots in the vacuum region (region 2−3) represent the space charge electrons which, at equilibrium, are continually emitted and re-absorbed by electrode surfaces (the main part come from the Ag–O–Cs layer on electrode $B$). Part of the electrons emitted by electrode $B$ have been definitely absorbed by electrode $A$. These are represented by the minus-signs on electrode $A$ and are responsible for the thermionically generated potential drop between 2 and 3 [1, 2].

Once again, conservation of energy demands that a test electronic charge $e$ conveyed around a closed path $\gamma$ in the device bulk of Fig. 3 through regions 1−2 (physical junction), 2−3 (vacuum gap) and 4−5 (open terminal leads) at equilibrium, must undergo zero net work from all the forces present along the path. At equilibrium, the only regions where the forces are allowed to be non-zero are 1−2, 2−3 and 4−5, and mathematically, we have,

$$\oint_{\gamma} dW_{\text{tot}} = \int_{1-2} dW + \int_{2-3} dW + \int_{4-5} dW = 0. \quad (4)$$

The integral $\int_{4-5} dW$ is equal to $e\Delta V_{\text{ext}}$, namely the voltage drop at the free ends of the thermo-charged capacitor, multiplied by the test charge $e$. The integral $\int_{1-2} dW$ has already been proved to be equal to 0 (previous Section and [2, 3]).

The point is then: is the integral $\int_{2-3} dW$ different from zero? I have already shown in the aforementioned publications that a voltage drop $\Delta V$ should arise inside the vacuum capacitor due to the thermionic emission charging process and thus an electric field $E_{\text{int}}$ (equal to $\frac{\Delta V}{d}$, where $d$ is the
Figure 3: Charged TCC at equilibrium with ambient heat at uniform temperature (with non-shorted terminal leads 4 and 5). As in Fig. II region 1 – 2 is the depletion region at the metal/Ag–O–Cs junction. Dots in the vacuum region (region 2 – 3) are the space charge electrons which, at equilibrium, are continually emitted and re-absorbed by electrode surfaces. $\gamma$ is the closed path traveled by the test charge $e$.

inter-electrode distance) should be present between the electrodes inside the capacitor (between 2 and 3).

Nevertheless, are we sure that a sort of compensating (thermally driven) diffusion force $F_{int}$, similar to that present in the contact junction 1 – 2, is not present inside the vacuum capacitor cancelling out the internal electric force $eE_{int}$? If this were the case, we would have,

$$-eE_{int} = F_{int}$$

and thus,

\[ \Delta V_{eq} \neq 0? \]
\[ \int_{\gamma} dW_{tot} = 0 + \int_{2-3} dW + \int_{4-5} dW = \]
\[ = \int_{2-3} (eE_{int} + F_{int}) \cdot d\vec{\gamma} + e\Delta V_{ext} = \]
\[ = 0 + e\Delta V_{ext} = 0. \quad (6) \]

This would mean that \( \Delta V_{ext} = 0 \), namely the TCC would have a zero voltage drop between its external leads.

Let me go into the possible nature of \( F_{int} \). As in the case of contact junction, this force could be seen as a collective and macroscopic manifestation of single microscopic actions on the electrons ejected by the thermionic surfaces (mainly, the Ag–O–Cs layer). At equilibrium, electrons are continuously emitted (due to the absorption of light quanta from black body radiation) and re-adsorbed by the surface of electrode \( B \) (the same process is going on also on electrode \( A \) but at a far smaller, negligible rate). The collective action of quanta absorption could be seen as a force acting in the opposite direction of \( E_{int} \): the field tends to pull the electrons just ejected from electrode \( B \) (and thus also the test charge \( e \)) back to electrode \( B \). The force \( F_{int} \) tends instead to push electrons (and thus the test charge \( e \)) away from electrode \( B \).

In the following Section I put forward three arguments which suggest that \( F_{int} \) is actually non-existent.

3 Discussion

In what follows I list three arguments, in increasing order of cogency, that appear to dismiss any concern about the possibility that \( F_{int} \) really exists and cancels out the internal, thermally generated, field force \( E_{int} \):

a) Cursory objection to \( F_{int} \): inside TCC there are no diffusion forces (\( F_{int} = 0 \)) since there is vacuum between electrodes \( A \) and \( B \).

b) Heuristic objection to \( F_{int} \): in [3] I have noticed that a kind of “force” \( F_{diff} \) acting upon the electrons must exist in the depletion region, otherwise the built-in electric field \( E_{bi} \) would go instantaneously to zero (there is a physical contact between metal and semiconductor in the junction). This close connection between \( F_{diff} \) and \( E_{bi} \) is expressed by the identity \( F_{diff} = -eE_{bi} \). In a fully charged TCC at equilibrium, if
we could “switch-off” the thermionic emission, the field inside the capacitor would still be there (maybe only becoming more uniform since space charge would cease) since some electrons from electrode B have already been absorbed/colllected by electrode A. Thus, we may heuristically conclude that, at equilibrium, $E_{\text{int}}$ and $F_{\text{int}}$ are not the one depending upon the other\footnote{The one does not exist only because of the other.} and there would be no reason to assume that $F_{\text{int}} = -e E_{\text{int}}$ exactly. There is no strict cause/effect relation between $E_{\text{int}}$ and $F_{\text{int}}$ as in the case of the contact junction.

c) Comparison with the behaviour of electrons in a photovoltaic tube: given the possible microscopic explanation/origin of the force $F_{\text{int}}$, this force would also be present on the active surfaces of a photovoltaic tube\footnote{The device depicted in Fig. 2 or Fig. 3 could equally work as a photovoltaic tube when illuminated by visible light.} with electrodes immersed in and illuminated by diffused light and with non-shorted terminals. This time, photovoltaic emission comes into play. If we apply the same closed-loop analysis performed on TCC and admit the equivalence $F_{\text{int}} = -e E_{\text{int}}$, then we would have a zero voltage drop between the (open) external leads of an illuminated photovoltaic cell. But this is experimentally not true.

Given a), b) and c), and the result of the closed-loop analysis performed in Section 2 with $F_{\text{int}} = 0$, a voltage drop does actually occur at the free ends (4 and 5) of a TCC.

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