A Note on Solid-State Maxwell Demon

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Abstract Since 2002, at least two kinds of laboratory-testable, solid-state Maxwell demons have been proposed that utilize the electric field energy of an open-gap $n$-$p$ junction and that seem to challenge the validity of the Second Law of Thermodynamics. In the present paper we present some arguments against the alleged functioning of such devices.

Keywords Second law of thermodynamics · Maxwell demon · $n$-$p$ junction

1 Introduction

Since 2002, two types of solid-state devices have been proposed \cite{1,2,3,4,5} that basically utilize the electric field energy of an open-gap $n$-$p$ junction and that seem to challenge the validity of the Second Law of Thermodynamics. They represent a sort of non-sentient solid-state Maxwell demons operating at room temperature, which are based on the cyclic electromechanical discharging and thermal recharging of the electrostatic potential energy intrinsic to the depletion region of a standard solid-state $n$-$p$ junction. The core of their functioning is the shaped junction depicted in Fig. 1.

It consists of two symmetric horseshoe-shaped pieces of $n$- and $p$-semiconductor facing one another. At Junction I (J-I), the $n$- and $p$-regions are physically connected, while at Junction II (J-II) there is a vacuum gap whose width $x_g$ is small compared to the scale lengths of either the depletion region $x_{dr}$ or the overall device $x_{dev}$; namely, $x_g \ll x_{dr} \sim x_{dev}$. All the scale lengths are in the micro-, nano-metric realm.

As is well known from solid-state physics, a built-in potential $V_{bi}$ forms across the junction J-I, whose numerical value depends on the doping characteristics of the two regions (concentrations of donors and acceptors, intrinsic

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carrier concentration) and on the environmental temperature (in the present case, room temperature). Its value can be estimated analytically.

This potential is the result of charge diffusion across J-I as soon as the two materials are physically joined. The depletion region is thus the region where, at equilibrium, a balance between bulk electrostatic and diffusive (thermally driven) forces is attained.

It is then claimed that an electric field must exist also in J-II. According to the built-in electric field in the J-I depletion region can be established either via Kirchhoff’s loop rule (conservation of energy) or via Faraday’s law ($\oint E \cdot dl = 0$). In fact, with regard to the latter condition, it would be more proper to talk about path-independence of conservative electric fields rather than referring to Faraday’s law. It is argued as follows. Consider a vectorial loop threading the J-I depletion region, the bulk of the device in Fig. 1 and the J-II gap. Since the built-in electric field in the J-I depletion region is unidirectional, there must be a second electric field somewhere else along the loop to satisfy $\oint E \cdot dl = 0$. An electric field elsewhere in the semiconductor bulk (other than in the depletion region), however, would generate a current, which contradicts the assumption.
Fig. 2 Physical characteristics versus position $x$ through Junctions I and II. Left ($x < 0$) and right ($x > 0$) sides of each graph correspond to $n$- and $p$-regions, respectively. (a) Energy levels for vacuum ($E_{\text{vac}}$), conduction band edge ($E_c$), intrinsic Fermi level ($E_F$), Fermi level ($E_F$), valence band edge ($E_v$). (b) Charge density ($\rho$). (c) Electric field magnitude ($|E|$). Note that vertical scales for $|E|$ are different for J-I and J-II ($|E_{\text{J-II}}| \gg |E_{\text{J-I}}|$). This sketch is from Fig. 2 of reference [1].

Therefore, by exclusion, the other electric field must exist in the J-II gap. Kirchhoff’s loop rule establishes the same result. Conservation of energy demands that a test charge conveyed around this closed path must undergo zero net potential drop; therefore, to balance $V_{bi}$ in the depletion region, there must be a counter-potential somewhere else in the loop. Since, at equilibrium, away from the depletion region in the bulk semiconductor there cannot be a potential drop (electric field) - otherwise there would be a non-equilibrium current flow, contradicting the assumption of equilibrium - the potential drop must occur outside the semiconductor; thus, it must be expressed across the vacuum gap J-II.

In Fig. 2 the energy, electric field and space charge profiles across J-I and J-II are represented according to the analysis done in [1]. Because the J-II gap is narrow ($x_g \ll x_{de}$) and the built-in potential is discontinuous (due to
the vacuum gap), there can be large electric fields there, which can be much greater than in the J-I depletion region. As a matter of fact, one can estimate the relative magnitude as follows: the J-II electric field is $|E_{J-II}| \approx \frac{V_{bi}}{x_g}$, while the average magnitude of the field in J-I is $|E_{J-I}| \approx \frac{V_{bi}}{x_{dr}}$, thus their ratio scales as $\frac{|E_{J-II}|}{|E_{J-I}|} \sim \frac{x_{dr}}{x_g} \gg 1$.

Through a mathematical treatment of the device, it has been shown that if some provisos on $x_g$ and $x_{dr}$ are met, then the electrostatic potential energy in J-II (electrostatic energy density times gap volume) is much greater than that in the entire depletion region J-I. Furthermore, if the open gap J-II is switched closed (thus becoming a second J-I junction), then such an excess energy is positively released. Most of the free electronic charges on each gap face (see Fig. 2) disperse through and recombine in the J-II bulk.

It is clear that if such a release can be made cyclical through an electromechanical nano-apparatus, then this kind of device can exploit the thermally driven diffusion across J-I to produce usable work. Namely, it appears to violate the Second Law of Thermodynamics in the Kelvin-Planck formulation.

In the literature, two kinds of such electromechanical apparatuses have been proposed and modeled so far (both analytically and numerically), one which uses a Linear Electrostatic Motor (LEM) [1,5], and the other using a Hammer and Anvil analogue [2,3,4,5]. The detailed description of these interesting devices is beyond the scope of the present paper.

In the following Section we present some arguments (heuristic and theoretical) which put the existence of the intense electric field in J-II into question. We simply believe that there is no electric field in J-II and thus no positive electromechanical energy release is possible by switching J-II gap closed.

### 2 Some arguments against Solid-State Demon devices

Now we try to argue that in the above scheme the electric field $|E_{J-II}|$ in junction J-II is non-existent.

It is easy to note that the amount of free electronic charge on each gap face at J-II depends upon the surface area of those faces. J-II being equivalent to a parallel-plate vacuum capacitor, the bigger is the surface area $S_{\text{face}}$ of the faces, the greater is the charge on them, the potential drop being fixed. In our case the potential drop is equal to $V_{bi}$, and:

$$Q_{J-II \text{ face}} = CV_{bi} = \frac{\epsilon_0 S_{\text{face}} V_{bi}}{x_g},$$

where $C$ is the electrostatic capacitance of J-II gap, $\epsilon_0$ is the vacuum permittivity, thus the greater is $S_{\text{face}}$, the greater is $Q_{J-II \text{ face}}$.

Imagine for a moment the following thought experiment. Let us have a device similar to that depicted in Fig. 1 with J-I still not closed and with an arbitrarily large surface area of J-II faces. As soon as J-I is switched closed, charge diffusion begins and a depletion region forms in J-I, together with the built-in potential $V_{bi}$. In order to satisfy the path-independence law and/or
the Kirchhoff’s loop rule, as argued in the cited literature, charges also must start to accumulate on each gap face in J-II. This means that a current must start to flow through the device bulk and through J-I, until the equilibrium is attained. It is easy to see that this current can be made arbitrarily high in intensity (if the ohmic resistance $R$ of J-I is suitably low) and/or arbitrarily long in duration (high $RC$ time constant), since $S_{\text{face}}$, and thus $Q_{\text{J-II face}}$, can be arbitrarily large.

All this is somewhat ‘unrealistic’: J-I can even melt if its section and ohmic resistance $R$ are the right ones; or cool down to extremely low temperatures, since the energy needed to maintain the current flow should come from the thermal agitation in J-I. As a matter of fact, in the case in which all the above really happens, the energy stored in the parallel-plate equivalent capacitor of J-II gap is $\sim \frac{1}{2}CV_{bi}^2$, and it comes exclusively from the thermal agitation in J-I. For high values of $C$, the stored electrostatic energy becomes huge: with

Fig. 3 Sketch of the first thought experiment described in the text.
A more household analogue can be obtained with two huge metallic plates, made of two metals with different work functions. Consider the device depicted in Fig. 3-a. We have two plates, one made of copper (Cu) and the other made of zinc (Zn), both placed in vacuum in order to eliminate electron exchange with (moist) air and thus avoiding spurious charging. They are spatially arranged in order to form a huge parallel-plate capacitor. A small wire of Cu starts from the Cu-plate and a small wire of Zn starts from the Zn-plate. Both plates are initially neutral and not connected to each other through the wires. All the system is at a uniform temperature $T$, in order to avoid charge accumulation due to the Seebeck/Thomson effects.

The plate capacitor can be made arbitrarily big, and thus having arbitrarily high electrostatic capacitance $C$, since $C = \frac{\varepsilon_0 S}{d}$, where $S$ is the plate surface area and $d$ the distance between the plates. As soon as the wire terminals are connected, a small Cu-Zn junction forms and a very thin (the junction being a metal to metal one) depletion layer is generated along the small contact surface (see Fig. 3-b). The local charge displacement, due to diffusion drift, originates a built-in potential $V_{bi}$. If we apply the arguments made in [1,2,3,4,5] and described in the previous Section, the same potential drop ($V_{bi}$) must originate also between the two plates with high electrostatic capacitance $C$. This means that an high amount of free charges must settle on both plates since, again, $Q = CV_{bi}$. As before, all this implies that an arbitrarily high current in intensity and/or arbitrarily long in duration must flow through the wires and that the small Cu-Zn junction must cool down very fast and significantly.

Fig. 4 Electrostatic behavior (charge diffusion and charge spreading) of Cu and Zn plates a) joined and then b) separated [6,7,8,9].
very fast and significantly. This behavior does not match what happens in laboratory experiments and in the real world.

It is already well known that this is not what really happens (see the Volta effect [6,9]). When two metals with different work functions (and similarly, an n- and a p-semiconductor) are joined, the charge drift is only local and the charge displacement remains localized within the thin depletion layer, in equilibrium. Far from the depletion region there is no free charge accumulation. A simple laboratory experiment with Cu and Zn plates and a gold-leaf electroscope can confirm such a behavior [6,7,8]. Only when the two metals are removed apart the charges, initially localized within the depletion layer, are free to spread across the surfaces of the metallic plates [7,8,9], satisfying electrostatic equipotentiality, see Fig. 4.

As is written in most introductory textbooks on the subject, the difference between work functions of two different materials (metal or semiconductor) cannot be measured directly with a normal voltmeter. With the thought experiment depicted in Fig. 5 it is easy to show that if a diodic or metallic vacuum gap generated and supported a capacitive electric field, then it would be possible to measure the difference of work functions directly with a normal voltmeter.

As said before, the existence of a capacitive electric field within the vacuum gap requires the accumulation of free charges (electrons and holes) on the gap faces. Consider now the device sketched in Fig. 5. We have three neutral chunks of metal: copper (Cu), zinc (Zn) and an unspecified metal (M). As in the previous thought experiment, these metals are placed in vacuum in order to eliminate electron exchange with (moist) air and thus avoiding spurious charging. We choose M such that \( \phi_{Zn} < \phi_{M} < \phi_{Cu} \), where \( \phi \) is the work function, as usual. If the contact between metals (or semiconductors) with different work functions generated a macroscopic charge drift to the opposite (free) sides of the metals (or semiconductors), far away from the junction, then the device depicted in the Figure would allow the measurement of the difference between \( \phi_{Zn} \) and \( \phi_{Cu} \) directly with a normal voltmeter, since we would have opposite free charges on the faces of a capacitor made of the same material (M), see Fig. 5.

Let us now comment the 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. Conservation of energy demands that a test electronic charge \( e \) conveyed around a closed path \( \gamma \) in the device bulk of Fig. 1 through J-I and J-II at equilibrium, must undergo zero net work from all the forces present along the path. Mathematically, we must have,

\[
\oint_{\gamma} dW_{ext} = 0. \tag{2}
\]

At equilibrium, the only two regions where forces are allowed to be non-null are the J-I and J-II regions, as already noted in Section 1. 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 \( F_{diff} \). We know that at equilibrium \( eE_{bi} = -F_{diff} \)
Fig. 5 Sketch of the second thought experiment described in the text.

and that $\mathbf{F}_{\text{diff}}$ is different from zero and constantly present, otherwise $\mathbf{E}_{\text{bi}}$ would soon drop to zero, thus,

$$0 = \oint_{\gamma} dW_{\text{ext}} = \int_{\text{J-I}} (e\mathbf{E}_{\text{bi}} + \mathbf{F}_{\text{diff}}) \cdot d\gamma + \int_{\text{J-II}} dW_{\text{ext}} = 0 + \int_{\text{J-II}} dW_{\text{ext}}. \quad (3)$$

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

$$0 = \int_{\text{J-II}} dW_{\text{ext}} = \int_{\text{J-II}} e \mathbf{E}_{\text{J-II}} \cdot d\gamma = e |\mathbf{E}_{\text{J-II}}| x_g \rightarrow |\mathbf{E}_{\text{J-II}}| = 0. \quad (4)$$

We have presented at least three arguments, the first two more heuristic, the third one more theoretical, that suggest that there is no electric field
within the J-II gap and thus no positive electro-mechanical energy release is possible by switching J-II gap closed.

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