RM-78-2

THERMAL RADIATION AND ENTROPY

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January 1978

PREFACE

As an approach to understanding the effectiveness of energy generating systems, the negentropy concept has been used recently at IIASA. It is inherent in Marchetti's "negentropy city" example and J. Thoma has described it via the modern "bond-graph" formalism of thermodynamics. An application of negentropy to an electromagnetic radiation source of energy--the sun--instead of a thermal source should be interesting; this paper attempts it.

ABSTRACT

In line with the "negentropy approach" currently pursued at IIASA, the thermodynamic properties of electromagnetic radiation are described. We use the photon description of the electromagnetic field and clarify the question of the entropy content of radiation. Entropy is found not in the spectral distributions but in the incoherence of individual modes. As an illustration, we calculate the efficiency of a highly idealized photocell.

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1. INTRODUCTION

Recently at IIASA, J. Thoma [1] has investigated various energy systems from a thermodynamical point of view, similar to C. Marchetti's "negentropy city". This approach is useful as an illustration of the simple, but nevertheless easily forgotten fact that no energy system ever produces energy (only entropy!) and to sharpen the awareness of the important role played by entropy in the performance of energy systems. It is interesting to look at solar radiation and photovoltaic cells from this point of view. This discussion of course, turns on the somewhat tricky concept of the "entropy content of electromagnetic radiation". It is the purpose of this note to collect well-known facts from theoretical physics--mainly statistical physics and quantum electrodynamics--and to present them with an eye on the problem above. Of course, a rigorous treatment of the subject would involve the full apparatus of quantum statistical mechanics; we shall therefore proceed quite informally.

2. THE PHOTON DESCRIPTION OF RADIATION

We imagine an ideally reflecting cavity, with a microscopic hole, connected for later purposes to a fixed temperature source (a large heat bath), as in Figure 1.

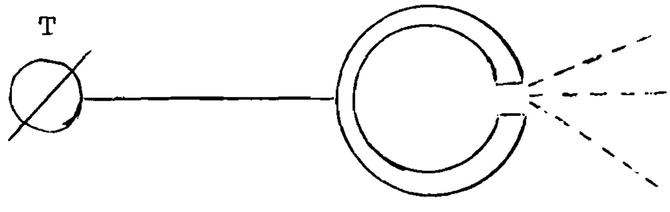

Figure 1.

The classical[1] electromagnetic (e.m.) field inside the cavity will have a discrete series of modes M_n, each with a frequency ν_n that behave like uncoupled harmonic oscillators. Each mode is given by a solution of Maxwell's equations of the form

$$\left.\begin{matrix}\vec{E}\\ \vec{B}\end{matrix}\right\} (x,t) = e^{2\pi i\nu nt} \left\{\begin{matrix}\vec{E}_n(x)\\ \vec{B}_n(x)\end{matrix}\right. \qquad (2.1)$$

(where $\vec{E}$ and $\vec{B}$ denote the electric and magnetic field strength respectively) and fulfilling boundary conditions appropriate to the walls of C. The most general classical e.m. field inside the cavity would then be a superposition of all modes with different amplitudes. But it is well known that classical physics cannot deal with the phenomenon of thermal e.m. radiation[2]. Intuitively speaking, instead of a continuous field one has to introduce discrete quanta of radiation: photons. A photon of frequency ν will carry an amount of energy given by $h\nu$ ($h = 6.626 \times 10^{-34}$ Js: Planck's universal constant). By using a description going back to Planck, a typical state of the "quantized" e.m. field inside C can be written as

$$|n_1; n_2; n_3 \ldots\rangle , \qquad (2.2)$$

meaning that n_1 photons of mode M_1, n_2 of mode M_2 etc. are present in the cavity. The total energy content of C is of course given by

$$E = \sum_i n_i h\nu_i \text{ }^{3)} \qquad (2.3)$$

The fact that E is a simple sum over all modes means that the modes are independent and uncoupled.

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1) "Classical" means here obeying Maxwell's equations.
2) Indeed, the famous "ultraviolet catastrophe" (the classical e.m. energy content of a cavity is infinite) was the starting point for the development of quantum theory.
3) Only a finite total number of photons should be present; i.e. all n_i are 0 except a finite number of them. Otherwise, E would be infinite.

One should not forget, however, that the states (2.2) do not exhaust all states of the e.m. field in C. These are states with fixed photon number , and with a completely undetermined phase[4]. In fact, $<\vec{E}\ (x,t)> = <\vec{B}\ (x,t)> = 0$ (the expectation values) in the states (2.2)--they could be called totally incoherent.

We contrast this result with the case of an ideal laser in the cavity radiating in exactly one mode M_i. The state of the e.m. field is then a so-called coherent state with sharp (non-fluctuating) values of $\vec{E}$ and $\vec{B}$. In this state, there are no photons in any mode except M_i. But the number of photons of mode M_i fluctuates (we can only say that in general its <u>average</u> number will be very large).

3. THE ENERGY DENSITY OF RADIATION (PLANCK'S FORMULA)

We now calculate the energy density and spectral distribution of the e.m. field in thermodynamic equilibrium at a temperature T ("black-body radiation of temperature T"). We can regard the field as a sum of independent modes; all of them must be at the same temperature T. From statistical physics we know that the statistical weight of a state of energy E at absolute temperature T is given by the Boltzman factor.

$$e^{-E/kT} \quad (k,\ \text{Boltzmann's constant} = 1.3807 \times 10^{-23} J/K \qquad (3.1)$$

Thus, in mode M_i, the state with n photons will have a probability ~ exp $(-h\nu_i \cdot n/kT)$. Normalizing the probabilities, we find for $<E_i>$, the average energy content of mode M_i

$$<E_i> = \frac{\sum_{n>o} nh\nu_i \exp(-h\nu_i \cdot n/kT)}{\sum_{n\geq 0} \exp(-h\nu_i \cdot n/kT)} = \frac{\nu_i\ h\nu_i}{\exp(h\nu_i/kT)-1} \qquad (3.2)$$

4) This is of course a special case of Bohr's famous "complementarity principle": number of quanta and wave phase are complementary quantities.

This expression has to be multiplied by the number of modes in a small frequency interval $\Delta\nu$ and divided by the volume V of the cavity in order to obtain ρ_ν, the energy density of black-body radiation in the frequency interval $\Delta\nu$. Since the first factor is $\frac{8\pi V\nu^2}{c^3}\ \Delta\nu$ [5], the result is

$$\rho_\nu \Delta\nu = \frac{8\pi h\nu^3}{c^3}\ [\exp h\nu/kT - 1]^{-1}\ \Delta\nu\,[J/m^3Hz] \qquad (3.3)$$

(Planck's formula. c = vacuum velocity of light = 2.9978×10^8m/s)

The energy flux F_ν into the solid angle 1 seen through a small hole (as in Figure 1) will be[5]

$$F_\nu \Delta\nu = \frac{c}{4\pi}\ \rho_\nu \Delta\nu = \frac{2h\nu^3}{c^2}\ [\exp h\nu/kT - 1]^{-1}\ \Delta\nu\,[J/m^2 sHz]\ . \qquad (3.4)$$

If we want to know the total energy density ρ and the flux F, (3.3) and (3.4) respectively have to be integrated over ν. Using the formula

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \pi^4/15 \qquad (3.5)$$

we obtain

$$\rho = \frac{8\pi^5}{15}\ \frac{k^4}{c^3h^3}\ T^4 \qquad [J/m^3]$$

$$F = \frac{2\pi^4}{15}\ \frac{k^4}{c^2h^3}\ T^4 = \sigma' T^4 \qquad [J/m^2 s] \qquad (3.6)$$

$$\sigma' = 1.805 \times 10^{-8} \qquad [J/m^2 sK^4],$$

the Stefan-Boltzmann law.

Note 1: Equations (3.3) - (3.5) cannot be immediately applied to solar radiation levels on earth, just by inserting T_{sun} = 6000 K. First one has to multiply by the solid angle covered by the sun as seen from the earth (approximately 10^{-5}).

5) We count both directions of polarization.

Actually, $T_{sun}:T_{earth} \approx 10^{5/4}:1$, expressing the energy balance of the earth: the same amount of energy is reradiated in all directions as is received out of the angle 10^{-5}.

Note 2: In the derivation of this result (as in any thermodynamic function for free particles) there is a kind of contradiction. The modes are supposed to be independent and uncoupled from each other and the walls (including the heat reservoir), yet they somehow obtained thermal equilibrium with the walls and with each other. To circumvent this difficulty, one introduces a small "coal dust particle" into the cavity which does not disturb the modes significantly, yet, through absorption and re-emission of e.m. radiation achieves equilibrium. Through this "Gedanken-mechanism", the temperature of all the modes are the same.

4. ILLUSTRATION: THE "FIRST APPROXIMATION" PHOTO CELL

We want to apply the above results to the efficiency of a "first order approximation" photocell in contrast to the "zero order" photocell efficiency given in a lecture by Prof. J. Thoma [2] and based purely upon entropy considerations. We recall the physical mechanism of a semi-conductor photocell (Figure 2):

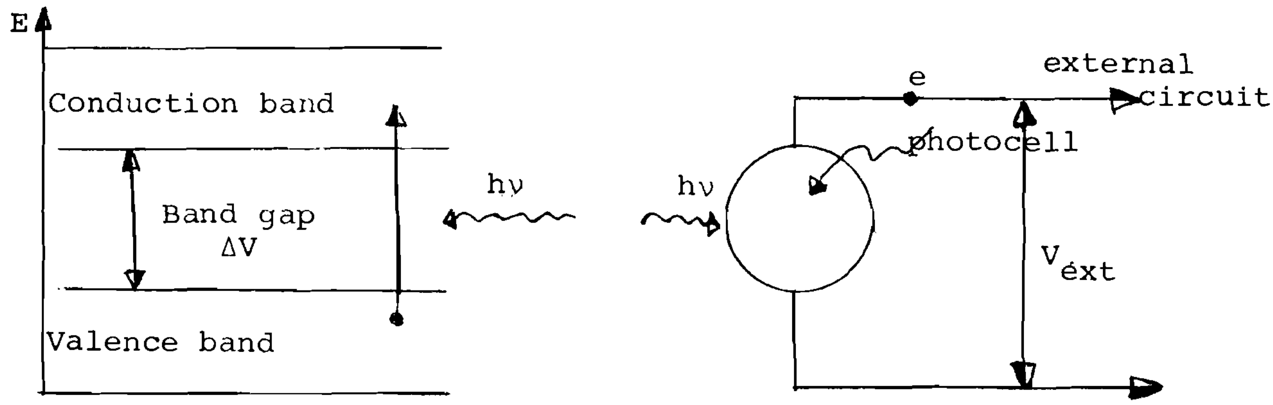

Figure 2.

Owing to the absorption of a photon of energy hν, an electron is raised across the band gap[6] into the conduction band; it is then removed into the external circuit. At the photocell we measure the external voltage $V_{est} \leq \Delta V$; thus one electron contributes eV_{ext} to the energy delivered by the photocell. ($e = 1.6021 \times 10^{-19}$ As). Any photon with energy less than eΔV will not be able to excite an electron; any excess energy (the difference $h\nu - eV_{ext}$) will be converted into lattice oscillations (thermal energy) inside the photocell. We call a "first-order approximation" an ideal photocell for which $V_{ext} = \Delta V$ and all dissipation mechanisms except the two mentioned are non-existent. This means, among other things, a quantum yield of 1 and no losses due to recombination inside the cell, as well as a full valence band. Using bond-graph techniques as described by Thoma [1] we can draw this ideal cell as in Figure 3:

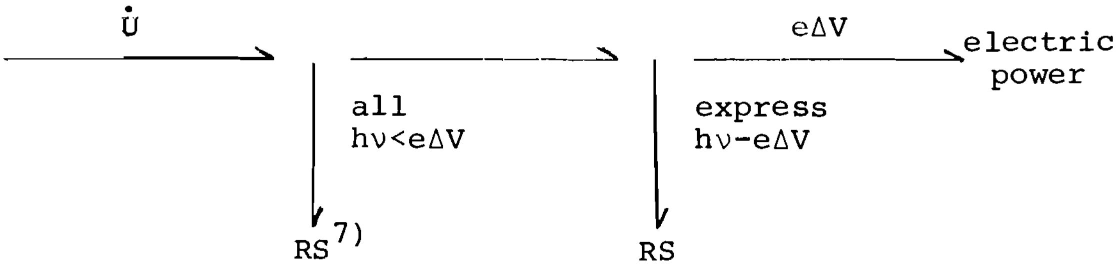

Figure 3.

Using equation (3.4), the "first order efficiency" becomes

$$\eta_1 = \frac{e\Delta\nu \int_{\nu o}^{\infty} F_\nu / h\nu \cdot d\nu}{\int_0^{\infty} F_\nu d\nu} \qquad (\nu o = \frac{e\Delta V}{h})$$

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6) We write the band gap energy as $e \cdot \Delta\nu$ with e the electron charge (1.6021×10^{-19} A·s).

7) Those photons--in the ideal case--will for instance be absorbed by the mountings of the semiconductor crystal.

$$= \frac{e\Delta\nu \int_{\nu o}^{\infty} \nu^2 d\nu\,[e^{h\nu/kT}-1]^{-1} d\nu}{h \int_{0}^{\infty} \nu^3 d\nu\,[e^{h\nu/kT}-1]^{-1} d\nu} \qquad (4.1)$$

$$= \frac{15}{\pi^4}\, x_o \int_{x_o}^{\infty} \frac{x^2}{e^x-1}\, dx \quad \text{with } x_o = \frac{e\Delta V}{kT}$$

for $T = T_{sun}$.

The last integral has been evaluated numerically. By the same technique it is possible to determine the percentages going into the first and second sink of Figure 3. We give a table of results, using as ΔV the band gaps of various semiconductors.

Table

Semiconductor	Ge	Si	InP	GaAs	CdTe	AlSb
band gap [V]	0.67	1.107	1.27	1.35	1.44	1.60
$x_o = \frac{e\Delta V}{kT_{sun}}$	1.296	2.141	2.456	2.611	2.785	3.094
above threshold	93.3%	78.8%	72.5%	69.1%	65.3%	58.6%
efficiency (η_1)	37.3%	43.9%	43.3%	42.6%	41.5%	39.0%
excess energy	56.0%	35.1%	29.2%	26.5%	23.8%	19.6%

5. ENTROPY AND COHERENCE

According to a recurrent statement in thermodynamics, thermal equilibrium is the state with maximum entropy, at a given average total energy. Which property of e.m. radiation is entropy connected to? (What makes black-body radiation "black"?)[8] It

8) The question can be put in the following form: "Imagine the cavity filled with coherent laser light. The introduction of "coal dust" makes the e.m. field approach equilibrium in a non-reversible way, i.e. with increasing entropy. What happens during this process?".

seems to be a natural pitfall to assume that the spectral distribution alone determines the entropy. To understand the real situation we note that the entropy of a system composed of independent uncoupled subsystems is the <u>sum</u> of the entropies of the subsystems. As the modes are independent, no entropy can be contained in the e.m. field that is not already contained in the modes. Black radiation is black because each of its modes is in thermal equilibrium at the same temperature T, i.e. each mode individually is in a state of relatively maximum entropy. As a closer analysis shows, thermal equilibrium of a mode M_i (i.e. it contains n photons of energy $h_{\nu i}$ with a relative weight of $e^{-\frac{nh\nu}{kT}}$) implies total incoherence. The thermodynamic state is composed of states with a definite photon number; not only the averages of $\vec{E}$ and $\vec{B}$ are zero in those states (section 2) but the correlation functions (for instance $\langle\vec{E}(x,t) \cdot \vec{E}(x+\Delta x,t+\Delta t)\rangle$) are significantly different from 0 only for very small Δx and Δt: the "coherence length" is of the same order of magnitude as the wavelength associated with the mode.

The entropy connected with M_i in thermal equilibrium can be calculated as $S_i = -k\sum_j p_j \log p_j$ where p_j is the probability for j photons in mode $M_i = e^{-jh\nu/kT}/(1-e^{-h\nu/kT})$ and k the Boltzmann constant. Using this expression as in (3.3), we obtain

$$s_\nu \Delta\nu = \frac{8\pi\nu^2}{c^3}\left[\frac{h\nu}{T} \cdot (e^{h\nu/kT}-1)^{-1} - k\ln(1-e^{-h\nu/kT})\right] \; [J/m^3HzK], \quad (5.1)$$

the entropy density contained in a frequency interval $\Delta\nu$.

By integrating over ν, the total entropy density and flux are

$$s = \frac{4}{3}\frac{\rho}{T}$$
$$\dot{S} = \frac{4}{3}\frac{F}{T}, \quad (5.2)$$

the "133%" of Prof. Thoma. This factor can also be obtained by thermodynamic reasoning using the fourth power law of Stefan and Boltzmann (equation (3.6).

For an illustration, we contrast thermal radiation with a laser radiating in the cavity. If the laser oscillates in mode M_i, the state of the e.m. field is a coherent superposition (not a stochastic one!) of states with different number of photons in M_i. While photons of thermal radiation are spread over many modes, in laser light they are all collected in one to a few modes: at optical wavelengths (λ=0.7μm and $T=T_{sun}$), the average number of photons in a mode is 0.03 while a typical giant ruby laser pulse of 10 J contains 3.5×10^{19} photons in a few modes. $\langle\vec{E}(x,t)\rangle$ and $\langle\vec{B}((x,t)\rangle$ are not equal to 0 (in fact, they are the solutions of the classical Maxwell equations corresponding to the mode M_i) and the coherence length is macroscopic. (This allows many optical experiments with laser radiation that are impossible with ordinary light sources.) The "thermalization" of laser radiation alluded to in footnote 8) is due to the incoherence of the radiation re-emitted by the coal dust particle. Thus the total energy is not only spread among the modes according to (3.2), but the modes themselves are incoherent.

We illustrate the connection between incoherence and entropy content by a "Gedanken-experiment": a form of energy will be recognized as entropy-free if under ideal conditions we could convert it completely to mechanical energy or electrical D.C. energy. We imagine a "laser oscillating circuit with rectifier" as if we were dealing with microwaves (Figure 4)[9]:

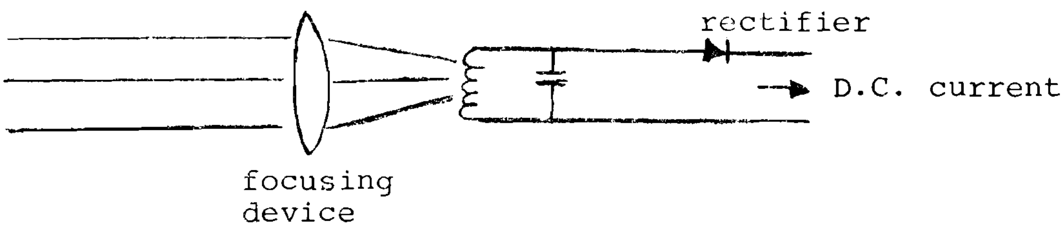

Figure 4.

The oscillating circuit cannot be larger than the wavelength of the incoming light, or it would radiate on its own.

To capture essentially all incoming radiation, it must therefore be possible to focus it onto areas of dimensions of the order of magnitude of the square of the wavelength. Because of diffraction effects, only coherent light can be thus focused.

REFERENCES

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