

# Read The Greats

## On The Theory of the Energy Distribution Law of the Normal Spectrum

by Max Planck - 1900

Sohrab Maleki

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## Preliminaries

### 1 Why and How Do Things Radiate?

Heat is known as the vibration of molecules and Maxwell's electromagnetism theory was well known. Therefore, It was convenient to consider the radiation due to the oscillation of charged particles in basic structure (note that the existence of atoms was still a "hypothesis").

From experience, there are several behaviors of matter in response to external electromagnetic wave:

- Reflection
- Absorption
- No response
- Emit radiation

Physicists could utilize classical physics to justify some of these phenomenon. Metals are usually great reflectors since they possess free electron (it's known from classical electrodynamics boundary-value problem). Electrons inside a metal has a long free-paths so the lattice perturbations affect them much less. These kind of statements suggest that *"good absorbers are also good emitters"*.

A more precise statement is that if a fictitious object absorbs light better than it emits, being in same temperature with it's environment, it gets heated and consequently the environment gets cooler. This obviously violates the

second law of thermodynamics: *"Entropy always increases"*. This was first stated by Kirchhoff. Therefore *"a body emits radiation at a given temperature and frequency exactly as well as it absorbs the same radiation"*.

## 2 Black Body

In general, the intensity and frequency distribution of the emitted waves depend on details of the object itself. To get rid of these variety, as usual, we seek for an idealization. an instance possible choice is to consider a "perfect" absorber and consequently a perfect emitter called *"black body"*. But how to verify the idea experimentally? Well, there's nothing really perfect in reality but there was a convenient suggestion made by Kirchhoff in 1859: a small hole in the side of a large box is an excellent absorber, since any radiation that goes through the hole bounces around inside, a lot getting absorbed on each bounce, and has little chance of ever getting out again. So, we can do this in reverse: have an oven with a tiny hole in the side, and presumably the radiation coming out the hole is as good a representation of a perfect emitter as we're going to find.

Kirchhoff challenged theorists and experimentalists to figure out and measure (respectively) the energy/frequency curve for this "cavity radiation", as he called it. In fact, it was Kirchhoff's challenge in 1859 that led directly to quantum theory forty years later!

## 3 What Was Observed?

**Stefan's Law (1879):** The total power radiated per unit area from a black body at temperature  $T$ , is proportional to  $T^4$ :

$$P = \sigma T^4 \text{ where } \sigma = 5.67 \times 10^{-8} \frac{W}{m^2 \cdot K}$$

**P.S:** Five years later, in 1884, Boltzmann derived this  $T^4$  behavior from theory: he applied classical thermodynamic reasoning to a box filled with electromagnetic radiation, using Maxwell's equations to relate pressure to energy density. (The tiny amount of energy coming out of the hole would of course have the same temperature dependence as the radiation intensity inside.)

**Wien's Displacement Law (1893):** As the oven temperature varies, so does the frequency at which the emitted radiation is most intense. In fact, that frequency is directly proportional to the absolute temperature:

$$f_{\max} \propto T$$

(Wien himself deduced this law theoretically in 1893, following Boltzmann's thermodynamic reasoning. It had previously been observed, at least semi-quantitatively, by an American astronomer, Langley.)

This shift in the frequency at which radiant power is a maximum is very important for harnessing solar energy, such as in a greenhouse. The glass must allow the solar radiation in, but not let the heat radiation out. This is feasible because the two radiations are in very different frequency ranges — 5700K and, say, 300K — and there are materials transparent to light but opaque to infrared radiation. Greenhouses only work because  $f_{\text{max}}$  varies with temperature.

## 4 More Accurate Observations

By the 1890's, experimental techniques had improved sufficiently that it was possible to make fairly precise measurements of the energy distribution in this cavity radiation, or as we shall call it black body radiation. In 1895, at the University of Berlin, Wien and Lummer punched a small hole in the side of an otherwise completely closed oven, and began to measure the radiation coming out.

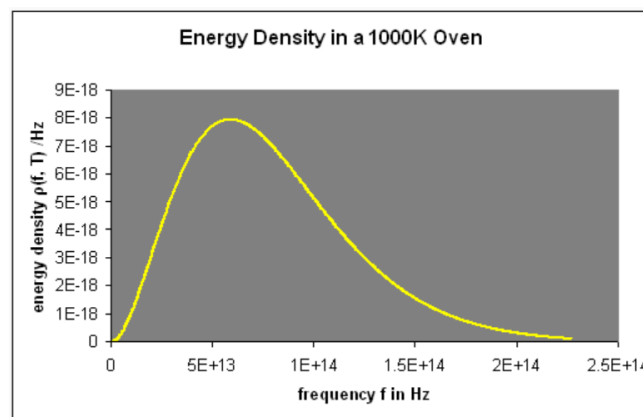


Figure 1: BBR experimental result (correct one)

They were also able to confirm both Stefan's Law  $P=T^4$  and Wien's Displacement Law by measuring the black body curves at different temperatures, for example:

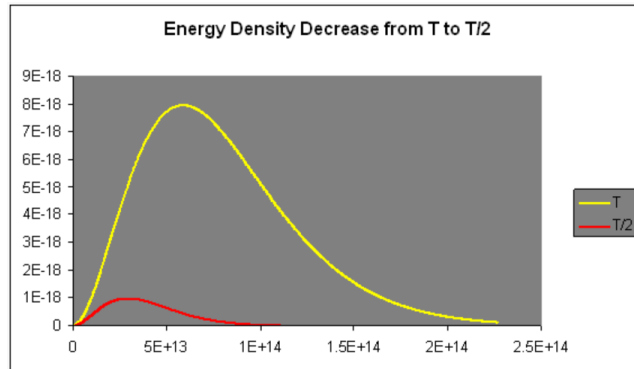


Figure 2: Wien's displacement law verification

## Planck's Story

### 5 Wien's Law

Wien proved using classical thermodynamics that the shape of the black body curve didn't change with temperature, the curve just grew and expanded. However, the thermodynamic methods didn't specify the actual shape. In 1893, Wien made a guess, based on the experimental data:

$$\rho(f) = \alpha f^3 e^{-\beta f/T}$$

his Radiation Law.  $\alpha, \beta$  are constants. In fact, this provided an excellent fit at that time.

### 6 Planck's Thermodynamics

Since (as Kirchhoff mentioned) BBR density doesn't depend on the shape and size of the object, Planck decided to consider the simplest possible material object that would interact with radiation: as always, it was "*simple harmonic oscillator*". Equations of motion are then

$$m\ddot{x} + m\omega_0^2 x - (2e^2/3c^3)\ddot{x} = eE \cos \omega t$$

Planck took  $\ddot{x} = -\omega^2 \dot{x}$ . He solved it to find the energy in the oscillator in terms of the strength of the driving field. Planck next replaced the single driving field by the incoherent field of radiation in an oven in equilibrium at temperature.

He was able to establish from his analysis (see the notes) an important correspondence between the wall oscillator's mean energy  $U(f, T)$  and the energy density  $\rho(f, T)$  per unit frequency in the radiation field:

$$\rho(f, T) = \frac{8\pi}{c^3} f^2 U(f, T)$$

It's worth emphasizing that this is a **classical** result: the only inputs are classical dynamics, and Maxwell's electromagnetic theory. Notice that the charge  $e$  of the oscillator doesn't appear: the result is independent of the coupling strength between the oscillator and the radiation, the coupling only has to be strong enough to ensure thermal equilibrium.

## 7 Planck Focuses on Entropy

Planck utilizes the Wien's law to find the energy of an oscillator:

$$\rho(f) = \alpha f^3 e^{-\beta f/T} = \frac{8\pi}{c^3} f^2 U(f, T)$$

$$U = \frac{\alpha c^3}{8\pi} f e^{-\beta f/T}$$

Finding the entropy through  $dS = dU/T$ :

$$S = -\frac{U}{\beta f} \left( \ln \left( \frac{8\pi U}{\alpha f c^3} \right) - 1 \right)$$

Taking the second derivative of  $S$  with respect to  $U$ :

$$\frac{\partial^2 S}{\partial U^2} = -\frac{1}{\beta f U}$$

guaranteed to be negative! He was impressed by this simplicity, and thought he must be close to a deep thermodynamic truth. He went on to argue that this indicated the Second Law plus Wein's displacement law most likely determined the black body curve uniquely. He was wrong.

Of course, it had been well known for years that statistical mechanics applied to an oscillator gives it energy  $kT$ . Why Planck didn't even mention this is a total mystery. He was familiar with Boltzmann's work, but he really didn't care for statistical mechanics. He was an old-fashioned thermodynamics guy.

## 8 Further Experiments

In October 1900, Rubens and Kurlbaum in Berlin announced some new experimental findings: the radiation intensity at low frequencies went as  $f^2$ , not

$f^3$ , and **the low frequency intensity was proportional to the temperature**.

This shook Planck. His simple result for an oscillator, was still very close to the truth for high frequencies, but at low frequencies equipartition was holding, the oscillator energy being  $U = kT$ . Together with  $dU = TdS$ , this gave immediately  $\partial^2 S / \partial U^2 = -k/U^2$ .

This certainly meant that his previous argument that the curve was uniquely determined by  $\partial^2 S / \partial U^2 = -1/\beta f$   $U$  had to be wrong. Abandoning thoughts of deep thermodynamic truths, he decided he'd better patch things up as best he could. How do you get from  $\partial^2 S / \partial U^2 = -k/U^2$  at low frequencies to  $\partial^2 S / \partial U^2 = -1/\beta f$   $U$  at high frequencies? Well, there's one simple way:

$$\frac{\partial^2 S}{\partial U^2} = -\frac{k}{U(hf + U)}$$

This was of course a completely unjustified guess. But pressing on, integrating twice gives the entropy:

$$S = k [(1 + U/hf) \ln(1 + U/hf) - (U/hf) \ln(U/hf)]$$

from which

$$\frac{\partial S}{\partial U} = \frac{k}{hf} \left[ \ln\left(1 + \frac{U}{hf}\right) - \ln\left(\frac{U}{hf}\right) \right] = \frac{1}{T}$$

giving

$$U = \frac{hf}{e^{hf/kT} - 1}$$

This yields the radiation curve:

$$\rho(f, T) = \frac{8\pi f^2}{c^3} \frac{hf}{e^{hf/kT} - 1}$$

This worked brilliantly! Of course, it matched Wien's formula for high frequencies, and was proportional to  $T$  at low frequencies. But it turned out to be far better: it matched the new high precision measurements within their tiny limits of error, throughout the entire range.

## 9 Birth of Quantum Mechanics

This surprisingly good news had Planck desperately searching for some theoretical justification! As always, he focused on his formula for the entropy:

$$S = k [(1 + U/hf) \ln(1 + U/hf) - (U/hf) \ln(U/hf)]$$

In the language of statistical mechanics:

$$\ln \Omega = [(1 + U/hf) \ln(1 + U/hf) - (U/hf) \ln(U/hf)]$$

The possible different arrangements of the  $N$  oscillators amount to: How many different ways can total energy  $NU$  be shared among the  $N$  oscillators? This is the total phase space that  $W$  measures. In fact, Planck realized, probably remembering Boltzmann's work, that his expression for  $W$  (above) closely resembles a well-known combinatorial expression: how many ways can  $M$  objects be distributed among  $N$  boxes, if we assume the objects are all identical? The answer is

$$\Omega' = \frac{(N + M - 1)!}{M!(N - 1)!}$$

Where using Stirling formula we have:

$$\ln(\Omega') = N [(1 + M/N) \ln(1 + M/N) - (M/N) \ln(M/N)]$$

And, staring first at this formula (or just remembering it?) and then at his expression for  $\Omega$ , it dawned on Planck that they are identical:  $\Omega = \Omega'$ , provided

$$\frac{U}{hf} = \frac{M}{N} \text{ or } NU = Mhf$$

That is to say, the total energy  $NU$  of Planck's array of  $N$  identical oscillators of frequency  $f$  is  $Mhf$ , and the entropy expression tells us this energy is distributed among the oscillators in discrete chunks each of size  $hf$ .

Planck did this work by December 1900, in two intense months after learning the new experimental results and feeling he had to justify his curve that fit so well. But he only half believed it. After all, the first part of his derivation, identifying the energy of an oscillator with that in the radiation field, was purely classical: he'd assumed the emission and absorption of energy to be continuous. Then, he suddenly changed the story, moving to a totally nonclassical concept, that the oscillators could only gain and lose energy in chunks, or quanta. (Incidentally, it didn't occur to him that the radiation itself might be in quanta: he saw this quantization purely as a property of the wall oscillators.) As a result, although the exactness of his curve was widely admired, and it was the Birth of the Quantum Theory (with hindsight), no-one — including Planck — grasped this for several years!

## References

- [1] Max Planck, *On an Improvement of Wien's Equation for the Spectrum*. University of Berlin, 1900.
- [2] Max Planck, *On the Theory of the Energy Distribution Law of the Normal Spectrum*. University of Berlin, 1900.
- [3] Michael Fowler, *Planck's Route to the Black Body Radiation Formula and Quantization*. University of Virginia.
- [4] Michael Fowler, *Black Body Radiation*. University of Virginia.