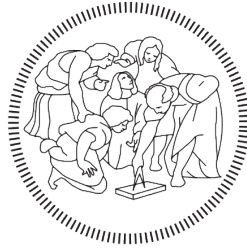POLITECNICO DI MILANO
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PLANCK: FROM THE CONCEPT
OF ENTROPY TO QUANTIZATION

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Contents

1 Introduction

During the past century many different physical discoveries and important steps have been made by scientists and physicists. Some problems have been easily resolved, while some others still remain unknown. One of the most challenging one has surely been the Black-Body problem; physicists took many years and proposed different theories before getting an actual description of the problem that did not falsify other universal physics laws.
The aim of this work is to present the steps that scientists, and in particular the pioneer of the Black-Body radiation theory Max Planck, followed to achieve what we all nowadays know.

In this work the first thing presented is the concept of Entropy, introduced in 1865 by Rudolf Julius Emanuel Clausius, a German physicist and mathematician who lived between the first and second part of the nineteenth century. Then the Planck's version of the second law of thermodynamics is discussed through the important statements that Planck himself made about thermodynamics. After that the Wien's displacement law introduced in 1892 is stated, explaining even the contribute made by Kirchhoff and Boltzmann. The main part of this work than focuses the attention on the use of combinatorials by Planck thanks to his statistical and thermodynamics knowledge. In the last part, it is described how he achieved the famous Planck's distribution law focusing in particular on the concept of discontinuity and quantization.

2 Planck and Thermodynamics

Thermodynamics played a central role in Planck's entire life as it was a relative novelty when he first encountered it in the 1870s. In 1824, in fact, Sadi Carnot derived some theorems concerning heat engines from the hypothesis that heat is a caloric fluid which does work as it passes from a higher to a lower temperature source. Any discovery or law we are going to introduce in this chapter was used by Planck to achieve his aim.

2.1 First Law of Thermodynamics

In 1850 Clausius made modifications over Carnot's assumptions and published his theory. The key point can be summarized in the following statement: heat can be converted into work and work can be converted back to heat. Moreover, Clausius introduced a new term that sums up the combination of interior heat and interior work: internal energy. Let's consider an ideal system with adiabatic walls in equilibrium with the environment; the internal energy therefore takes into account all the different types of energies the system owns, such as kinetic energy, potential energy and so on. This is why the internal energy is such an important tool to use. In 1865 the German mathematician introduced his version of the first law of thermodynamics

$$\Delta U = Q - W \tag{1}$$

where ΔU is the change in internal energy, Q the heat being absorbed or released by the system and W the work done by the system during the transformation. The first law of thermodynamics basically describes the conservation of energy in an isolated system.

2.2 The Concept of Entropy

Sadi Carnot (1796-1832) was one of the first scientists to approach thermodynamics at the beginning of the nineteenth century. At that time the new technology of steam was arising and for this reason everyone was giving attention to this topic. In particular, Carnot had to deal with the transfer of heat between systems. In 1850 a German scientist, Rudolf Clausius, using the first law of thermodynamics - thus the conservation of energy - and further analysis on Carnot's theorems, stated that heat cannot itself pass from a colder to a warmer body while the rest of the universe remains unchanged. In fact, the primary thermodynamics systems considered by Clausius were always in thermal and mechanical interaction with the environment: this is the fundamental condition that ensure his principle to be valid in any portion of the universe. After that, Clausius studied what happens to such systems when they are carried through a closed cycle. In 1854 he came up with his principle in the form

$$\oint \frac{dQ}{T} \leq 0 \tag{2}$$

where dQ is the quantity of heat absorbed and released by the system from its environment and T is the absolute temperature of the system. The equality sign applies only if the cycle is reversible. At that point Clausius considered relation (2) when such systems had to be carried through closed cycles. Finally, in 1865 he introduced both the symbol S and the name entropy for the value of that integral

$$S_B - S_A = \int_A^B \frac{dQ}{T} \tag{3}$$

where the path from configuration A to configuration B must be reversible.

Applying the second law of thermodynamics Clausius demonstrated that entropy must be a single-valued function of a system's configuration. We conclude with Clausius's derivations by showing in summary his version of the two laws of thermodynamics:

1 The total energy of the universe is constant;

2 The entropy of the universe tends to a maximum.

Thanks to these achievements, Planck was able to explain how the entropy changes by itself in thermal and mechanical isolation from its environment with time as the corresponding system developed. Subsequently, in 1887, Planck presented the enunciation of his version of the second law: the principle of the increase of entropy

$$S' - S \geq 0 \tag{4}$$

where S' is the entropy after the system has changed and S the entropy before the transformation. Though recognizing its mathematical equivalence to Clausius's form, there still are three differences:

1 Just as the Clausius's form governed the behavior of energy over time, so the Planck's version governed that of entropy.

2 Planck's version highlighted their decisive difference: the total energy of an isolated system must remain constant over time; its entropy can only increase or, in the ideal limiting case, remain constant.

3 Planck's version prohibited not simply the spontaneous passage of heat from a lower to a higher temperature but any process which would decrease the entropy of an isolated system.

Since Planck considered the Black-Body problem a case of thermal equilibrium, he looked for a solution corresponding to a maximum of entropy; in fact, as entropy increases in time, a system at its equilibrium has the maximum value of entropy. In order to go on with our treatment, we still need to introduce some key concepts that helped Planck to reach his aim.

3 Wien's displacement law and The Black-Body problem

Since the Wien's displacement law derives from Kirchhoff radiation law and Boltzmann radiation arguments in 1892, we need to have introduce these two laws in order to better understand what comes later.

3.1 The Kirchhoff's Law

In 1859 Kirchhoff announced his theorem about the thermal radiation of a body. Let's consider $d\sigma$ as an element of the interior surface of the wall of an arbitrary cavity and let $a_\lambda(T)$ be the fraction of the incident energy with wavelength between λ and $\lambda + d\lambda$ absorbed by that element when the cavity is maintained at temperature T. The rate at which energy in that range is absorbed by $d\sigma$ is then $\pi a_\lambda K_\lambda d\sigma$, where the factor π has been introduced by an integration over $d\Omega$. In the same way, let $\pi e_\lambda(T) d\sigma$ be the rate at which energy in the same range is radiated into the cavity from $d\sigma$. Obviously, in order to reach the equilibrium condition, total emission and absorption must be equal, or $\int_0^\infty a_\lambda K_\lambda d\lambda = \int_0^\infty e_\lambda d\lambda$.

Kirchhoff managed to show, by considering a cavity made by different materials, that the equality of emitted and absorbed energy must also apply separately to each infinitesimal wavelength range, so that $a_\lambda K_\lambda = e_\lambda$. Moreover, since K_λ is constant in all the cavity walls, the ratio of e_λ to a_λ must be the same for all materials, eventhough those materials could emit and absorb in a different way.

Those results led Kirchhoff to state his radiation law:

$$\frac{e_\lambda}{a_\lambda} = K_\lambda(T) \tag{5}$$

where the intensity distribution K_λ is a universal function that does not depend on the size or shape of the cavity or on the material of its walls but only depends by the temperature and the wavelength. For a cavity with black walls, $a_\lambda = 1$ because the radiation is fully absorbed and $e_\lambda = K_\lambda$. The radiation emitted by a black body is therefore identical, in its intensity distribution, to the equilibrium radiation contained in a cavity of any material for which $a_\lambda \neq 0$ at all wavelengths. This result was very important because if someone managed to know the emission power e_λ of the Black-body under these conditions he directly achieved the evaluation of the universal function $K_\lambda(T)$.

3.2 The Stefan-Boltzmann's Law

In 1884 Ludwig Boltzmann stated that for equilibrium the net flux of energy across the surface of any volume in a cavity's interior must be zero, and this

condition is satisfied only when the density u of radiant energy was related to its intensity K by the equation

$$u = \frac{4\pi K}{c} \tag{6}$$

where c is the velocity of propagation.

In 1879 Josef Stefan, after some experimental results he managed to achieve himself, proposed an equation that relates the energy density of black radiation and the cavity temperature

$$u = \sigma T^4 \tag{7}$$

were σ is a universal constant. The last expression is also known as the Stefan-Boltzmann law. Less than ten years later Wilhelm Wien used these results to derive a fundamental property of the distribution functions u_λ and K_λ in case of equilibrium. Wien's result is called displacement law because it shows how the curve for u_λ is displaced as the temperature of a cavity changes. It takes the following form

$$u_\lambda = \frac{4\pi}{c} K_\lambda = \lambda^{-5} \phi\left(\lambda T\right) \tag{8}$$

where σ is an arbitrary function of a single variable.

In 1887, W.A. Michelson combined the Stefan Boltzmann law with a statistical hypothesis about the mechanism of emission to derive the radiation formula

$$K_\lambda = b\lambda^2 e^{hT - \left(\frac{a}{\lambda^2 T^2}\right)} \tag{9}$$

where a,b and h are three disposable constants. Finally, the Wien's displacement law takes the form

$$K_\lambda = b\lambda^{-5} e^{-\frac{a}{\lambda T}} \tag{10}$$

Both the previous laws were already discovered when Planck first started to work on the Black-Body problem in 1894. The results we have presented in this section helped Planck to better understand the physics behind the Black-Body radiation and provided a starting point to his work a few years later.

4 Planck's Distribution Law

4.1 Derivations

Let's return to the concept that a distribution function would be one that maximize the total entropy of the radiation in the cavity. Planck tried to understand what was the relation between the entropy and the energy; he asked himself what characteristic the function $S(U)$ must have if it has to possess a local maximum.

For this purpose he imagined a system full of resonators initially in equilibrium and displaced from it by adding a small extra energy ΔU to one of them. The system will subsequently return by itself to equilibrium; the transition, Planck shows, is governed by a manipulated form of his "fundamental equation", which describes the relation between the energy of the resonator and the actual field intensity. The expression is:

$$\frac{dU}{dt} + 2\sigma\nu\Delta U = 0 \tag{11}$$

where ν is the frequency of the resonator, U the total resonator energy, and σ is the damping constant of the resonator.

Further manipulation, using relationships between energy and field strength, leads to an equation for the change in total entropy dS_t, in a time interval dt during the system's return to equilibrium

$$dS_t = dU\Delta U\frac{3}{5}\left(\frac{\partial^2 S}{\partial U^2}\right)_0 \tag{12}$$

where dU is the change in resonator energy during time dt.

Since by equation (11) dU and ΔU must have opposite sign, dS_t will be positive and the equilibrium position must be a local maximum provided that

$$\frac{3}{5}\left(\frac{\partial^2 S}{\partial U^2}\right) = -f(U) \tag{13}$$

where $f(U)$ is any positive function of U.

Suppose now that instead of displacing a single resonator from equilibrium by an amount ΔU, we displace n of them by that amount, so that the total displacement of the energy of the system would be $\Delta U' = n\Delta U$. Since the entropy is additive, the corresponding change is dS_t should be $dS_t' = ndS_t$. Making the assumption that the total resonator entropy S' depends on the total resonator energy U' in the same way that the entropy S of a single resonator depends on its energy U, we must have:

$$dS_t' = -dU'\Delta U'f(U') = -n^2 dU\Delta U f(nU) = ndS_t = -ndU\Delta U f(U) \tag{14}$$

or

$$f(nU) = \frac{1}{n}f(U) \tag{15}$$

Equation (15) is satisfied only when $f(U)$ is proportional to $\frac{1}{U}$ or when

$$\frac{\partial^2 S}{\partial U^2} = -\frac{\alpha}{U} \tag{16}$$

where α is an opportune constant. From the last equation, the standard relation

$$\frac{\partial S}{\partial U} = \frac{1}{T}, \tag{17}$$

the displacement law previously introduced and the Wien distribution law, the expression for resonator entropy can be derived.

Despite the fact that for Planck everything seemed good, the Wien-Planck distribution law still did not represent the measurements on black radiation in the full spectrum. In September 1900 Planck was aware of this problem and made the assumption that the entropy of n oscillators must depend not only on their total energy U', but also on the energy U of a single oscillator. This leads to replace the term $-\frac{\alpha}{U}$ in equation (16) with a term that yield S as a logarithmic function of U.

Therefore, the new form follows directly by addition of a term proportional to U^2 and we obtain:

$$\frac{\partial^2 S}{\partial U^2} = -\frac{\alpha}{U(\beta + U)} \tag{18}$$

This step was made by Planck thanks to his knowledge about Boltzmann's results on probability theory, as we will further discuss in section 5.1. With equation (17) and equation (18), two integrations and the application of the displacement law we obtain the distribution law

$$K_\lambda = \frac{C\lambda^{-5}}{e^{\frac{c}{\lambda T}} - 1} \tag{19}$$

where K_λ is the energy intensity distribution, λ is the wavelength of the radiation, T the temperature, c the velocity of light propagation and C a proper constant. Equation (19) can be rewritten to make the average energy resonator in function of frequency ν and temperature T

$$U_\nu = \frac{b\nu}{e^{\frac{a\nu}{T}} - 1} \tag{20}$$

with a and b suitable constants. Forward manipulations showed that entropy is maximized only if $U'_\nu s$ are governed by the following expression

$$U_\nu = \frac{h\nu}{e^{\mu h\nu} - 1} \tag{21}$$

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where we substituted $b = h$ and $\mu h T = a$. Moreover, μ can be evaluated by applying the standard relation

$$\frac{\partial S_{E_0}}{\partial E_0} = \frac{\frac{\partial S_{E_0}}{\partial \mu}}{\frac{\partial E_0}{\partial \mu}} = \frac{1}{T} \tag{22}$$

which gives $\mu = \frac{1}{kT}$ that put into equation (21) gives

$$U_\nu = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \tag{23}$$

Finally the corresponding distribution for the field, $u_\nu = (8\pi\nu^2/c^3)U_\nu$ satisfies the displacement law so that we obtain the final density of radial energy distribution function or Planck distribution law

$$u_\nu = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} \tag{24}$$

4.2 Recourse to Combinatorials

As it should be clear so far for the reader, Planck assumed the second principle of thermodynamics as a fundamental condition for his treatment. Moreover, he made the assumption that the entropy of a physical system in a definite state depends only on the probability of the state. Hence

$$S = f(W) \tag{25}$$

where W has to be considered as a "thermodynamics probability". Equation (20) can be manipulated to yield $\frac{1}{T}$ as a function of U and ν, taking into account that $\frac{\partial S}{\partial U} = \frac{1}{T}$. One integration thus gives:

$$S = \frac{b}{a} log \left[\frac{(1 + \frac{U}{b\nu})^{1 + \frac{U}{b\nu}}}{(\frac{U}{b\nu})^{\frac{U}{b\nu}}} \right] + \text{constant} \tag{26}$$

That formula for entropy is the one for which Planck was looking for, thus the universal function with argument W, that is the same argument of the logarithm in expression (26). This result had been obtained by Planck by using Boltzmann's expression for the logarithmic relation between entropy and probability. Equation (26), however, applies only to a single resonator with average energy U in equilibrium with a radiation field. It is, therefore, not yet suitable for interpretation in probabilistic terms, as it takes into account only one single item. Planck's attempt to reformulate it may well have constituted an early stage of "the most strenuous work" of his life.

Imagine n independent resonators of frequency ν in equilibrium with their radiation field. Their total entropy must be N times that given by equation (26), and their total energy must, since all have the same average energy over time by NU. If combinatorial are to be introduced, that total energy must be subdivided into P elements of size ϵ, so that $P_\epsilon = NU$. Multiplying equation (26) by N and substituting $\frac{P_\epsilon}{U}$ for U yields:

$$S = \frac{b}{a} log \left[\frac{(N + \frac{P_\epsilon}{b\nu})^{N + \frac{P_\epsilon}{b\nu}}}{N^N (\frac{P_\epsilon}{b\nu})^{\frac{P_\epsilon}{b\nu}}} \right] + \text{constant} \tag{27}$$

Last equation yields to the entropy due to a number of resonators, so that the probability corresponding to the equilibrium case should be proportional to the expression in square brackets on its right-hand side.

To obtain an expression involving only integers, the size of the energy element ϵ must be set equal to $b\nu$. The quantity in square brackets then reduces to $\frac{(N+P)^{N+P}}{N^N P^P}$, an expression for which Planck in his published papers adopts the special symbol R. For larger N and P, the preceding expression for R may be written:

$$R = \frac{(N + P - 1)!}{(N - 1)! P!} \tag{28}$$

That equation is the standard expression for the number of ways in which P indistinguishable elements can be distributed over N distinguishable boxes. Where W is, according to Planck, "the combinations with repetitions of N elements taken P at a time".

What sort of probability is Equation (28)? Planck says, "The number of all complexions which are possible with a given distribution in space we equate to the thermodynamics probability W of the space distribution". Planck used the term "probability" with the meaning of "number of permutability" or, much more often, to indicate proportional to probability. In December 1900, Planck used Boltzmann's results, especially his 1877 paper, and said that by introducing probability considerations, he could derive an expression for the entropy of a resonator. He argued that the entropy of a system of resonators with given energy is proportional to the logarithm of the total number of possible complexions. This is what we are going to talk about in the next section.

5 Probability and Quantization

We have already stated that the second principle of thermodynamics played a central role in Planck treatment; actually, it was the funding condition for solving the Black-Body problem. Furthermore, he reached the fundamental proposition that states: "*The entropy of a physical system in a definite state depends solely on the probability of this state*". In order to better understand that statement, we need to explain in further details where his knowledge about probability came from.

Moreover, one point is still not clear so far: what made Planck think about a logarithmic expression that relates the entropy S with the energy resonator U as expressed in equation (26)? In order to answer to this question, we need to introduce the model stated by Boltzmann in 1877 that recovers the most probable state of a system in function of the energy of the state, thus the probability of the state.

5.1 Boltzmann Theory of Probability

Boltzmann starts his treatment suggesting a collection of n molecules with energy $k\epsilon$ of finite value: 0, ϵ, 2ϵ, 3ϵ, ... , $p\epsilon$ where $p\epsilon$ is the total available energy. If ω_k is the number of molecules in the collection with energy k, then the set numbers: ω_0, ω_1, ... , ω_p is sufficient to define a particular state of the gas. Since individual molecules are, for Boltzmann, distinguishable, a state can be achieved in various ways, each of which is called complexion by Boltzmann. Each complexion was assumed then equally probable and the more generally for a complexion of n molecules a second complexion can be achieved by any permutation of two molecules which have different energies. The number of such permutations is a known combinatorial techniques:

$$Z = \frac{n!}{(\omega_0!)(\omega_1!)...(\omega_n!)} \tag{29}$$

where Z is the permutability and not the probability. The most probable state will be the one for which Z is largest, so it can be determined by maximizing Z subject to the two constrains:

$$\sum_{k=0}^{p} \omega_k = n \tag{30a}$$

$$\sum_{k=0}^{p} k\omega_k = p \tag{30b}$$

Since n is fixed, this problem is equivalent to minimizing the denominator of equation (29) which is equivalent to minimizing its logarithm. Boltzmann there-

fore seeks the minimum of:

$$X = \sum_{k=0}^{p} log[(\omega k)!] \tag{31}$$

a formula which can, for large values of ωk, be rewritten by a standard approximation now called Stirling's formula. The quantity to be minimized then becomes

$$X' = \sum_{k=0}^{p} \omega k log(\omega k) \tag{32}$$

Where X' differs from X by a constant which has no effect on the location of the minimum. Standard variational techniques led directly to the conclusion that, for $p \gg n$, Z will be the maximum if the ω_k's are given by

$$\omega_k = \frac{n\epsilon}{\mu} e^{\frac{-k\epsilon}{\mu}} \tag{33}$$

where μ is the average energy of a molecule. Equation (33) specifies the most probable energy distribution, which is what Boltzmann was looking for.

Despite the fact that, as we have just seen, the logarithmic connection between entropy and probability was first discovered by Boltzmann, equation (27) differs from the one he discovered in an essential point. While Boltzmann left an additive constant undetermined, Planck managed to assign a definite value to the entropy S. This important step led to two fundamental consequences: first, the hypothesis of quanta came up and second it led Planck to make a definite law of distribution of energy of black body radiation.

Moreover, Planck considered that the connection between entropy and probability - that now should be more clear - of a state had also to be defined in order to obtain a posteriori justification of the introduction of energy quanta, which is the last argument we are going to talk about in our work.

5.2   Quantization of Energy

During his entire career Max Planck considered mechanics and in particular Maxwell's electromagnetic theory - which was almost universally accepted - a model science. The assumption that the energy had to be divided into elements of finite size actually provided a physical controversy. In fact, Maxwell's theory offered no place for the introduction of discrete values of energies. Planck was aware of this problem, eventhough he published nothing about it before he became involved with the special theory of relativity after 1905. Moreover, until that time neither the law nor its derivation provided a basis for a claim to fundamental innovation in physics.

In order to recover the entropy of an arbitrary distribution Planck, as we have already seen in part 4.2, had to introduce combinatorials and for this purpose he followed Boltzmann in subdividing the energy continuum into elements of finite size. For his purpose, the size of the energy elements ϵ, ϵ', ϵ'', etc., for reasons that will not be considered in this paper, must be proportional to the frequency ν.

Hence Planck stated:"*Let's consider the distribution of energy E over the N resonators with frequency ν. If E is regarded as infinitely divisible, an infinite number of different distributions is possible. We, however, consider - and this is the essential point - E to be composed of a determinate number of equal finite parts and employ in their determination the natural constant $h = 6.55 \cdot 10^{-27} (erg \cdot sec)$. This constant multiplied by the frequency ν of the resonators gives the energy element ϵ in ergs, and dividing E by ϵ, we obtain the number of P of energy elements to be distributed over the N resonators*".

When Planck first announced his derivation of the Wien Distribution law, he also reported values for the two constants it contained: $a = 4.818 \cdot 10^{-11} deg \cdot sec$; $b = 6.885 \cdot 10^{-27} erg \cdot sec$. If Planck's law was to coincide with Wien's in the high frequency limit, the value of h would have to be very nearly to that of b, and h/k of a. During his derivations papers, Planck actually never evaluated the energy of a single resonator with an integral multiple of $h\nu$, while he repeatedly uses the expression $U_N = Ph\nu$, with P an integer and U_N the total energy of N resonators. Planck's subdivision of total energy into an integral number of equal finite elements is entirely modeled on Boltzmann's. For this reason, if quantization is the subdivision of total energy into finite parts, then Boltzmann is its author.

From the previous statement one question should naturally arise: why do we associate the quantization of energy to Max Planck and not to its actual author Boltzmann? Actually, the matter is a bit more complicated, in fact despite its generally classical nature, Planck's statistical radiation theory differed from Boltzmann's gas theory presented on his paper in 1877 in one fundamental aspect. For Boltzmann, the subdivision of the energy continuum was just a mathematical device, and the size of the element employed to introduce it had no actual importance. For Planck, that subdivision was a physical necessity, and the size of the element was fixed by the relation that we all know

$$\epsilon = h\nu \tag{34}$$

Early in 1900 Planck described that relation as "the essential point" of his theory, where h had finally become the "quantum of action" or "element of action".

6　Conclusions

Planck's route to his distribution law and later to the idea of quantization of energy has not been easy and clear: he made mistakes, he had many tries and sometimes he did not trust what he found. Moreover, as we have seen, Planck was not the only one that gave his contribution to understand what actually happens behind the thermal radiation process; Wien, Boltzmann, Einstein and many others played a central role, each one of them focusing on a specific topic. Everything we have presented in this paper and in particular the results we have achieved, represent the starting point of an entire new vision of physics that still holds nowadays: the quantum mechanics.

Additionally, following the introduction of the quantization of energy, the concept of "photon" came just after. As we all know in our era - the *Information Era* in which everything is connected by the Internet Traffic - information is transmitted thanks to a technology constituted by bits transported by photons. Both bits and photons share the same origin; thermodynamics and, in particular, one of the main concept of our work: entropy. This is the reason why we decided to focus our attention on the Black-Body problem in the course of *Optical Communications*.

In physics, as well as in other sciences, important discoveries take years or even decades to be found and then proved. Sometimes we do not even obtain a proper result, but this does not mean that what we have done so far has been useless; there will always be someone that will use your work as a starting point for a new physical discovery.

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