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1905, ANNUS MIRABILIS: THE ROOTS OF THE 20TH-CENTURY REVOLUTION IN PHYSICS AND THE TAKE-OFF OF THE QUANTUM THEORY

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RESUMEN

¿Cuál fue la naturaleza y el verdadero papel del annus mirabilis *(1905) en la física? En este trabajo se discuten y analizan históricamente las contribuciones de Planck, y con una conciencia metodológica mucho más clara las de Einstein, como el paso fundamental en las transformaciones científicas que llevaron del enfoque mecanicista y reduccionista de la física del siglo XIX hasta la culminación de la revolución formal de la Mecánica Cuántica. Se estudian dichas transformaciones, con sus sucesivas rupturas, en el contexto de la situación económica y social, así como el papel de la ciencia y la técnica en las mismas. El enfoque mecanicista, dominante en la física a finales del siglo XIX, por un lado generó dificultades y contradicciones, pero sobre todo resultó ser una limitación para el ulterior desarrollo científico. Los químicos fueron los primeros, en aquellos años, en darse cuenta de estas limitaciones e introdujeron un enfoque termodinámico, cuyo papel en la revolución de la física es preciso subrayar. Planck fue el primer físico en introducir un procedimiento que rompía con el mecanicismo, aunque difícilmente se le pueda atribuir el concepto de cuanto como entidad física. Resaltan la capacidad y el papel de Einstein en completar la superación del reduccionismo e introducir una nueva metodología física.*

ABSTRACT

What were the real nature and role of the annus mirabilis, *1905, in Physics? In this paper we discuss in a historical perspective Planck's and Einstein's contributions as the fundamental steps in the scientific transformations (the latter with a sharper sense of methodological awareness) that led from the mechanistic and reductionist approach of 19th century physics to the fulfillment of the formal revolution of quantum mechanics. This process underwent with further scientific breaks, in the context of the social and economic situation and the corresponding role of science. The mechanistic approach adopted in physics at the end of the 19th century not only produced difficulties and contradictions, but resulted in the limitation of further scientific development. Chemists were the first, at that time, to perceive such limits, and introduce a thermodynamic approach, whose role in the revolution in physics must be underlined. Planck was the first physicist to introduce a procedure that broke with mechanism, although he can hardly be attributed with the concept of the* quantum *as a physical quantity. It was Einstein's ability that stands out for his role in overcoming reductionism and introducing a new physical methodology.*

Palabras clave: Física, Mecánica Cuántica, Einstein, siglo XX.

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1. A conceptual and methodological revolution

The crucial importance of the year 1905 for the development of physics with its current concepts and theories, ranging from the infinitely small up to the scale of the universe, is widely acknowledged, as is demonstrated by the choice of 2005 as the «International Year of Physics». As a matter of fact, it opened a process that led to the abandoning of the 19th century world view and the creation of a completely new one. These developments have deeply influenced even common sense, although ordinary people are far from mastering scientific notions, which in fact present difficulties, both from the conceptual and the formal point of view. In our opinion, however, a possible way in which even common people could perceive at least the real purport of this progress, consists in putting the hard physical concepts into the context of the methodological transformations that took place at the turn of the 19th century, the change in attitude of scientists in relation to the (often new) scientific and technical problems they had to solve, the very concept of a scientific «solution» or explanation, all within the framework of deep technological and social changes. Even within the scientific community I [we] think there are but few who have grasped the real nature, purport and role of the specific concepts introduced by Einstein, and above all the profundity of the methodological changes that he fostered. Not only that, but the majority are not even aware of the fact that in 1900 there were not just one, but two papers by Planck on blackbody radiation, or that Einstein in his early papers, between 1902 and 1904, had laid the foundations of *statistical mechanics*, that are commonly attributed to Gibbs. Actually, Einstein's formulation was independent of, but equivalent to, that of Gibbs (so we would have kept this theory in any case), but had greater potentialities, that played a fundamental role in the conceptual and methodological path that led to the ideas of the *annus mirabilis*.

All the more so since the majority of physicists have a simplified and largely distorted idea of the evolution and changes in physics during those years: an idea that they have inherited from counterfeit and *ad hoc* historical reconstructions provided in physics textbooks. These tend to be *a posteriori* rationalizations of the evolution of science, conceived as a purely internal and cumulative process, in which changes are simply rational answers to the problems that arise inside science itself, and objectively reflect the features of the new physical phenomena. So, for instance, the story goes that Planck introduced the *energy quantum* as a reaction to the failure of Rayleigh's formula to explain the black body spectrum. Actually, as we will see, Planck does not even cite Rayleigh. He had originally obtained his formula *without* introducing the quantum, through *purely thermodynamic* reasoning, and the subsequent *discretization* process, introduced as an «act of desperation», can hardly be interpreted as the true introduction of the *quantum* as a physical entity, as it has been interpreted *a posteriori*. Likewise, Einstein's 1905 *light quantum* hypothesis is commonly presented as an extension of Planck's *energy quantum*, deriving from the necessity to explain the frequency threshold of the photoelectric effect. On the contrary, Einstein did not mention either this threshold, nor Planck's hypothesis (just as in the paper on special relativity he did not even mention Michelson and Morley's experiment); he actually introduced the *light quantum* for completely different reasons, and *predicted* that threshold in search of a confirmation of his hypothesis (a confirmation that had to wait for ten years).

In order to understand what happened in concrete terms, we must take into account the fundamental fact that around a century ago economy and society were deeply changing, shaken by a crisis of the nineteenth century order, that was to lead to, but would not even be resolved by, the First World War. In such a tormented process, the mechanistic structure of nineteenth century science and technology showed its limits in the face of new developments and needs. We will see how these changes had already manifested themselves in chemistry in the last decades of the nineteenth century. At the beginning of the twentieth century a radical process came about in physics, through a conceptual and methodological breakthrough, in the very way in which physics was «produced», and a *scientific explanation* was conceived.

The depth of the break introduced by quantum mechanics (QM) in relation to the treatment provided by so-called «classical physics» is really disconcerting. One has to wonder —even though the majority of the scientific community has accepted and use, often in a rather pragmatic way, the so-called «orthodox», or «Copenhagen» formulation of QM— why some of the most eminent founders of the quantum concepts (like Einstein, Schrödinger, de Broglie, to name but the most famous) never did acknowledge it as the final and complete physical theory of the microscopic world. It should be mentioned that initially there was strong ideological opposition against QM in the Soviet Union. A considerable number of physicists, some of them quite authoritative, most of them free by now of the pragmatism and conformity expected at the beginning of their career), are still investigating the «Foundations of QM», thus showing persistent discontent regarding its logical and conceptual foundation. As Planck declared in his *Scientific Autobiography*

> A new scientific truth does not triumph because its opponents are converted and see the light, on the contrary because in the end they die, and a new generation is born to which the new concepts become familiar [PLANCK, 1948, p. 22 Italian transl.]

How did such a breakthrough originate? What was its true nature and purport? What were its stages? I am convinced that, behind and at the basis of the development and formulation of QM, there are some very strong and radical *choices* about the kind of description of phenomena, that is not solely imposed by the nature of the atomic processes. Is not such an impression to be drawn from reading, for instance, the first words of the Introduction to the first edition of Dirac's textbook, *The Principles of Quantum Mechanics*, of 1930?

> The methods of progress in theoretical physics have undergone a vast change during the present century. The classical tradition has been to consider the world to be an association of observable objects (particles, fluids, fields, etc.) moving about according to definite laws of force, *so that one could form a mental picture in space and time of the whole scheme*. This led to a physics whose aim was to make assumptions about the *mechanism* and forces connecting these observable objects, to account for their behaviour in the simplest possible way. It has become increasingly evident in recent times, however, that nature works on a different plan. Her **fundamental laws do not govern the world *as it appears in our mental picture* in any very distinct way**, but instead they control a ***substratum*** **on which *we cannot form a mental picture without introducing irrelevancies***. [...] **The new theories**, if one looks apart from their mathematical setting, **are built up from *physical concepts which cannot be explained in terms of things previously known*** *to the student*, which ***cannot even be explained adequately in words at all***. [the italics are mine] [DIRAC, 1930, Preface, p. V]

Does it not seem that there is here some sort of *a priori choice* about the kind of physical or formal description of physical processes? A choice that leaves out others (which Dirac does mention), that were possible in principle, but were not appropriate for the new purposes of physics. Einstein, as we will see, explicitly denounced these choices. In fact, alternative formulations, or interpretations, have been proposed. I am actually convinced, in absolutely general terms, that in principle more than one theoretical framework may exist which can reproduce, or explain a specific context of phenomena and experimental data (although the consensus of the scientific community on the prevailing one makes an alternative framework quite difficult, especially faced with the increasing use of material and human resources required by modern scientific enterprise. Nevertheless, we will examine at least one concrete example, that of Lorentz): if extraterrestrial, intelligent and highly-developed beings exist, I do not believe that they have explained the same phenomena in the same form or with the same concepts and theories as we have.

The quantum revolution was the final result of a process that went through distinct stages. The change in concepts, methods and planning has been the result of decades of evolution and methodological breakthroughs [BARACCA, LIVI and RUFFO, 1979-80]. The *annus mirabilis* was of fundamental importance in such a process, and in many other fields; but in order to really understand it, one has to place it historically in the framework of the changes in the social and productive environments, in the social role played by science and the scientists, in the internal and external organisation of scientific research, of its cultural and philosophical surroundings. In general, the *production* of science is a social, *committed* process, immersed in the reality, both economic and cultural, of its time. Both the role of science, its organization, its logic and conceptual structure and method, have deeply changed over the different epochs, along with its relationships with technology, social and productive problems, the cultural context. Of course, these changes were not only reflected in science. For instance, can it be fortuitous that in the 20th century also painting, or literary forms moved away from a naive representation of reality? Or that psychoanalysis traced back psychological features and behavior to deep roots, which cannot be reduced to their direct manifestations? Thus, summing up, not only the role and mode of expression of science have changed, but the expression of everything cultural and intellectual.

In fact, the process of formalization and abstraction in Physics went through various steps, whose specific features and reasons can be reconstructed, thereby providing an explanation of these changes. The basic idea of my analysis is that at the turn of the 19th century science was characterized by a *mechanistic setting* which (apart from implying specific contradictions, such as thermodynamic irreversibility, or the electromagnetic «aether wind») proved itself to be a limitation of the potentialities of science. Yet, the endeavour to overcome it actually led to new results and possibilities of focusing and solving, with increasing effectiveness, the problems that arose in connection with the economic and technical development of the *second Industrial Revolution*. It is to this limitation that the roots of the abandonment of concrete physical models can be traced, referred to by Dirac as if it were required only by the physical properties of the atomic systems. The depth of the changes that occurred is confirmed for instance by the harsh clashes between different schools: Planck recalls that at the end of the 19th century

> It was absolutely impossible to be listened against the authority of men such as Ostwald, Helm and Mach. [PLANCK, 1948, p. 20 Ital. transl.]

While Sommerfeld recalls that at the Congress of the *Naturforschergesellshaft* in 1985

> The battle between Boltzmann and Ostwald was much like the duel between a bull and a supple bull-fighter[1] [SOMMERFELD, 1944].

As regards Boltzmann, there is a touching tone of despair in his 1898 Introduction to the second volume of his *Lectures on Gas Theory* (note that in 1906 he committed suicide)

> I am conscious of being only an individual struggling weakly against the stream of time. [BOLTZMANN, 1896-98, in BOLTZMANN, 1964, p. 216].

We will see that such conflicts were actually typical of the environment of the physicists: the chemists, on the contrary, urged by exigencies to solve concrete and very complex problems, were the first to succeed in overcoming mechanism as a general outlook at the end of the 19th century, when in its place they introduced *a basic framework based on thermodynamics*. As for the physicists, the historian of physics Martin Klein analyzed the *fundamental role played by Thermodynamics in the birth of the quantum concepts at the beginning of the 20th century* [KLEIN, 1963, 1965, 1966, 1967].

From the point of view of the connection with society, it is significant that the majority of the above mentioned changes happened in Germany, the country that guided the recasting of technology (or in neighboring countries, such as Austria, Switzerland, or Denmark). Even the names of the eminent physicists testify that up to the end of the 19th century the British and French brought major contributions (Maxwell, Lord Kelvin, Poincaré, and so on), while the birth and development of 20th century theories were due mostly to Central European physicists, with some eminent exceptions, like those of de Broglie, Dirac, Fermi, Slater.

We shall now analyze the phasing of change in the scientific setting, the progression of physical abstraction and formalization, and their roots. It can be worth specifying that with the term *mechanism* we intend the mechanical conception of nature, searching for a reduction of all the physical concepts and disciplines to mechanics.

2. A first change by the middle of the 19th century (1850-1870)

By the middle of the 19th century deep ferments emerged, that prepared a fundamental change in science: let us briefly review the roots of this process which I analyzed in more detail in previous papers [BARACCA, 2002, 2005].

2.1. *Eighteenth century science*

Modern science had developed during the 18th century first industrial revolution in Britain, on the basis of the rejection of the speculative attitude of the previous centuries, adopting instead the methodological principle of basing itself upon experimental quantitative data: such an attitude reflected an initial dependence of science on invention and technical innovation. These features substantially persisted during the first half of the 19th century: a basic assumption of science during this period was in fact *the rejection of any concept or model that were not based* *upon rigorous experimental data*. Such an attitude, though it allowed great scientific progress, actually limited in a substantial way the possibility of reaching radically new fields or knowledge. For instance, although Dalton had already formulated the atomic concepts at the beginning of the nineteenth century, the atomic-molecular model was not accepted, since it was based on non-observable entities: actually, the molecular hypothesis, proposed by Avogadro (1811) and Ampére (1814), was rejected. This prevented the true scientific advance of various disciplines, such as organic chemistry. In fact, the Frenchman Gerhardt proposed a classification of organic compounds based on «structural types», i.e. on purely empirical properties «without the need of resorting to hypotheses, but strictly remaining inside the limits of experience» [GERHARDT, 1844-45, p. 22]: it is evident, however, that the true nature of organic substances can be grasped only by making reference to the internal structure of their molecules, an aspect that was not accepted at that time.[2] In general, the prevailing scientific attitude was based on a prescription of strictly conforming to objective and well ascertained experimental facts and data, avoiding any recourse to concepts or entities that were not directly measurable.

2.2. *Social and technological changes around the middle of the 19th century*

This situation began to change by the middle of the 19th century, parallel to deep economic changes, which posed new tasks for science: in the new context the approach of early nineteenth-century science showed its inadequacy. Apart from the 1789 French Revolution, in the other continental European countries the old aristocratic social classes had held their power, and after Napoleon's defeat this power was re-established even in France. Britain was then the only country in which a capitalistic industrial economy had been established. After the 1848 revolutions on the Continent, the middle class extended its control on economic development and began to transform the economic and productive structures.

The most astounding development occurred in Germany, though the country was still divided into various states: for instance, Krupp's ironworks, and new chemical plants, such as BASF and Hoechst, were established. Economy evolved towards an overcoming of protectionism, a free trade area grew up, while capitalistic enterprise developed, driven by the setting out of new forms of credit and banking systems. Economic development acquired a new impetus. In Germany, in particular, the capitalistic system grew up without a comparable change in the social system: the definition of «development without democracy» is sometimes used. The middle class developed an increasing entrepreneurial and innovative initiative. It did however face an enormous problem, since the rising continental capitalistic economies had to compete with the overwhelming powerful structure reached by the British industrial system, that was one century ahead. The point is that, in this ascending phase of capitalism, this initial developmental undertow turned out to be a formidable innovative drive: the main tool that allowed such an economic miracle to be reached was actually the deep renewal and integration of science and technology. The industrial structure and the technological basis of the first Industrial Revolution proved to be backward and rigid in relation to the new dynamics of growth: innovative economic mechanisms and *a huge technological jump* were necessary (our analysis follows that of LANDES [1965, 1969]).

These developments proceeded through successive stages. A spectacular process of inventions and technical innovations started in the first decades of the second half of the century, which reached a pace absolutely unknown in the past, and was concentrated mainly in Germany: however, during a first phase these advances still remained essentially independent of scientific progress. Let us limit ourselves here to some relevant examples. New techniques were introduced for steel production (Bessemer, Siemens, Gilchrist-Thomas). Unlike British industry —which had already created in the course of the previous century a massive, but rather rigid structure, that proved to be quite difficult to reorganise— the German steel industry was essentially built on the basis of these new processes: at the beginning of the twentieth century the average size of the German steelworks was about four times that of the British ones, and the overall production of German iron and steel overtook that of the British. Something similar happened in soda production when Solvay introduced a new and much more efficient method of synthesis. British industry, based on the old Leblanc process, held a monopoly on world soda production, but it was not flexible enough to respond quickly to the new process, trying instead to improve the old one as far as possible. The emerging German industry, on the other hand, adapted the new process, and outstripped British production within a few decades, becoming the main world producer. Chemical production in general advanced rapidly in Germany, in particular organic chemistry, and the new-born dye industry, which grew up as a science-based branch. Another important instance of innovation was the invention of the internal combustion engine.

In the course of these developments, there was growing awareness that leaving the process of innovation to almost haphazard activity or to the ingenuity of inventors was becoming inconvenient. Some kind of guide to technical and industrial innovation was needed, which could only be provided by scientific research, if the latter could overcome the substantially empirical approach that strongly limited the possibility of new results or discovering new processes. Obviously, such a change did not result from a conscious decision, but was instead a response to a new spirit of inquiry and investigation into natural phenomena that broke with the old, traditional methods, and reflected the increasing involvement of science and technology in the new social and economic developments. It was a process of general maturation which spread in all aspects of activity of the members of the emerging class.

2.3. *The turning point in science: from empiricism to the adoption of mathematical models*

In fact, by the middle of the century a real inversion occurred in the methodological criteria of early century science, a first step towards a departure from direct experience, and a process of marked formalization and abstraction. Stephen Brush explicitly speaks of a «second scientific revolution» [BRUSH, 1976, Vol. 1, pp. 35-51]. Actually, *models based on non-observable entities, which had previously been rejected, began to be adopted as useful tools to lead to the prediction of new properties, or to the discovery of new phenomena or empirical facts*. To this end, however, models could no longer be used in a speculative form, but had to be formulated and developed in mathematical terms, in order to be tested rigorously. As Maxwell maintains in one of his early papers:

> In order to obtain physical ideas without adopting a physical theory we must make ourselves familiar with the existence of *physical analogies*. By a physical analogy I mean that partial similarity between the laws of one science and those of another which makes each of them illustrate the other. [...] we find the same resemblance in mathematical form between two different phenomena» (he italics are mine) [MAXWELL, 1856; p. 156 (*I*) of 1890 repr.]

where evidently (in the light of Maxwll's scientific production) «physical analogy» is a synonymous for «model». Boltzmann confirms the same concept:

> The most surprising and far-reaching analogies were seen to exist between natural phenomena which were apparently quite unlike. [...] The same differential equations hold for the most diversified phenomena. [...] philosophy at last generalized Maxwell's ideas in the doctrine that cognition is on the whole nothing else than the discovery of analogies. [BOLTZMANN, 1893, p. 42, 44]

> Every hypothesis must derive indubitable results from mechanically well-defined assumptions by mathematically correct methods. If the results agree with a large series of facts, we must be content, even if the true nature of facts is not revealed in every respect. No one hypothesis has hitherto attained this last end, the Theory of gases not excepted. [BOLTZMANN, 1895, p. 413-414]

A true theoretical physics was thus born, based on a hypothetical-deductive approach. The predictions reached on the basis of these models might turn out to be right or wrong when tested against experiments: in the first case, the model was to be considered as substantially correct, in the second case it had to be rejected, improved or changed. In Maxwell's words, the method consists of

> forming a hypothesis, and calculating what would happen if the hypothesis were true. If these results agree with the actual phenomena, the hypothesis is said to be verified, so long, at least, as someone else does not invent another hypothesis which agrees still better with the phenomena. [MAXWELL, 1875]

It is implied that, in any case, new insights and advances are reached in the understanding and practical control of physical processes, or new ones are predicted. In other words, the model, treated in a rigorous mathematical form, turned into *a «probe» to explore unknown aspects or regions of phenomena*. Already in his first paper on kinetic theory [MAXWELL, 1860] he found in fact the unexpected prediction that the viscosity of gases is independent on pressure, a property that he really verified wit an accurate experiment [MAXWELL, 1866; BRUSH, 1976, *1*, pp. 189-194]. But the most astonishing and far reaching example was Maxwell's prediction of electromagnetic waves, which was made possible by the mathematical representation of the electromagnetic field in terms of a model of fluids.

It is emblematic that this change occurred almost simultaneously in physics and in chemistry during the 1850s, starting with the adoption of the atomic molecular theory, although the subsequent implications were to be quite different in the two fields. In 1859, in a Conference in Germany, Cannizzaro simply re-proposed Avogadro's hypothesis —with a few changes, and furthermore in the form of a summary of a graduation course [CANNIZZARO, 1858]— and at that moment the latter was not only immediately accepted but, as we will see, it turned into a tool for renewing and going much deeper into chemical knowledge. Already some years before KRÖNIG [1856] and CLAUSIUS [1857] had published the early papers on the kinetic theory of gases,[3] based on the assumption that a gas is composed of very small bodies that move chaotically and whose collisions generate the macroscopic properties of the gas: actually, these initial papers had the rather limited purpose of justifying Boyle's law and the equation of state of the gas on a kinetic basis.

It is also important to observe the displacement in the centres and countries of these developments: «though the pioneers in these new fields had been technologists-scientists of Scotland and England in the period of industrial revolution and those of France in the period of French revolution, the systematic scientific researches in these new fields were commenced by German scientists in the 19th century. The term 'Physics' (*Physik*) itself was introduced during the German university reformation in the early 19th century.» [JUNGNICKEL and MCCORMMACH, 1986, Chap. 1].

The implications and developments of the adoption of this new method were quite different in physics and in chemistry. While, in fact, this approach raised deep difficulties both in the kinetic approach and its generalizations, as in the electromagnetic theory, chemists found out more efficient paths to reach new concrete results. Let us briefly analyze the two branches.

2.4. *Models in chemistry*

For chemists the atomic molecular model turned into a real tool to «probe» new properties and obtain new chemical compounds. Actually, the kind of models developed by chemists did not, strictly speaking, have a mathematical form: all the same , they were rigorous models, that made it possible to draw exact results that could be tested, reproduced and generalized. Through operations that one could term «molecular engineering», the chemists developed *models of the internal structure of molecules, i.e. of the spatial disposition of atoms*, looking in such a way both for new method of synthesis suitable for industrial processes, and for other molecules with required chemical properties. Such developments were substantially concentrated in Germany and in surrounding countries, and allowed the technical progress that was at the base of its powerful chemical industry. In France, on the contrary, this approach still met with opposition, shown in the scientific and technological lag accumulated by this country after the splendour of the first half of the century

In the first place, models of the internal structure of complex molecules were systematically developed, connecting the macroscopic properties to the spatial disposition of atoms and their connections, or to specific atomic groups: this allowed the design of new molecules with specific chemical properties, starting from known atomic groups and of more efficient industrial processes of synthesis. One of the most astounding results was Kekulé's hexagonal model of the benzene molecule [KEKULÉ, 1865-66], which became the basis for the modern classification of organic compounds [BENFEY, 1966; ROCKE, 1985,1988, WOTIZ, 1992]. Although these chemical models were not mathematical in the strictest sense, the new level of abstraction and formal reasoning is evident in this new approach.

Another fundamental advance made possible by the new conception was the concept of chemical equilibrium. It emerged from the complexity of the new chemical and technologic processes that were carried out: in the past only the simplest chemical processes that proceeded till the exhaustion of one of the reactants were used, but the more complex reactions, in particular the organic ones, show a *chemical equilibrium*, and often do not even occur in normal thermodynamic conditions, but require exceptional values for pressure and temperature. In 1864 the Norwegians Guldberg and Waage enunciated this concept [GULDBERG and WAAGE, 1864, 1879], in terms that anticipated those of kinetic theory. Apart from the rather obscure terms they used, their hypothesis was that the velocities of a chemical reaction of the kind $A+B \rightleftarrows C+D$ in the two opposite directions, are proportional to the product of the concentrations of the molecules that collide, that is respectively $k_1.[A][B]$, and $k_2.[C][D]$, where k_1 and k_2 are two constants (depending on the kinds of molecules, and on the values of the thermodynamic parameters, see later): chemical equilibrium occurs when the two velocities are equal, whence the law for chemical equilibrium (*mass action*) derives

$$\frac{[C][D]}{[A][B]} = \frac{k_1}{k_2} = K_{eq} \quad (1)$$

There were more advances stemming from chemistry that played an important role in subsequent developments. It is worth recalling Bunsen and Kirchhoff's discovery in 1860 of the characteristic spectral lines of elements, which led to the discovery of rubidium and caesium, and triggered off problems that opened up, through Kirchhoff's theorem, the general field of radiant energy, its spectrum and the black body problem.

2.5. *The birth of theoretical physics*

2.5.a. *Kinetic theory*

It is important to remark that the approach of Guldberg and Waage to chemical equilibrium is conceptually equivalent to the slightly posterior Boltzmann's *Stosszahlansatz* («hypothesis of molecular chaos»), namely that the number $n_{u,v}$ of collisions between molecules having respectively velocities $\vec{v}$ and $\vec{u}$ is proportional to the product of their respective numbers

$$n_{u,v} \propto f(\vec{r},\vec{v},t).f(\vec{r},\vec{u},t) \quad (2)$$

Boltzmann's proof of the Maxwell's velocity distribution derived therefore from a procedure analogous to (1), corresponding in the case of the gas to the condition that the numbers of the direct and inverse collisions are the same.

In physics resorting to mathematical models led to fundamental results in several fields. After the pioneering papers of Krönig and Clausius, the kinetic theory of rarefied gases was fully developed in absolutely general terms by MAXWELL [1860, 1867], and especially by Boltzmann.[4] The latter in 1872 proposed his transport equation, based on assumption (2), and derived from it the so-called «H theorem», which provided a kinetic definition of entropy and explained its increase with time, justifying the second law of thermodynamics, i.e. the irreversibility of the evolution towards the equilibrium state of gases [BOLTZMANN, 1872]. Boltzmann introduced the fundamental distinction between the «microscopic» (or «dynamic») state of a gas, determined by the exact positions and velocities of all atoms, and its «macroscopic» (or «thermodynamic») state, determined by a restricted number of macroscopic magnitudes, defined as averages over atoms [BARACCA, 1991, 1993]: he maintained however the belief that the relationship he had established between the two, namely the calculation of the latter from the kinetic treatment of the former, provided a *mechanical explanation* for the thermodynamic properties of the gas. In Boltzmann's view, this foundation of thermodynamics obtained for this simplest physical system, would have paved the way for the subsequent extension of this theory to more complex systems: for this purpose, he tackled the treatment of the behavior of the gas in its most general state, both of equilibrium and even very far from equilibrium.

2.5.b. *Light and electromagnetism*

On the other hand, the use of mathematical models based on *fluids* produced no less interesting results. Stokes developed the mathematical theory of physical optics, identifying light with waves propagating in a highly elastic fluid, the *luminiferous aether* [STOKES, 1845, 1880]. An analogous treatment was introduced by Lord Kelvin, and was fully implemented by Maxwell for electric and magnetic phenomena, as a development of Faraday's early qualitative approach in terms of contact actions, in contrast with the traditional approach, introduced by Newton, but adopted mainly by the French school, based on forces acting at a distance. As an example, Maxwell assumed

> Let us now suppose that the phenomena of magnetism depend on the existence of a tension in the direction of the lines of force, combined with a hydrostatic force [...] The explanation which most readily occurs to my mind is that the excess of pressure in he equatorial direction arises from the centrifugal force of vortices or eddies in the medium having their axes in directions parallel to the lines of force. [MAXWELL, 1861, p. 165]

Vortices materially represent the vector operator «curl». On these grounds Maxwell developed a complex mathematical treatment, identifying electric and magnetic actions with the states of pressure, stress or torque inside the hypothetical fluid [TRICKER, 1966]. He thus formulated the general laws of the electromagnetic field (*Maxwell equations*) [MAXWELL, 1873], fulfilling the unification between electric and magnetic phenomena. This theory provided the best example of the power of the new method in physics, since it was just on the basis of this fluid that Maxwell was led to the prediction of the existence of transverse *electromagnetic waves* and of their properties: this followed in fact from the highly elastic properties that the aether had to possess in order to reproduce the features of the electromagnetic phenomena. On the same basis Maxwell also predicted the *electromagnetic nature of light*, since the properties of his «electromagnetic aether» turned out to be identical with those of Stokes' «luminipherous aether», so that

> if the luminiferous and the electromagnetic media occupy the same place and transmit disturbances with the same velocity, what reason have we to distinguish the one from the other? By considering them as the same, we avoid at least the reproach of filling space twice with different kinds of aether [MAXWELL, 1876; p. 322 (*II*) of 1890 repr.]

The existence of electromagnetic waves was experimentally confirmed by Hertz in 1888. These results brilliantly confirmed the benefit of the new theoretical approach based on mathematical models, since such conclusions would have been quite difficult, if not impossible, to reach through an empirical approach: electromagnetic waves constitute in fact one of the discoveries that have more deeply transformed and renewed technology, production and social relations. The road was paved to make way for new technological and productive branches in the subsequent decades.

2.5.c. *Mechanism*

The leap in the level of scientific abstraction and formalisation carried out by these models must be noted, as well as the interplay between the microscopic and the macroscopic descriptions, and the association of the macroscopic magnitudes and properties with sets of microscopic states. Such developments brought about an increase in mathematical complexity: models and theories in fact grew into *highly formalised systems of differential and integral equations* (such as Maxwell's equations for the electromagnetic field, and the Boltzmann equation for a rarefied gas). The common feature of the whole scientific production in physics in this epoch was however its mechanistic basis. Mechanics was at that time the «queen of sciences», namely the scientific branch that had reached the most fully grown and coherent form, and it was natural that it should constitute the model to which every other branch attached itself: *the models that were introduced in this phase were in fact formulated in mechanical terms*. In other words, *mechanics provided the common basis and the methodological framework for the increasing proliferation and specialisation of scientific branches*.

With the further development of this approach, by the end of the nineteenth century a massive scientific system had been built that seemed to demonstrate the triumph of mechanics, notwithstanding serious difficulties that it brought with it. Actually, mechanism fitted into a more general philosophy, namely *reductionism*: macroscopic properties were in fact traced back to hypothetical underlying microscopic structures and configurations. The electric and magnetic fields are manifestations of the electromagnetic fluid, whose properties determine the laws of electromagnetism; *in Boltzmann's approach the expression of the thermodynamic functions is built up from the dynamics of collisions between the molecules of* *gases*. Actually, the mechanical description of the underlying structures was not the only one: as we will see, there were also reductionist theories based on electromagnetic properties.

2.6. *Hypotheses and models in other fields of science*

The use of hypotheses and models also became commonplace in other scientific disciplines, according to the level they had attained, and allowed important advances. For instance, in the biological theory of evolution, formulated by Darwin in 1859, a great advance was made possible by the conscious use of hypothetical, but rigorous (however qualitative) considerations:

> I have always considered the doctrine of natural selection as an hypothesis that, if it should explain wide orders of facts, would merit to be considered a theory worthy of acceptance. [DARWIN, 1903]

It is interesting that Boltzmann himself acknowledged this aspect of Darwin's theory, which allowed him to go beyond purely empirical facts:

> Darwin's hypothesis made it possible not only to describe the various living forms and phenomena, but also to explain them. [BOLTZMANN, 1893, p. 40]

3. Difficulties and paradoxes raised by the kinetic and electromagnetic theories

The spectacular results obtained by the new scientific approach notwithstanding, the last decades of the 19th century were marked by extremely harsh controversies among the major physicists, as may be perceived from the remarks by Planck, Sommerfeld and Boltzmann quoted at the beginning. How was it possible that the latter, in view of the epochal relevance of his scientific contributions, could feel like «an individual weakly against the stream of time»? Indeed, such an issue sounds complex and contradictory in many respects, but it can be thoroughly analysed if one goes back to the concrete roots of these disputes, beyond their purely physical aspects. The latter, in fact, concerned just the *mechanistic formulation and interpretation* of models and theories, rather than their true nature and structure.

First of all, the new theories raised difficulties and contradictions with regard to the world view held by physicists: in effect, as we will see, chemists were not at all bothered by such problems. We will briefly review the main difficulties raised by the kinetic and electromagnetic theories respectively, with a particular regard for the former, since it is more closely related to our analysis.

3.1. *The reversibility paradox and the introduction of probability*

The first difficulty in connection with kinetic theory, namely the *reversibility paradox*, was raised in 1876 by LOSCHMIDT [1876], who was not an opponent of the atomic theory (he introduces the «Loschmidt number», a forerunner of «Avogadro's number»). The Boltzmann equation was based on molecular collisions, and was interpreted therefore as a *mechanical equation*. Now, with mechanics being reversible, the derivation of irreversible behaviour from such an equation appeared to be inconsistent. Boltzmann's answer to this criticism was immediate, and introduced the fundamental concept in the microscopic interpretation of thermodynamics, namely the concept of *probability*. Assuming as the probability of a macroscopic state the number of distinct microscopic states compatible with it, Bolzmann obtained a probabilistic definition of entropy, with the state of *equilibrium derived as the most probable one*.

> One could even calculate, from the relative number of the different state distributions, their probabilities, which might lead to an interesting method for the calculation of thermal equilibrium. [...] Loshmidt's theorem seems to me of the greatest importance, since it shows how intimately connected are the second law and probability theory, whereas the first law is independent on it [BOLTZMANN, 1877 *a*, Engl. transl. BRUSH, 1965-72, I, p. 192-193]

It is worth recalling that Maxwell had already moved in this direction, with the argument of the so-called «Maxwell demon», that he exposed in 1867 in a letter to Tait [reported in KNOTT, 1911, p. 213]. His argument led him to write Lord Kelvin in 1870 that

> The second law of thermodynamics has the same degree of truth of the proposition that if one throws a glass of water into the sea, he cannot extract the same glass of water. [Reported in STRUTT, 1968, p. 47]

The origin of this, along with other «paradoxes», is a basic constituent in our analysis. Far from reflecting a contradiction between thermodynamics and mechanics, it stemmed in fact from a lack of distinction between the macroscopic and the microscopic levels of description of the system (in the end, therefore, between mechanics and thermodynamics as independent theories): Boltzmann performed the fundamental steps in this direction, although he was not always capable of fully exploiting its consequences. His basic step was the splitting of the phase space for the single particle into *cells* of finite volume: the set of average numbers n_i of molecules in each cell define the macroscopic state. He then *assumed* as the definition of the *probability* of a macroscopic state the number of distinct microscopic states W

$$W=N!/\prod_i n_i! \qquad (3)$$

and demonstrated that the equilibrium distribution, namely Maxwell's distribution of velocities, derives from purely probabilistic considerations, without the need of any mechanical argument, as the most probable distribution, while entropy is defined as

$$S=k_B \ln W \,. \quad (4)$$

> The initial state of the system will be, in the majority of cases, a state of very small probability and the system will tend towards more probable states, till when it reaches the most probable state, namely the state of thermodynamic equilibrium. If we apply this to the second law of thermodynamics, we will be able to identify the magnitude usually called entropy with the probability of the corresponding state. [BOLTZMANN, 1877 *b*]

Substituting the expression for entropy (4) with the definition of probability (3), one gets (using Stirling's approximation)

$$S=-k_B\sum_i n_i \cdot \ln n_i + \text{constant}, \quad (5)$$

where the value of the arbitrary additive constant depends on the arbitrariness of the volume *dv* of the cells: in fact, in each cell every molecule has this volume at its disposal, so that the number of microstates (3) would actually be

$$W=\left\{N!/\prod_i n_i!\right\}\cdot(\delta v)^N \quad (6)$$

so that $const = N\cdot ln(\delta v)$. It is well known that QM determines the volume of the elementary cell, $\delta v=h^s$, *h* being Planck's constant (see later): this in turn determines the value of the additive constant of entropy, according to the third law of thermodynamics, that will be discussed later on. We will not discuss in this paper «Gibbs' paradox» which, as is well known, is related to expression (3), although «the identity of classical point-like particles has nothing to do with quantum mechanics» [MEHRA and SUDARSHAN, 1970].

3.2. *The recurrence paradox*

Twenty years later one more objection was raised against the Boltzmann theory, known as the «recurrence paradox» [ZERMELO, 1896]. In order to appreciate its relevance, it must be recalled that Zermelo was a young assistant of Planck, and Boltzmann was aware that behind this criticism lay the negative attitude of Planck himself to the kinetic approach and the philosophy behind it: it was on this occasion that Boltzmann expressed himself in the sorrowful terms we have already mentioned. The paradox was based once more on a theorem of dynamics: Poincaré had shown in fact that a (bound) mechanical system has to return to a state arbitrarily close to the initial one over a sufficiently long period of time: this behaviour seemed to imply that entropy could not always go on growing, but sooner or later it has to decrease and return to a value close to its initial value. Boltzmann, upset and depressed by this criticism, retorted that his previous considerations had not been understood, reaffirmed that the evolution of the system towards equilibrium was a probabilistic process, and evaluated that the «recurrence time» for a macroscopic system is tremendously long, much more than the life of the universe:

> this is practically equivalent to *never*» [BOLTZMANN, 1964, p. 444]

In spite of the relevance of such considerations and calculations, he seemed however to miss the fundamental point, which is again that Poincaré's theorem concerns the «microscopic state» of the system, but has nothing to do with the «macroscopic», since the latter is defined in terms of an ensemble of microscopic states: a concept that he himself had introduced. Such a failure betrays, in my opinion, the fact that Boltzmann had not yet overcome a fundamentally mechanistic view. The full appreciation of the distinction between the two levels would have opened the way to a wider perspective, in which dynamic properties such as recurrence could be viewed as manifestations of thermodynamic fluctuations: one had however to wait for Einstein in order to attain a full awareness of this.

3.3. *Contradictions with the specific heats of gases*

The kinetic theory raised more contradictions. The one related to the specific heats of gases, whose values were correctly predicted on the basis of the theorem of equipartition of energy, appeared to be particularly problematic if one takes into account only the translational and rotational degrees of freedom of atoms and molecules. But increasing evidence was accumulating of the existence of an internal structure of these systems: this fact raised a deep contradiction, since the inclusion in the theory of the internal degrees of freedom, in addition to the translational and rotational ones in the theory, would have led to values for specific heats at variance with the experimental ones.

> I have now put before you what I consider to be the greatest difficulty yet encountered by the molecular theory. [MAXWELL, 1875; p. 433 (*II*) of 1890 repr.]

Such a contradiction was of a different nature from the previous ones, and was to be solved only when the quantum theory showed that the internal degrees of freedom are «frozen» at ordinary temperatures, in the sense that they cannot be excited by thermal motion, since the energy differences between both the vibrational and the electronic states of atoms and molecules, are much larger than the average kinetic translational or rotational energies.

At the end of the century a strong debate took place on the validity of the equipartition theorem and the ergodic hypothesis, whose mechanistic premises and bases were evident: it involved significantly, besides Boltzmann, almost only British physicists [BARACCA, 1980, Sects. 7.7, 7.8], testifying an increasing lag of that country in science and technology that we will discuss in the following.

3.4. *The «aether wind»*

In a similar context, one may consider the difficulties that arose in electromagnetic theory, as the latter was formulated on the basis of the electromagnetic aether, conceived as a classical fluid: the most generally known was the paradox commonly called the «aether wind». At the end of the nineteenth century, in fact it seemed obvious (as a consequence of the use of the Galilean transformations for uniform translations) that the behaviour of the electromagnetic phenomena was to depend on the motion of the experimental apparatus (or the Earth) with respect to the aether, just as we experience wind when moving through still atmosphere. A series of experiments tried to measure such effects, culminating in the negative results of the Michelson and Morley experiments (from 1881 up to 1904).

4. The roots of 19th century mechanism

Let us discuss the true nature of the above mentioned difficulties and paradoxes, since they illustrate the roots of the 19th century mechanistic reductionist approach. In fact, these difficulties were not really inherent to the structure of the physical theories, but derived from their mechanistic interpretation, which was not the only possible one: and they can simply disappear if these theories are interpreted and developed abandoning the mechanical relationship between the macroscopic and the microscopic descriptions, as emerged at the beginning of the 20th century. In the case of electromagnetism, the contradiction was to be clarified by EINSTEIN [1905 *c*], and depended on the application of the Galilean transformations, valid for Newtonian mechanics, while the Maxwell equations are correctly Lorentz covariant. In the case of kinetic theory, the paradoxes arose because the distinction between the macroscopic and the microscopic descriptions was not fully appreciated: since the former is defined by assigning the (average) number of molecules contained inside small but finite intervals of positions and velocities (the *cells* in phase space), the position and velocity of each molecule are not exactly known, as would be required in order to reverse velocities, or to apply the theorems of mechanics. Actually, these two levels of description turn out to be distinct and complementary: in other words, *thermodynamics cannot be reduced to mechanics*.

Boltmann's work suffered in this respect from a contradiction, or at least a still inadequate development [see for instance BARACCA, 1980, 1991, 1993]. Actually, the concept of probability he had introduced in 1877 went well beyond mechanics, but he did not succeed in really going beyond a substantially mechanistic point of view.[5] In fact, only the state of macroscopic equilibrium is obtained through probabilistic considerations, as the most probable (Sect. 3.1): this approach offered the basis for a generalisation applicable to systems other than gases, as was carried out by Gibbs and Einstein at the beginning of the 20th century (Sect. 6.1). Boltzmann's program was on the other hand more ambitious, aiming at the full treatment of states of non-equilibrium, which could derive from a generalisation of the kinetic treatment for the simplest physical system, i.e. rarefied gas. But for states of non-equilibrium probabilistic considerations alone were non sufficient, and he had to resort to his general equation, based on molecular collisions. However, he did not fully appreciate the probabilistic basis of the *Stosszahlansatz*, eq. (2), that was the real basis of the theory. In the end, his hope of generalising this general treatment to physical systems more complex than a gas, without restricting to the equilibrium state, did not come true.

On the other hand, it is important to note that the mechanistic and reductionist approach offered possible ways out of the difficulties, and contained great potentialities for very valuable physical developments that, however involved they might appear, were likely to have opened a path of evolution for contemporary physics completely different from the one actually developed at the beginning of the 20th century.

It may be supposed that these routes were interrupted by the start of the twentieth-century revolution in physics: **the evolution of science, in effect, implies choices that are not merely of a scientific nature, but involve more general factors**. Boltzmann, for instance, performed calculations of the «recurrence time», as well as considerations on statistical ensembles [GALLAVOTTI, 1995], anticipating current developments on «dynamic systems», that updates and makes his approach valuable. On the other hand, Lorentz proposed a solution of the negative result of the Michelson and Morley experiments, namely the «Lorentz contraction», usually considered as a hypothesis, but which had on the contrary a solid theoretical base. In fact, he had developed the «theory of electrons» [LORENTZ, 1892, 1895, 1909], in which matter was conceived as being composed of elementary charged particles (a hypothesis that preceded the discovery of the electron by J. J. Thomson in 1897).

This theory, in a sense, complemented Maxwell's theory of the electromagnetic field, by unifying it with the theory of matter: the basic equations of the theory of electrons are in fact Maxwell's equations together with Lorentz's equation for the motion of a charged particle in an electromagnetic field [HIROSIGE, 1969; MCCORMMACH, 1970 *b*]. Such a theory had therefore a reductionist structure, as it was based on interaction among the elementary components of matter, and appeared as an electromagnetic equivalent of mechanistic theories.

Lorentz's theory, which embodied the concept of aether, was quite successful. In particular, the electromagnetic nature of the interacting forces in matter implied a contraction of bodies in the direction of their motion throughout the aether (*Lorentz contraction*), that exactly counteracted the «aether wind». It was not therefore (as it is sometimes presented) an ad hoc hypothesis, but rigorously followed on electromagnetic theory, and was the same as that predicted in Einstein's theory of special relativity, which retains electromagnetism while rejecting Newtonian mechanics and Galileo transformations [MCCORMMACH, 1970 *a*; HIROSIGE, 1976; BERGIA, 1979, 1988 *a*]. At the time, moreover, all experiments confirming the theory of electrons were also in agreement with special relativity, and vice versa. Actually, the *electromagnetic conception of nature* played an important role at the turn of the century: since Joseph Larmor tried to understand the atomic structure of matter [LARMOR, 1894-97; GIANNETTO, 2005], and in 1902 proposed a physical interpretation of Planck's constant [LARMOR, 1902, 1903; GIANNETTO, 2005].

We can therefore conclude that, *from the point of view of physics*, probably there was no real need or urgency to overcome the formulations that were at the basis of 19th century physics. The reasons for the radical changes at the beginning of the 20th century were mainly of a different nature, and were rather rooted in the fact that *the mechanistic-reductionist approach was not able to meet the needs of the social, cultural, economic and productive system with respect to science*. This approach suffered in fact from an internal contradiction, and a crucial limitation. In fact, once the recourse to models had been adopted as a powerful way to investigate and forecast new properties and phenomena, the full potentiality of this approach lay in the complete freedom of their formulation, while the restriction to mechanical models (or to a reductionist treatment, such as Lorentz's «theory of electrons») constituted a deep and unjustified limitation. The true contradiction was, therefore, between the adoption of models and non observable physical entities on the one hand, and the limitation to models of a mechanical nature on the other. The clash that developed between «model-makers» and «phenomenologists» was essentially fictitious: the real solution, as we will see, came out of a third line, that consisted in going beyond both positions, overcoming both «phenomenalism» and «mechanicism», and adopting the widest freedom in the formulation of physical concepts and theories.

Not surprisingly, at the end of the 19th century a dramatic dispute opened, in which Boltzmann felt extremely isolated. W. Ostwald, the only chemist who took an active part in it, developed a theory, called «Energetics», that claimed to get rid of every difficulty by reducing all phenomena to fluxes and transformations of energy. This was very popular at that time, but clashed with the ideas of both Boltzmann and Planck: in 1895 he gave a famous lecture on «The overcoming of scientific materialism» [OSTWALD, 1895].

> The central point of this lecture is the proof that the mechanistic interpretation of natural phenomena is inadequate and can be replaced by that of energetics, with the result of removing the inadequate aspects.

The criticism of mechanicism was explicit, but Ostwld's route looked backwards, as Planck pointed out:

> I retorted, among other things, that a volume energy in the sense specified by Ostwald did not exist. For instance, the energy of an ideal gas does not depend on volume [...] [Ostwald's] point of view resulted in the irreversibility hypothesis being considered useless in order to prove the second law of thermodynamics. [PLANCK, 1948, p. 19-20 Ital. transl.]

The cultural milieu in central Europe were dominated by schools of thought that refuted the new insights into natural phenomena and the very legitimacy of using models based on non-observable entities. They critically re-examined positivistic philosophy, in their support of a scientific approach restricted to observable phenomena and data. The most profound, authoritative and influential trend was critical empiricism, formulated by Ernst Mach and Avenarius, who both denied the reality of anything beyond direct empirical evidence, which they reduced to mere sensations. Although this viewpoint also produced important results, such as studies on the connections between sensations and perceptions, and the development of psychophysics, it implied the rejection of the reality of atoms, considered as purely «economic» tools, and led to idealistic positions denying the existence of matter itself. Nontheless, this anti-mechanistic polemic reached a deep level of critical awareness; so much so that Einstein acknowledged his debt towards Mach in limiting the role of mechanics.[6] The diffusion of this philosophy (Sommerfeld recalls that «The champion for energetics was Helm, behind him stood Ostwald; and behind both of them the philosophy of Ernst Mach» [BRUSH, 1964, p. 14]) led Lenin to write down in 1908 a harsh criticism, in his essay, *Materialism and Empiriocriticism*. Botzmann retorted with deep considerations, as in the following quotation:

> It is said: only sensory perceptions are given, and we have no right to perform one more step. However, those who say that this was consistent, should ask one more question: are our sensory perceptions of yesterday also given? Directly, only one sensible perception, or only one thought, is given, precisely only what we are thinking at the moment. Therefore, if one wants to be coherent, not only the existence of other persons outside my ego should be denied, but also the existence of every idea of the past. [BOLTZMANN, 1905, p. 132]

In such a situation, it is not surprising that Boltzmann's points of view attracted attention and raised a discussion only in the scientific British milieu [BRUSH, 1967, Sect. 9; 1976, Sect. 10.9; BARACCA, 1980, Sect. 7.8]. His loneliness was increased by the fact that the representatives of the new scientific generation, like Planck, were not sympathetic to his ideas (Sect. 7.1).

The situation was further complicated by the fact that, while the physicists were making a great effort to complete such a mechanical construction, convinced as they were of reaching the final explanation of natural phenomena, a series of completely new processes were being found. The discovery of X-rays, radioactivity, cathode rays, the electron, the internal structure of atoms, and the determination of the complete spectrum of electromagnetic radiation, were in fact posing the need for new physical concepts and theoretical frames. This meant that the difficulties and contradictions had to be overcome in a completely different context, and this was to introduce a further deep change in the very basis of science, marking the breakpoint with mechanistic philosophy. However this turning point in physics was preceded, and indirectly prepared, by a different scientific change, in the same direction.

5. The second industrial revolution in Germany (1870-1900)

5.1. *Industrial and technical innovation under the German Empire*

The absence of chemists (with the exception of Ostwald) in the debate we have just discussed was not a fortuitous circumstance, and constitutes one of the central points of our analysis. In order to appreciate this, we must briefly consider the economic and social developments in Germany at the end of the century. Although it was not until 1870 that the country overcame the division into small independent states, one of them, Prussia, had reached a remarkable economic level (as had been shown in the Austrian-Prussian war of 1866). In fact, when unity was reached, in 1870, the power of the new German Empire immediately manifested itself by routing the imperial French army in the French-Prussian war (1870-71), for which the recently founded Krupp ironworks provided the German army with 300 new guns. Although the period between 1873 and 1896 is considered as a «long depression», a completely renovated system of economy and production was being built up, founded on a deep technological revolution, whose bases we have seen come about in the previous decades. At the end of the century the process reached so quick a pace that it is not out of place to speak of a *second industrial revolution*, which had its centre in Germany. The impetuous course of such a process stands out if one considers that the order of the most advanced industrial powers was completely overturned in a short period of only a few decades: around 1850 Great Britain had an overwhelming lead, and France was in second place, but by the start of the twentieth century they had been outstripped by Germany, and in part by the US, when several of the leading productive sectors in Britain almost collapsed, faced with increasing German technical leadership and competition.[7] As an example, while in 1870 Great Britain produced more than half of the steel produced by the first four European countries all together, as early as 1873 the German production overtook that of the British!

How could Germany overcome the powerful British industry in so short a period? One of the main factors was *technological innovation* (for a more extensive analysis we refer to the already cited study by LANDES [1965, 1969]): the German industry arose on the basis of the new techniques, while the powerful British industry, based on old ones, became obsolete, could not be recast at a comparable pace, and was rapidly soon unable to compete.[8] When the Solvay process was introduced for soda production, the British industry, based on the old Leblanc process, held a monopoly on world soda production, but it was not flexible enough to respond quickly to innovation, trying instead to improve the old process as far as possible. The emerging German industry, on the other hand, adopted the new processes from the beginning, and outstripped British production within a few decades, becoming the main world producer. Chemical production in general advanced very rapidly in Germany, in particular the organic chemistry industry, and above all the new-born dye sector.

Something similar happened in the metallurgical sector, in which Great Britain had developed a powerful industry in the course of the previous century. The young German steel industry was developed on the basis of the new processes: at the beginning of the twentieth century the average German steelworks was about four times the size of a British one, and German production overtook that of the British. One more important instance of innovation was the invention of the internal combustion engine.

Much research was also taking place within the German electric industry. In Berlin the large and very advanced *Physikalische Technische Reichsanstalt* (*Imperial Institute of Physics and Technology*) was established in 1884 [PFETSC, 1970], in which the fundamental measures on the spectrum of electromagnetic radiation were obtained in 1900 (Sect. 7): it owed its origins and development to very specific economic factors, namely, the needs of the German scientific precision instruments industry. Its greatest expansions occurred in periods of economic slowdown, in which scientific and technological development were viewed as appropriate solutions to economic difficulties that required governmental and industrial investment.

German economy was characterised by the rapid growth of a modern industrial system, based on continually renewed processes, intensive and programmed technological progress, and scientific investigation, both fundamental and applied. The index of German industrial production grew 7 times between 1860 and 1913, in comparison with not even 3 times for British production (but 12 in the US). The most important advances in the banking and the credit system, in company structure, in the formation of the huge industrial *konzern*, and so on, took place in Germany.

These developments, moreover, took advantage of a very advanced educational system, which could satisfy the growing need both for a working class with a good basic preparation [LEXIS, 1904 *a*, *b*; TURNER, 1971; MCCLELLAND, 1980], and for a wide category of specialised and trained scientists and technicians. Besides the universities, which had radically modernised their laboratories and teaching methods, there was a system of polytechnics (*Technische Hochschulen*) unknown in other countries, that prepared highly qualified technicians with a university education in applied research. At both levels strict collaboration with the main firms provided a close link between the academic milieus and the concrete problems of production and technical innovation [MANEGOLD, 1970; RINGER, 1969; 1979, pp. 3, 37-54].

The German schools of chemistry became the most advanced in the world, and those chemists who wanted a thorough training went to study in Germany. Not surprisingly, the best source of information regarding the German educational system is given by the Reports of the Parliamentary Commissions that were appointed in these decades, to investigate the reasons for the worrying decline of British education and to suggest solutions: in 1867 the chemist Roscoe declared in one of them:

> In Cambridge there are not the means to prepare, for instance, a chemist [...] a person who thinks to distinguish himself in chemical science would not remain satisfied with the preparation that he could get in Cambridge, and would go abroad for this. [PARLIAMENTARY PAPERS, 1867-68, p. 286]

At the beginning of the 20th century it was estimated that there were in Germany almost 7.250 chemists engaged in research, industry and teaching [PARLIAMENTARY PAPERS, 1901, pp. 32-33; HABER, 1958, p. 188]; at the end of the first world war this number reached the order of 30.000 [CARRÉ, 1918].

One more aspect of the German situation is worth mentioning. The impulse of *Wissenschaft* and industrial development by the state had been a consciously pursued policy of the Prussian government since the early nineteenth century, after its defeat by Napoleon, and it remained an integral part of the state-building in Prussia and some of the other leading German states in the following decades. In particular, *the inadequate development of Germany's national consciousness and the lack of a political consensus in the German empire justified a claim by both industry and science to positions in the nation far beyond what was happening in the other societies: in other words, science and industry became substitutes not only for power, but also for national identity*. We will see the relevance and the repercussions of this spirit during, and especially after WW II.

5.2. *The German chemical industry in the eighteenth century*

The chemical industry (especially organic chemistry, and in particular the dye industry, which accounted for 85-90% of world output of dyes at the end of the nineteenth century) and the electric industry were the leading German sectors. The annual compared rates of growth of the German chemical industry were [HOHENBERG, 1967]

1872-1913	Production:	chemical industry	6.2 %
		Global industrial	3.7 %
1850-1913	Employment:	in chemistry	4.0 %
		in industry	1.9 %
1875-1913	Labour productivity:	in chemistry	2.3 %
		in the whole industry	1.6 %

The recently established modern chemical firms (BASF, Bayer, Hoechst, Geigy, Agfa) grew very rapidly in these decades, built up huge research laboratories and developed intensive scientific investigation. In Germany, in fact, the chemical industry assumed its modern, science-based structure, based on programmes of team investigation, and gradually shifted direction towards the research laboratory [HABER, 1958; HOHENBERG, 1967; BARACCA, RUFFO and RUFFO, 1979, Chap. 6]. The percentage of workers with a university degree in the principal German chemical firms at the end of the century was comparable with today's figures (in 1900 the German chemical industry employed 3,500 chemists out of a total of 80,000 employees, 40% of whom worked in plants with more than 200 employees). In 1900 BASF employed 148 chemist out of 6,500 workers, Hoechst 120 chemists and 36 engineers out of almost 4,000, Bayer 145 chemists and 27 engineers. There was in Germany a total of more than 7,000 chemists with an academic preparation, 4,000 of them working outside the educational and academic system. The laboratory was the brain behind the planning and the development of the chemical firm, as a British observer remarked in 1909:

> Control of big chemical plants in Germany is to a great extent in the hands of chemists; it is relatively unusual to find persons skilled only from the financial or commercial point of view in responsibility places of direction. … one of the most peculiar features is the large amount dedicated every year for scientific purposes. Researchers are used with the purpose of discovering new products and improving the existent fabrication methods. These men proceed from the universities and the polytechnic schools. [BARON, 1909, p. 43]

Agfa was established by two chemists, Martius and Mendelshon-Bartholdy. In 1868 BASF, among other chemists, appointed to the direction of its laboratory the chemist H. Caro, who kept up direct contacts with the most qualified chemists in the universities. A similar role was played by Carl Duisberg in Bayer. Research proceeded through strict interchange and collaboration between industries and universities. A BASF report stated: «Great importance was ascribed at that time to maintaining personal relationships with scientists, in the interests of useful research». On the contrary, the situation was completely different in Britain, as the chemist Frankland replied to an inquiry commission in 1867:

> I had the occasion to visit many chemical industries in Lancashire, which I had not visited in the last 11 years, and I was struck to see that the processes in use at that time are still in use, and exactly in the same way. There are many attempts of inventions, but in general they fail; so that if one gets a new patent, nobody believes it; and with reason, since it is probable that it has no value. … There is in this country a great waste of intellectual work and time. [PARLIAMENTARY PAPERS, 1867-68, p. 271]

In 1845 the Royal College of Chemistry of London appointed as director a German chemist, A. W. Hofmann. Later on, when he resigned, the British chemist Roscoe, previously mentioned, declared to a Commission: «I think that Prof. Hofmann went back to Germany only because he has understood that it is impossible here to build a true school of science» [PARLIAMENTARY PAPERS, 1867-68, p. 284].

Particularly advanced technical scientific developments happened in the organic chemical industry [IHDE, 1964, pp. 614-615; JOHNSON, 1990, pp. 25, 34-36]

> … organic chemistry had helped to lower the barriers between pure and applied chemistry by a remarkably fruitful cooperation between the German academic and industrial chemists who built up the industry of coal-tar products […] Germany had by the early 1880s gained world leadership in most areas of pure and applied organic chemistry.» [JOHNSON, 1990, p. 25]

The most advanced sector was that of synthetic dyes [BEER, 1959]. The first artificial dye had been obtained in 1856 by Perkin, one of Hoffmann's assistant in London: until 1869 small dye plants were established in France and Britain. In that year Graebe and Liebermann, at the Berlin Polytechnic obtained alizarin:

their process was not industrially usable, but in collaboration with Caro's laboratory in BASF, the patent for an industrial process was achieved just a few days before a similar application by Perkin. This allowed BASF to become one of the biggest world industries in this sector. Similar developments happened in the whole of the German industry, in particular in the five main research-intensive dye firms (BASF, Bayer, Hoechst, Agfa and Cassella). In 1880 A. Baeyer, after many attempts, obtained synthetic indigo: Caro established with him a research agreement that took 17 years in order to find an industrial process, at the expenditure of one million pounds, the efforts of dozens of technicians and researchers, and the contributions of several collateral processes.

> The advent of synthetic indigo opened the way to reducing competition and cutting the costs of research in many other dyes [JOHNSON, 1990, p. 34]

At the end of the century Germany produced 75 % of the world production of dyes, with a value that, from 1.2 million pounds in 1874, had reached 6 million in 1898 [HABER, 1958, p. 126].

Another notable technical scientific undertaking was the so-called «fixation of nitrogen» (or ammonia synthesis), carried out in 1913 by Fritz Haber, of the Karlsruhe polytechnic, and the BASF chemist C. Bosch. Nitrogen is a common component of the atmosphere, in its molecular form N_2, and can be easily separated by fractional distillation (refrigeration techniques were developed in connection with sea commerce and the shipment of perishables), but is used as a compound in fertilisers and explosives: at the end of the 19th century the only source of nitrogenous compounds was guano (bird dung) from Chile, which besides being subject to exhaustion, was moreover subject to the British control of the seas.

> Germany's growing dependence on imports of certain key inorganic resources also became a matter of concern to many chemists in Germany around the turn of the century. [JOHNSON, 1990, p. 39]

A compound of nitrogen, NO, can be produced by an electric arc, but this process is too expensive for industrial production. The reaction $3H_2+N_2\leftrightarrow 2NH_3$ does not proceed at ordinary temperatures and pressures, so the basic problem consisted in determining the dependence of the chemical equilibrium of this reaction on thermodynamic conditions: the progress that we will discuss in the next section in physical chemistry was essential in order to establish that, being an exothermic process with 4 initial and 2 final molecules, ammonia can be obtained at relatively low temperature but very high pressure. After numerous attempts, in 1905 Haber concluded that such a process was not industrially usable. In 1906 Walter Nernst, in his investigations on the third principle of thermodynamics (Sect. 9), critically reviewed Haber's results. Some years later the latter reconsidered the problem and found the solution in collaboration with Bosch (Nobel Prize, 1932), solving enormous technical problems, including the finding of a suitable catalyst, the manufacture of very high pressure-resistant equipment (Krupp provided steel converters in a single block) and the regularity of the process. A huge plant was established at Oppau, for 8.700 tons of ammonia per year, raised to 60.000 during the war (employing 5.000 workers, 40 chemists, 60 engineers, 500 technicians; the energy plant produced 10 MW), and a second plant set up in Leuna. This process for ammonia synthesis allowed Germany, while completely surrounded, to continue to resist for years during the First World War, since it could synthesise explosives and fertilisers (this had in fact been the main motivation behind the Germans' effort to develop these the new methods of synthesis). When an Ally commission inspected the Oppau plant for ammonia production in 1919, it could ascertain the great technical progress that had been made. Ammonia was not the only case: Germany had become able to replace expensive, naturally occurring substances, which would have been imported from abroad, with synthetics and artificially produced substitutes based on cheaper, domestically available substances.

In this connection, it is worth recalling Haber's direct involvement in war research: as the director of the *Kaiser Wilhelm Institute* of Chemical Physics in Berlin, he was the organiser, and the real father (violating international laws) of the German manufacture and use of chemical weapons (at Ypres in 1915) [JOHNSON, 1990, Chap. 9]: a role that he proclaimed in his Nobel Lecture (1918). Nernst too, who had been rejected from the army when he was young, but as the war broke out enlisted as a volunteer, was called on among others as a technical advisor at the High Headquarters, where he devoted himself to chemical warfare (the relationship between the German chemists and the Imperial government was complex. This aspect, that lies outside the aims of this paper, is extensively and critically examined by JOHNSON [1990]).

It is important to remark that *the German chemical industrialists, such as Carl Duisberg, with their scientist-allies, such as Emil Fischer and Fritz Haber, took the initiatives and provided the models for the relationship between industry and science within physics*.

5. The chemists beyond mechanicism

We are now in a position to understand why chemists, mainly in Germany, were absent from the disputes on fundamental and methodological issues at the end of the century. This, in fact, was not a sign of backwardness: on the contrary, they introduced a fundamental change, that for the first time enabled them to overcome the mechanistic approach, and turned out to be of the greatest importance for the revolution in physics at the beginning of the 20th century. The fundamental point is that the chemists tackled problems of an unusual complexity and great practical and economic relevance, for whose quick and efficient solution they were subject to very strong direct and indirect pressure.

We have seen, for instance, the relevance of the problem of determining chemical equilibrium. What was the situation after Guldberg and Waage's paper of 1864? We have noted the similarity of their approach to Boltzmann's *Stosszahlansatz*, eq. (2). Such an approach, based on molecular collisions, without doubt achieved outstanding results in the kinetic theory of gases, but it could hardly have had any prospect of practical success in the calculation of equilibrium even of the simplest chemical reaction: for instance, even such a «simple» reaction as $2H_2+O_2\leftrightarrow 2H_2O$ is a very complex process, which never proceeds through the collision between three molecules, but through chains of binary dissociations and recombinations, that, to make matters worse, change according to thermodynamic conditions.[9] Therefore, whatever attempt to perform explicit calculations based on the kinetic-mechanistic method could not have any hope of success.

Faced with such complex problems, however, the position of chemists had a great advantage, since they were not bound to any rigorous or rigid methodological rule, and had to satisfy in the first place a practical criterion of efficiency and speed in solving problems and finding concrete and viable results. It seems quite natural, in this respect, that thermodynamics offered a much more flexible and nimble context, besides being more suitable, than mechanics in the study of complex systems composed of a very large number of particles that undergo complex processes. *Thermodynamics is in fact a set of phenomenological laws, compatible with different models of the structure of the system*:[10] and, above all, *the thermodynamic state functions do not depend on the specific behaviour of a transformation, but only on the initial and final states* (for a chemical reaction, they depend on the concentrations and thermodynamic conditions of the reactants and the products, but not on the intermediate steps of the reaction). In fact, it does not appear that chemists further developed Guldberg and Waage's approach, nor that they had disputes of the kind of those that bothered physicists: they refined and applied instead the concepts of theoretical thermodynamics, as a part of chemical physics, in particular the concepts of *free energy*, a set of state functions whose minimum value directly corresponds to thermodynamic equilibrium in specific thermodynamic conditions. In 1876 the American physical-chemist W. Gibbs (the same who in 1902 was to formulate statistical mechanics, Sect. 6) published a fundamental paper [GIBBS, 1876] that contained all the basic results: Gibbs' free energy $G=U-TS+PV$, the «phase rule», and so on. It was a lengthy, formal and complex paper, that was in fact ignored for a decade. However, in the meanwhile, the main useful partial results were independently obtained and applied by Van't Hoff, Le Chatelier [1884] and others: among them, those criteria that, as we have seen, were used by Haber in the synthesis of ammonia. The consideration of the minimum of free energy for the reactants and the products of a reaction leads to the law of mass action, eq. (1), *without any consideration of molecular collisions, and independently on the intermediate steps of the reaction* (Appendix, *1*).

An important remark must however be added in this respect. The equilibrium constant is obtained from free energy through an exponential [Appendix, *1*, eq. (a)]. It obviously depends on the temperature at which the reaction proceeds, and the determination of this dependence is crucial for technical applications. But *the additive constant S_0 of entropy is reflected into an arbitrary multiplicative constant in the expression of the equilibrium constant, preventing its absolute «scale» to be obtained*. We will fully appreciate the importance of this fact in the formulation of the third principle of thermodynamics (Sect. 9).

It is worth insisting on the central aspect of this path taken by the chemists, namely the fact that *thermodynamics provides a basic framework in which models and techniques can be conceived and developed that are more general than those allowed in a mechanistic framework*.

This choice can be verified also in problems such as chemical kinetics, that do not fall within equilibrium thermodynamics, but need the consideration of molecular collisions: Van't Hoff, for instance, explicitly wrote

> Reaction speed … can be considered from two points of view. In the first place, we find support in thermodynamics, since the laws that govern speed must be compatible with the laws of equilibrium that settle at the end. In the second place, we can place on the ground of kinetic considerations. We will develop in the order: a) reaction speed and equilibrium; b) kinetics of the reaction. [VAN'T HOFF, 1898, p. 175]

This amounts to saying that thermodynamics, and not mechanics, provides the basic framework in which even models of chemical kinetics are specified. We will see that the approach adopted by Planck in 1900 followed just these steps.

As a conclusion, the overcoming of mechanicism was carried out at the end of the Nineteenth century by the chemists, who did find in thermodynamics a less restrictive and more flexible framework, allowing greater freedom for the development of fruitful and innovative models.

6. The revolution in physics at the beginning of the 20th century: the first break with mechanicism

6.1. *New horizons and tasks*

We are now in a position to analyse the changes in physics at the beginning of the twentieth century. It is important to remark that **so radical a change** as had come about, **could hardly have arisen from a purely internal and autonomous process within the community of the physicists**; in other words, it could hardly have simply derived neither from the complexity of the physical phenomena, nor from a cumulative evolution of concepts, since we have discussed the deep and fruitful potentialities of the nineteenth century approach. Instead, **such a change must have been connected to a radical overturn of formulation and viewpoint, of the concept itself of a physical explanation**, its legitimacy and acceptability: **it must** therefore **have been the result of**, or have been connected to, **more general and deep transformations of the social and cultural environment in which scientists operated**, implying a change in their social role and organization.

We have analysed the peculiarity of the change of the scientific attitude within the chemists community. The delay and specific features of the reaction of the physicists can be attributed to the fact that their involvement in social and technical developments was less direct, and had different characteristics. In advanced societies (Germany, Great Britain, United States) life styles, culture, outlook, production, technology were rapidly changing, and with them even man relationship with nature, the attitude towards natural (and artificial) phenomena. Scientific and technical innovations, such as electricity, the internal combustion engine, telephone and wireless telegraph, oil, new materials, and so on, induced deep changes in habits, the daily way of life, and mentality. Technology appeared as something extremely powerful (one can refer, for instance, to Jules Verne's novels), as it was building an artificial «second nature», interposed with «true» nature, feeding the illusion of a boundless capacity of controlling, subjecting, and exploiting natural phenomena. Science had grown enormously. The number of scientists had multiplied, their role amplified; new scientific institutions had been established, industrial laboratories had developed and their relevance had grown.

The context of natural phenomena was itself also subject to a growing and unexpected pace of renovation, change and enlargement. Many scientists of the old generation were convinced that the «construction» of physical knowledge — mechanics, thermodynamics and electromagnetism— was almost complete, knowledge of nature almost exhausted, apart from some difficulties —such as the problems of aether, irreversibility, the radiation field—, whose solution was to come rapidly. In contradiction with this belief, just at the end of the century, completely new phenomena were being discovered, that did not fall within this context: X rays (1895), radioactivity (1896), the Zeeman effect (1896), the photoelectric effect (1897), the discovery of the electron (1897). The plot was thickening.

In the face of such developments there were, naturally, «conservative» and «innovative» reactions (we recall Planck's words, cited at the beginning). In order to understand the path of the innovators it seems worthwhile, from the methodological point of view, remarking that it implied, in the first place, the overriding of the mechanistic framework, which appeared as an arbitrary and unjustified limitation of the potentiality of possible models and schemes, in order to reach more general frameworks in which more general hypotheses could be freely conceived. This is evident, for instance, for the special theory of relativity of 1905, that will not be discussed here, which in the end retained electromagnetism as correct albeit reformulated mechanics.[11] In any case, in order to give a correct interpretation of the revolution, I consider it important to remark that, as previously mentioned, the overrunning of the mechanistic approach was not an absolute need, from the point of view of physics, in the sense that in its context fundamental advances could have been attained: in other words, I do not share the opinion that the new physical theories were made necessary by the characteristics themselves of the phenomena that were being discovered. **In the evolution of science several alternatives are always possible, and the one that has really been developed does not merely depend on its capability of reproducing the phenomena, but also on more general factors, of a cultural, social, and generational kind**. In the framework of mechanism, the problems of reversibility and recurrence induced important developments [for instance, it was established that the «molecular chaos hypothesis» (2), and therefore the second law, have a probabilistic meaning], and Boltzmann and Paoincaré made significant findings on the behaviour of a dynamical system in the phase space (Poincaré anticipated basic ideas, resumed at present by the so-called «science of chaos» for non-linear systems). That debate, however fruitful it was, broke off at the beginning of the 20$^{\text{th}}$ century. In particular, the formulation of statistical mechanics adopted a different point of view, though several current results in this branch are from many points of view nearer to Boltzmann's position than to Gibbs' (in spite of the extremely important results obtained during the last century, like the theory of solids, semiconductors, and so on).

In the case of electromagnetism, we have recalled that Lorentz's theory of electrons reached results that were equivalent to those of special relativity

[HOLTON, 1976]. It is interesting to note the way in which Lorentz himself discussed Einstein's theory in lectures at Columbia University in 1906:

> His results about electromagnetic and optical phenomena … are in general in agreement with those we have obtained in the previous pages, the principal difference being that *Einstein simply assumes what we have deduced* , with some difficulties and not always in a satisfactory manner, from the fundamental equations of the electromagnetic field. In doing this, he can surely be credited with the merit of showing in the negative result of experiments like those of Michelson, Rayleigh and Brace, not a fortuitous compensation of contrasting effects, but the manifestation of a general and fundamental principle. (the italics are mine) [LORENTZ, 1952]

Actually, Einstein's formulation of special relativity substantially overcame the difficulties in a peculiar way, namely *by assuming as postulates, on the basis of experimental evidence, the very problems that had to be solved*: as it was for the relativity postulate. Einstein's methodological breakthrough is testified to by the difficulties in the acceptance of special relativity abroad (for instance in Britain, GOLDBERG [1970]). «The process by which Einstein's theory was gradually accepted during the latter half of the first decade of the [the 20th] century confirms the importance of the complete emancipation from the mechanistic world-view» [HIROSIGE, 1976, p. 74].

6.2. *The new role of thermodynamics and statistics as a reference framework*

By these considerations I do not mean that everything could have been obtained in the old framework, without the need of the new physics. Rather, the basis of the change lay principally in a new way of conceiving the nature and structure of a theory, and practising scientific activity: in short, the role itself of science was changing. To the «new generation» of physicists, to whom Planck made reference, the purpose ceased to be the search for general representations of the world, along with established methodological criteria (in particular, the mechanical framework). The contradictions with respect to mechanics ceased to bother them, and the most topical problems were set out and solved in the most efficient way and without prejudice (as chemists had already done), leaving aside the fact that the procedures were compatible with the general criteria previously accepted. For instance, calculations in Lorentz's theory of electrons, based on Maxwell's equations plus the one for the Lorentz force, were much more complex than in relativity theory. The latter solves the same problems in a much simpler way, breaking however with Newtonian mechanics. In a similar way, the probabilistic approach adopted by statistical mechanics is simpler than the kinetic approach based on the Boltzmann equation. In general, this change resulted from the *superseding of the reductionist method of «building» the properties of a system through the detailed, dynamic treatment of his components*: this implied at the same time the *overcoming of mechanicism*. In this way, the first step was taken towards the extreme level of abstraction and formalisation reached by quantum mechanics. This methodological change also led in many cases to a shift in problems and formulation.

It is interesting to quote the terms in which Planck some decades later recalled the situation in German theoretical physics at the end of the 19th century and the subsequent change:

> At that time all physicists held the opinion that the future development of theoretical physics would have had as its essential aim the application of the above mentioned principles [Hamilton's least action, conservation of energy, and the second principle of thermodynamics], and nobody thought that to these basic pillars of science others would have been associated, completely different, independent of them, and of the same dignity. [...] apart from the execution in the details, theoretical physics around the end of the past century presented the aspect of an impressive building, compact and solid in itself [...] One easily understands that a physical theory cannot by itself transform its contents, and indeed it will oppose every transformation, with so much greater a force, so much greater its completeness and breadth. [...] Therefore the intervention of strong external forces, incontrovertible results of experimental research were necessary, which compelled to abandoning certain theoretical principles, accepted till then as universally valid, and with this to a basic revision of the whole construction of theoretical physics. [PLANCK, 1930 *a*]

What we have being saying about this change, can be seen in a concrete way in the theories that constitute the core of the revolution in physics at the beginning of the Twentieth century: namely, statistical mechanics, the Brownian motion, special relativity, and the quantum theory. From our point of view, it is important to insist on the *role assumed by thermodynamics in the search for new theoretical frameworks*: the latter was in fact the concrete guide, or at least the source of inspiration, in all these fields of innovation in Physics. In the case of Einstein, his early program of research was based on the atomistic view, its statistical foundation, and the role of fluctuations. As Holton, for instance, acknowledges: «While the three papers of 1905 … seem to be in entirely different fields, closer study shows that they arose from the same general problem, namely, the fluctuations in the pressure of radiation. In 1905, as Einstein later wrote to von Laue, he had already known that Maxwell's theory leads to a wrong prediction of the motion of a delicately suspended mirror 'in a Planckian cavity'. This connects on the one hand with the consideration of the Brownian motion as well as the quantum structure of radiation, and on the other hand with Einstein's more general reconstruction of 'the electromagnetic foundation of physics' itself.» [HOLTON, 1960]. Einstein himself did acknowledge that:

> [Thermodynamics] is the only physical theory of universal content which, within the framework of the applicability of its basic concepts, will never be overthrown. [EINSTEIN, 1949, pp. 32-33]

In this respect, the enlargement and generality of Einstein's conception of thermodynamics are also worth noting, since from the very beginning of his program of research, as we will see, the atomic molecular basis of thermodynamics and its statistical foundation have played a fundamental role (see for instance NAVARRO [1990], especially Chap. II, Par. 5-7; KLEIN [1982]). One should take into account, moreover, that, connecting to a problem which after the discovery by Brown [BROWN, 1828] had remained marginal in eighteenth century physics, Einstein opened a further new field of investigation, really «inventing» [RENN, 2005 *a*] the Brownian motion.

Let us briefly summarize the main features of the innovative fields in physics.

a) *Quantum Theory.* The case of the quantum theory will be discussed in detail in the next sections, where we will see in concrete terms how thermodynamic and statistical considerations played a basic role, offering the most general framework for the elaboration of non-reductionist hypotheses and models, in order to cope with the wider phenomenological context, substantially taking the place played in the past by mechanistic considerations.
b) *Statistical Mechanics.* In the case of statistical mechanics, it is well known that it was formulated in 1902 by Gibbs (whose role in the renovation of thermodynamics we have already seen), but independently by Einstein in three papers between 1902 and 1904 [EINSTEIN, 1902, 1903, 1904]. Although Einstein's formalism was equivalent to Gibbs', there were some very remarkable differences [MEHRA, 1975; EZAWA, 1979; BARACCA RECHTMAN, 1985; NAVARRO, 1991, 1998; ABIKO, 1991; RENN, 2000]. In the first place, from a methodological point of view, Einstein's framework was *thermodynamics*, and his purpose was to lay the statistical foundations of its laws; Gibbs, instead, developed «statistical *mechanics*» as a «wider point of view» with respect to mechanics, when we «imagine a large number of systems of the same nature, but differing for the configurations and velocities that they have at a given time», and we study not indeed «a particular system through its succession of configurations», but rather how «the entire number of systems is distributed between the various possible configurations and velocities» [GIBBS, 1902, p. VII]. «Einstein's theory is more properly called 'statistical thermodynamics', a more general theory than Gibbs' 'statistical mechanics'» [ABIKO, 1991, p. 11].

Einstein's approach, above all, really shows a wider generality. Gibbs, in fact, limited himself to the conclusion that in macroscopic systems fluctuations are negligible, while Einstein explicitly aimed to single out relatively small systems in which fluctuations can be observed, in order to get a confirmation of the atomic structure of matter: it was precisely this attitude that led him to the paper on the random (Brownian) motion[12] [EINSTEIN, 1905 *b*]. As he himself acknowledged:

> My main aim in this was to find facts which would guarantee as much as possible the existence of atoms of definite size. In the midst of this I discovered that, according to atomic theory, there would have to be a movement of suspended microscopic particles opened to observation, without knowing that observations concerning the Brownian motion were already long familiar. [EINSTEIN, 1949, 47]

As far as the 1905 revolution is concerned, we want to stress that *the formulation of statistical thermodynamics, in terms of ensembles, «turned upside-down» the logical structure of kinetic theory*, in a way that was in a certain sense analogous to what we have remarked concerning relativity: *the characteristic thermodynamic function of the system, in a specific state —which in the kinetic approach is «built up» from molecular dynamics— is formally defined by the normalisation of the expression of the abstract probability function, assigned in the G phase space* (see Appendix, *2*). It is important to stress that such a change was made possible by *a substantial shift in the physical problem and approach*: Boltzmann's program, in fact, had started from the *simplest physical system*, namely the rarefied gas, in order to treat its *most general state* (i.e., both equilibrium and non-equilibrium, whence the paradoxes arose); statistical thermodynamics, on the contrary, has attained an absolute generality, namely the power of treating *every thermodynamic system*, at the price of *confining the problem to thermodynamic equilibrium*.

> Einstein's establishment, independently ofWillard Gibbs, of statistical mechanics between 1902 and 1904 was motivated by the quest [...] to extend the methods of the kinetic theory beyond gases to include a vast change of physical systems such as the electron gas in metals and heat radiation, not least in order to provide additional evidence for the atomic hypothesis. The methods he developed imposed only the most general requirements on the systems studied and did not depend on the knowledge of the detailed interaction between the constituents of a system as is the case in kinetic theory, where collision dynamics plays a major role. [RENN, 2005 *a*, p. 29]

This change was polemically acknowledged by Boltzmann himself in a lecture on statistical mechanics in 1904 in St. Louis, commented on by a historian as follows: «One can gather, in the distinction that [Einstein] proposes between statistical dynamics and statics, a criticism as much justified as discreetly veiled: since Gibbs had essentially treated equilibrium states, arriving considerably less far than Boltzmann in the definition of the entropy of a whatever state» [DUGAS, 1959, Part I, Chapt. X].

In return, the generality reached by equilibrium statistical mechanics stands out, for instance, even in the formulation of quantum statistics, since probability density becomes a density operator, having the same formal expression, with a mere change of functions for Hermitean operators (Appendix, *2*). This is obvious since, as we have already remarked, thermodynamic laws are the same independently of the fact that the underlying microscopic system is supposed to obey the classical or the quantum laws. Therefore, since macroscopic probability is defined in a formal way according to the requirement that it has a direct correspondence with the characteristic thermodynamic function of the system, the functional dependence of this probability on the Hamiltonian must remain the same, independently of the fact that the latter is an operator.

c) *Brownian motion*. Proceeding once more from his program of research, and again without reference to previous discovery and work, Einstein at the same time opened a new field of study concerning stochastic processes, and in concrete terms accomplished the atomistic revolution [RENN, 2005 *a*, *c*].

«By 1905, Einstein's views of the observability of fluctuation phenomena had changed. [...] Einstein's invention of the Brownian motion was just as much prepared by his quest to identify evidence in favour of the atomic hypothesis as by the specific research problems he had tackled, in particular, in the course of his long-standing interest in the theory of solutions. Combining a model that had assumed a central role in this pursuit —the model of suspended particles undergoing diffusion in a liquid— with his search for observable fluctuation phenomena, he was naturally led to consider the irregular motion that must be exhibited by such particles.» [RENN, *a*, p. 30].

As Renn remarks, Einstein's «invention» of the Brownian motion stems, as for the whole 1905 triad, from a *conflict* he perceived/noticed, this time between thermodynamics and kinetic theory. His results paved the way for Perrin's demonstration of the reality of atoms [PERRIN, 1908, 1911, 1913; BRUSH, 1976, *2*, pp. 693-701], which led even Ostwald to reverse his opinion.

d) *Special relativity.* The case of this «revolutionary» theory, special relativity, seems at first sight to have had a different conceptual origin and physical motivation, namely that of overcoming a contradiction between Newtonian mechanics and electromagnetic theory. However, over the years several historians have pointed out the influence of *Einstein's thermodynamical thought* in its formulation [HOLTON, 1960; MILLER, 1986; ABIKO, 1991, 2005 *a*]. Abiko's analysis is very detailed, and his main conclusions are:

> … special relativity derives from chemico-thermal studies, promoted as a result of the industrial revolution, and pursued vigorously by Albert Einstein at the start of his scientific career. … Einstein's initial field of independent inquiry was the relation between the thermodynamical macroscopic quantities and molecular theoretical microscopic quantities. He retained this interest in his paper through 1905. … in 1905 Einstein was fully immersed in chemico-thermal research. … The transformation of the concept of time in the formulation of the special relativity can be interpreted as a transition from the absolute mechanical time common to all coordinate systems to the thermodynamical time based on the irreversible transfer of signals. This point is substantiated by the special status of the light velocity in the theory. The light velocity is nothing else but the velocity with which the free energy stored in the light source diffuses into vacuum, that is, the velocity of the most fundamental process of nature, and can be regarded as a more primitive quantity than artificially prescribed space-time coordinates. [ABIKO, 1991, pp. 1, 10, 24]

Such a central role of thermodynamic and statistical inspiration, reasoning and approaches in the origins and the formulation of the basic theories of the revolution in physics at the beginning of the 20th century, confirms that they derived from the overcoming of the nineteenth century mechanistic and reductionist approach. It is interesting to recall that Einstein indicated later on, in his Autobiographical Notes, the two points of view that constituted for him the invariable prerequisite and guiding criteria for the assessment of physical theories in general: they are «external confirmation», in the sense that the theory must not contradict experimental facts, and «internal perfection», consisting of the »naturalness» and «logical simplicity» of its premises [EINSTEIN, 1949, p. 8 Ital. transl.]. From both viewpoints he was criticising mechanics as the foundation of physics [ABIKO, 2005 *b*].

7. Planck's two 1900 papers on the spectrum of radiation

7.1. *The basis of Planck's approach*

Along these lines we are in a position to analyse the birth of the quantum concepts. Planck's contribution in 1900 is commonly mentioned as the earliest introduction of the energy quantum; but in my view its relevance was quite different. In the first place, it is not true that Planck introduced quantisation as a consequence of the failure of Rayleigh's calculation [RAYLEIGH, 1900]: in none of his papers did Planck make reference to such an approach. This fact appears to be logical if one thoroughly analyses Planck's point of view, as we will do.

Without doubt, the radiation field was in those years a very advanced field of research, in connection also with the growth of electric and electromagnetic technology. In Berlin, an advanced research institute in this field (it was situated right in the vicinity of the Institute of Theoretical Physics directed by Planck) the

Technische Physikalische Reichsanstalt, had been established. There were spectacular advances in the construction of instruments of exceptional sensitivity and precision: scientists of the level of Paschen, Lummer, Pringsheim, Rubens, Kurlbaum (the last four performed in 1900 the determinations of the full spectrum of cavity radiation) built up new radiometers, bolometers, photometers, thermopiles, and so on [see for instance LUMMER, 1900; BARACCA, RUFFO, RUSSO, 1979, pp. 243-246].

It is worth recalling that Boltzmann too studied the problem of radiation, obtaining a fundamental result (the Stefan-Boltzmann law). But Planck's approach was completely different, as already mentioned in connection with Zermelo's recurrence paradox (Sect. 3.2). It is interesting to consider how Planck himself recalled this, since his words throw an interesting light on the interpretations of the second principle and their evolution:

> Boltzmann knew that my point of view was fundamentally different from his. He was especially upset for the fact that I was not only indifferent, but in a certain sense hostile towards atomic theory, which was at the basis of all his researches. The reason was that, in that moment, I considered the principle of entropy increase as no less immutably valid of the principle itself of the conservation of energy, while Boltzmann treated it simply as a law of probability. […] Boltzmann answered the young Zermelo in a tone of bitter sarcasm, that obviously was in part directed to me, since Zermelo's paper had been published with my approval. This was the reason of that malevolent tone that, in other occasion too, Boltzmann kept on showing me, both in publications and in our personal correspondence. It was only in the years of his life, when I informed him of the atomistic basis of my radiation law, that he assumed a more friendly attitude. [PLANCK, 1948, pp. 21-22 Italian transl.]

To Planck, therefore, thermodynamics played the most fundamental role, before the atomic structure of macroscopic systems, and the law of the increase of entropy was of an absolute nature. In his treatise on thermodynamics he intended in fact:

«not to place in the first priority the mechanical nature of heat, on the contrary, carefully avoiding the formulation of specific hypotheses on the ultimate essence of heat, to limit starting directly from some absolutely general experimental facts.» [PLANCK, 1911]

Planck had initially studied the energy exchanges between the field and the material oscillators, but he had met difficulties, and had acknowledged that

«I had no other alternative than to resume the problem from the beginning, this time from the opposite point of view, from the side of thermodynamics: here I felt on my own ground.» [PLANCK, 1948, p. 24 Ital. transl.]

We could conclude, therefore, that in 1900 *Planck had already followed, rejected and surpassed an approach of the kind Rayleigh was adopting in his study of the* *spectrum of radiation, concluding that it was unsuitable, as well as Boltzmann's : at that time he was already following a different approach, based on pure thermodynamics, as a guide to finding a solution to the problem of the radiation field.* In this respect, it is very important to remark that there were two papers by Planck in the year 1900 on the radiation spectrum: in the first, which is hardly ever cited, he deduced his radiation formula on the basis of a purely thermodynamic parametrisation, and only in the second, trying to provide a foundation for this successful result, he introduced what is commonly interpreted as the «quantum of energy». We will analyse both papers in detail.

7.2. *The first one of Planck's 1900 papers*

Rubens and Kurlbuam's results in 1900 on the spectrum of cavity radiation contradicted an heuristic exponential formula proposed by Wien, that at that time was generally accepted (as we will see, it constitutes at present the high frequency approximation)

$$u(\upsilon,T)=a\upsilon^{3}\cdot\exp\left(-b\frac{\upsilon}{T}\right)\quad(7)$$

Planck, as we said, had clarified the connection between Wien's formula and thermodynamics: this research had led him to choose as the thermodynamic function to treat this phenomenon the inverse of the second derivative of the entropy *s* of a material oscillator coupled with the field, with respect to its energy *e* [PLANCK, 1899, 1900 *a*; see Planck's reconstruction of these early researches in Planck (1949)]:

$$\left(\frac{\partial^{2}s}{\partial\varepsilon^{2}}\right)^{-1}\quad(8)$$

(we will comment on the physical meaning and the deep implications of such an expression, Appendix, *6*). Obviously, thermodynamics does not specify the form of this function, but Planck had verified that Wien's law (7) corresponded to the simplest, linear, parametrisation (this reinforced the reliance in this formula),

$$\left(\frac{\partial^{2}s}{\partial\varepsilon^{2}}\right)^{-1}=-a\varepsilon\quad\text{(see Appendix, 3).}$$

Planck's procedure is discussed in detail in Chapt. IV of KUHN [1978].

As Planck recalled:

> While I was minutely concerned with this problem, I had the luck that en external circumstance, that I previously felt as disagreeable, that is the lack of interest by part of my colleagues for the direction of my researches, now was on the contrary of advantage for my work, as a sort of facilitation. In fact, a great number of eminent physicists was devoted to the problem of the normal distribution of energy in the spectrum, both on the experimental and the theoretical sides. Everybody however was investigating only in the direction of representing then intensity of radiation as a function of temperature *T*, while I supposed the deeper connexion in the dependence of entropy *s* from energy *e*. Since the meaning of the concept of entropy at that time had not yet found the right appreciation, nobody cared the method that used, and I was allowed to carry out my calculations with complete ease and deepness, without the fear that somebody could disturb or surpass me. [PLANCK, 1949]

When Rubens and Kurlbaum presented their results, showing a discrepancy with respect to Wien's formula, Planck was therefore in the condition of trying other thermodynamic expressions, simply adding higher degree terms to the parametrisation of his function (8): one can remark the generality of such an approach, which in principle can lead to practically every possible kind of physical law. Some days before Planck had learned from Rubens that above 100º C the intensity of the long wavelength components of the spectrum increased linearly with temperature [KANGRO, 1970, pp. 200-206]: his relationship between the entropy and energy of the resonator indicated the presence of a term [KUHN, 1978, note 12, pp. 281-282]. In fact, he could immediately realise that the next, quadratic, parametrisation was sufficient

$$\left(\frac{\partial^2 s}{\partial \varepsilon^2}\right)^{-1} = -a\left(\varepsilon^2 + \gamma\varepsilon\right) \quad (9)$$

and led to a new law for the spectrum, precisely Planck's law (see Appendix, *3*), that he published in this form in his first 1900 paper [PLANCK, 1900 *b*]. In fact, he had immediately communicated his result to those experimenting, and

> The following morning I received a visit from Rubens. He told me that after the meeting, the same night, he had compared my formula with the results of his measurements and had found good agreement in every point. Lummer and Pringsheim too. [PLANCK, 1948, p. 26 Ital. transl.]

The first deduction of Planck's law was thus founded on a procedure entirely based on thermodynamics, and had nothing to do with quantisation. Obviously it was not «deduced» from thermodynamics (which is obviously impossible, as it follows on from Wien's general, thermodynamic law): but thermodynamics provided the reference framework, the most general one, in which to work out the allowed «models». Moreover, it is evident that such a procedure *had nothing to do with a reductionist approach*, as did Rayleigh's one. Planck's words are very expressive in this sense:

> … at last I reached the point of constructing an *absolutely arbitrary* expression for entropy which, though more complicated than Wien's expression, seems to *satisfy with the same perfection every requirement of the thermodynamic and electromagnetic theories*. (the italics are mine) [PLANCK, 1900 *b*]

The absolute independence, besides indifference, of Planck's approach with respect to Rayleigh-Jeans', is confirmed by the fact that the quadratic term alone in parametrisation (9) provides exactly Rayleigh's formula (see Appendix, *4*): but *Planck does not even mention such a possibility*. Anyhow, it is interesting to remark that, from the physical point of view, Planck's law can really be interpreted, in this formulation, as an *interpolation* between Rayleigh's and Wien's formulas, that reproduce respectively the low and the high frequency intervals of the spectrum (fig. 1). We will see more consequences of this interpretation.

Incidentally, in this respect one should remark that even the history of the so-called Rayleigh-Jeans formula was quite different from how it is known and reported by physicists, who reduce it simply to the application of equipartition to the normal modes of the field. Since the present paper is devoted to the turn towards non-mechanistic physics, it will suffice to mention that Rayleigh's paper [RAYLEIGH, 1900] did *not* contain the so-called Rayleigh-Jeans law [KANGRO, 1970; KLEIN, 1962], but only an heuristic modification of Wien's exponential law [KUHN, 1978, pp. 144-152]: actually, Rayleigh had questioned the general validity of the equipartition theorem (Sect. 3.3), and was convinced that that it holds only for long wavelengths. One could observe that really Rayleigh's research between 1900 and 1905 seems more interested in the validity of equipartition, than in the form of the black-body spectrum: he never seems to have had the ambition of establishing a general expression for it, but only an approximation, that he was aware could be suitable «when *?T* is large» [RAYLEIGH, 1900]. In 1905 he concluded that: «[…] this is sufficient to show that the equipartition law cannot be applied in its integrity. […] It seems to me that we must admit the failure of the equipartition law in these extreme cases» [RAYLEIGH, 1905].

7.3. *The second of Planck's 1900 papers*

Only a few weeks later the second paper by Planck appeared, the (only) one which is universally (but superficially) cited, as containing the early introduction of the quantum of energy. After the success of his heuristic procedure, he felt the need to provide a sounder foundation for

> the very simple *logarithmic expression for the dependence of the entropy of the radiant oscillator*, vibrating in a monochromatic way, on its vibration energy. (which derives from integrating eq. (9), see Appendix, *3*; the italics are mine) [PLANCK, 1900 *c*]

(One may remark that he seems to assign a more fundamental meaning to the thermodynamic parametrisation, than to the final law he had obtained). To this end, for the first time he turned his attention towards the statistical concepts, that he seemed to have disdained till that moment, finally acknowledging that «entropy implied disorder». Nevertheless, we will see that his approach could hardly fit into the framework of what was acknowledged at that time as the procedure founded by Boltzmann: but the main departure from it was not his discretisation procedure. Planck, indeed, formally adopted Boltzmann's statistical definition of entropy, eq. (4), but assumed for the probability W, instead of eq. (3), which was naturally associated with Boltzmann's formalism, an expression that nobody among the mechanistic physicists of the «old generation» could accept, nor even understand. Later on, in his talk for the award ceremony of the Nobel prize in 1918, he was to qualify his approach as an «act of desperation» [PLANCK, 1931]. As he himself stated in advance in the paper,

> In the procedure that follows, it will seem to you that there is something arbitrary and complicated. [PLANCK, 1900 *c*]

These remarks are of prime importance in order to interpret the substance of Planck's procedure. In particular, as regards the energy quantum, my opinion is that he did not really introduce it, as a physical quantity. The point is that, in order to apply Boltzmann's fundamental expression (4) for entropy, he had to calculate the number of distinct ways in which the total energy of the oscillators coupled with the field can be distributed among the individual oscillators. The numbers z_n of oscillators of frequency n, $z_{n'}$ of frequency n', and so on, play in his considerations the role of Boltzmann's cells for the gas. Out of the total energy E_t, Planck had to distribute the fractions E among the z_n oscillators, E' among the $z_{n'}$, and so on, with the condition that E_t=E+E'+E''+... . The new problem he had to solve consisted therefore in the division of a *continuous* quantity E among a *finite* number z_n of oscillators: this can clearly be made in an infinite number of ways, with which the statistical counting loses meaning! There was a mathematical technique that was very common at that time: namely, to *discretise the problem, and take the continuum limit at the end of the calculation*. This was just what Planck started to do:

> We have now to divide energy over the oscillators of each kind, in the first place the energy E among the z_n oscillators of frequency n. If we consider E as a magnitude infinitely divisible, the division is possible in an infinity of ways. We however —and this is the most essential point in all the calculation— will consider E as

> composed of a determined number of equal finite parts, and use then the physical constant $h = 6{,}55\cdot10^{-27}$ erg◊s [which, as we will see, is determined by the comparison with the experimental data, note is mine]. This constant, multiplied by the common frequency n of the resonators, gives us the *energy element* e_0 in erg; dividing E by e_0, we get the number n_n of the energy elements which must be divided over the z_n resonators. *When the ratio thus calculated is not an integer, we take for* n_n *an integer in the neighbourhood.* (the italics are mine) [PLANCK, 1900 *c*]

There are therefore serious doubts that Planck's «element of energy» could really be considered as the physical quantum! Such a conclusion is shared by other authors, like KUHN[13] [1978] and ABIKO [2005 *b*]. Planck himself later acknowledged that

> For many years again I always made new attempts of inserting in some way the quantum of action in the system of classical physics. But I did not succeed. [PLANCK, 1949, p. 34 Italian edition, 1973]

The more so, since the mathematical procedure of discretisation was quite common at that time. Boltzmann had regularly adopted it, according to his *finitist* conception of mathematics [DUGAS, 1959, p. 26]: he in fact had posed the problem whether the continuum is more adequate than the discrete to represent reality (quite a real problem, in my view, although it is not usually considered, since we are used to the power of the infinitesimal calculus: the velocities of the molecules of a gas, for instance, are always a discrete set [AGENO, 1992])

> If one considers that in nature infinities only mean a passage to the limit, one cannot conceive the infinite multiplicity of the velocities that each molecule is susceptible to acquire in another way than the limiting case when a molecule receives an ever growing number of velocities. [BOLTZMANN, 1877 *b*]

To Boltzmann, the integral was nothing more than a symbolic notation that expresses a sum over infinite infinitesimal terms: in the early formulation of his kinetic theory each molecule could have only discrete values of the kinetic energy, corresponding to integer multiples of an elementary quantity e, namely e, $2e$, $3e$, …, pe, and so on. In spite of this, we would firmly disagree from every claim that Boltzmann had already introduced quantisation.

Anyhow, there are several surprising «anomalies» in Planck's calculation (probably to be found in every pioneering work). In the first place, after the process of discretisation, *he did not take the continuous limit at the end of his calculation. Nor, although he «formally» adopted Boltzmann's fundamental expression for entropy, did he calculate the most probable distribution*, i.e. the maximum of (4), corresponding to the equilibrium condition between the oscillators and the field. The interpretation of these anomalies is relevant to our analysis. Einstein himself was to remark in his Autobiographical Notes (we will comment further on this):

> Planck got his radiation formula if he chose his energy elements e_0 of the magnitude e_0 = *hn*. The decisive factor in doing this lies in the fact that the result depends on taking for e_0 a definite value, that is to say that one does not go to the limit $e_0 = 0$. This form of reasoning does not make obvious the fact that it actually contradicts the mechanical and electrodynamical basis, on which the derivation otherwise depends. [EINSTEIN, 1949, pp. 44-45]

On the other hand, the finite value of Planck's constant *h* does not represent in itself the quantum hypothesis either: in fact, it is important to remark, with ABIKO [2005 *b*], that «in fact, the value of *h* had already been introduced by Planck into Wien's radiation formula (under the notation '*b*') in his 1899 paper [PLANCK, 1899], that is, *before* the construction of his own radiation formula. Also, it was only in 1906, i.e. after the introduction of the term 'light-quantum' by Einstein, that Planck designated *h* as the 'quantum of action' [PLANCK, 1906, Par. 149]».

As for the second «anomaly», M.J. Klein [1962] has argued that Planck's number W_n (see later) of distributions of the energy elements on the oscillators of frequency n is in fact equivalent to Boltzmann's sum *SW*, i.e. the normalisation factor, in which the contribution of the equilibrium state is overwhelming: such an argument, however valid from a physical point of view, seems historically groundless. It seems evident, instead, that the expression Planck immediately obtained for entropy was just that «very simple logarithmic expression» of his first paper (Appendix, *5*), that he was trying to «justify» (see the first citation by Planck at the beginning of this sub-paragraph): at this point, he was sure that the problem had been solved, and he no longer needed to proceed any further. This is the sole origin of the interpretation of Planck's paper as the introduction of the energy quantum. Thermodynamics was therefore the true framework in which Planck's derivation of his radiation formula was first of all derived, and subsequently «justified», without any prejudicial acknowledgement of the universally recognised formal rules.

There was however one more disconcerting anomaly: Planck, in fact, did not assume, in keeping with what was interpreted at that time as «Boltzmann's theory», the expression (3) for probability, but wrote down, without any justification, an absolutely anomalous expression

$$w = \prod_{v=1}^{k} \frac{(n_v + z_v)!}{n_v! z_v!} \quad (10)$$

He did explicitly acknowledge this a year later:

> In my opinion, this hypothesis essentially corresponds to a *definition of the probability W* (the italics are mine) [PLANCK, 1901]

24 years were to elapse before acknowledging, in expression (10), an approximate form of the Bose-Einstein statistical counting [14] (Planck's discrete «energy elements» are obviously indistinguishable, and do not obey any exclusion principle). Actually, it seems plausible that Planck inferred expression (10) from the expression for the energy of oscillations he had already obtained from (9) in his first paper, and its relation with entropy and temperature, using Stiling's approximation, as usual in statistical calculations [KUHN, 1978, pp. 100-101].

One really has to wonder how physicists familiar with the traditional approach and formalism could have even understood Planck's completely anomalous procedure! The true, and in any case great, value of Planck's papers of 1900 was not, in my opinion, the introduction of the energy quantum, but *the break with Eighteenth century mechanicism and reductionism, the entire procedure in the two successive papers being merely based on a thermodynamic reasoning*. Such a break derived from a deep change in the scientific attitude and in the final aim of scientific activity, namely the search for the most efficient, open-minded solution, that allows the reproducing and «control» of the phenomenon, outside traditional prescriptions, which imposed standard treatments and justifications of a fundamental type. Much later Planck declared:

> It was a purely formal hypothesis, and I certainly did not devote much attention to it: the only thing that interested me, at any cost, was to arrive at a positive result. [PLANCK, 1931]

In fact, Planck was so unhappy with the discrete quantum hypothesis, that his scientific efforts in the following years were devoted to the purpose of getting rid of it: they culminated in 1912 with the so-called «second quantum postulate», in which absorption is a continuum process, while only emission proceeds in a discrete way [PLANCK, 1912]. As it has been observed, «Although Planck was intimately associated with the two major innovations in physics in the 20th century, quantum physics and relativistic physics, he never intended to participate in a revolution in physics.» [GOLDBERG, 1976]. It is important to remark that in his procedure Planck explicitly kept his distance both from the phenomenal and mechanistic approaches, declaring complete freedom in choosing a hypothesis:

> Since the creator of an hypothesis has a priori complete freedom as to the way of formulating it, he has the *faculty of choosing as he wants the concepts and the propositions* [without the constraints of mechanics, this note is mine], provided that they do not contain contradictions. It is not true, as many claim [i.e. phenomenalists, this note is mine], that in posing an hypothesis one has to accept only those concepts whose meaning is a priori rigidly fixed by measures, that is independent of

> any theory. In fact, whatever hypothesis, as a constituent part of the physical image of the world, is a product of *complete speculative freedom* of the human mind. (the italics are mine) [PLANCK, 1930 *b*, pp. 231-232 Ital. transl.].

The logarithm of expression (10) is equivalent to the parametrisation (9) (see Appendix, 5). The average energy of each oscillator turns out to be, in place of equipartition,[15]

$$\bar{\varepsilon}(\nu, T) = \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} \qquad (11)$$

Apart from the issue of the quantum and the break with mechanicism, this paper by Planck presents one more remarkable aspect, that would by itself have made it an exceptional contribution: he was in fact able to calculate the values of an incredible number of universal constants, with a much higher degree of precision than the known values. The black body spectrum depends on the constants h and k_B, whose values he fixed from the fit to the experimental data. One has to note that, although k_B is known as the Boltzmann constant, the latter had never expressed its value, probably because the quantitative aspects of kinetic theory raised the objections that we have discussed. As Planck himself appraised much later:

> Boltzmann did never introduce this constant, neither, as long as I know, never did he think to search for its numerical value. [...] in his calculations he never abandoned the possibility that the kinetic theory of gases represented only a mechanical model. [PLANCK, 1948, p. 27 Ital. transl.]

From the values he had obtained for h and k_B, Planck was able to calculate the Avogadro number, $N_A=R/k_B$, getting the value $N_A=6{,}175\cdot 10^{23}$, much nearer to the current value $6{,}02\cdot 10^{23}$ than the one quoted by Meyer, $6{,}4\cdot 10^{23}$. Finally, knowing the electric charge of the monovalent gram-ion, Planck got for the charge of the electron the value $e=4{,}69\cdot 10^{-10}$ u.e.s., much nearer to the actual value $4{,}8\cdot 10^{-10}$ than that given by J.J. Thomson in 1898, $6{,}5\cdot 10^{-10}$.

Planck's 1900 paper did not raise an immediate debate [KUHN, 1978, pp. 134-140]. It would seem really that, notwithstanding his scientific authority, the majority of physicists could hardly understand, or even take his approach seriously. Only in 1905 did Rayleigh acknowledge «not being able to understand Planck's procedure» [RAYLEIGH, 1905], and Jeans criticised Planck for having arbitrarily chosen the expression for W_n and not having taken the limit for the continuum:

> ... statistical mechanics provides the further information that the true value of h is $h=0$. [JEANS, 1905].

It may be interesting to remark that Jeans, well aware of the agreement of Planck's law with experience, went back to considerations made by Boltzmann, considering that for short-wave excitations of the aether the exchange of energy with material oscillators take an extremely long time, so that these oscillations are not in equilibrium: considerations of this nature have been reconsidered in recent times [CERCIGNANI, 1998].

8. Einstein, 1905: the «light quantum»

Einstein's paper of 1905 [EINSTEIN, 1905 *a*] can really be considered as the introduction of the quantum as a physical entity. Without doubt, its genesis and logical structure were quite different from what is commonly reported in the textbooks of quantum mechanics, in spite of several serious historical reconstructions, to which we have been referring. As we have already pointed out, Einstein's full scientific program in the first years of his career was based on thermodynamic considerations and was focussed on the connection between the macroscopic and the microscopic aspects of matter, including the statistical foundation of thermodynamics, the Brownian motion, and the problem of the radiation field: Planck's paper of 1900 had then immediately attracted Einstein's attention, but from a different and more general point of view [NAVARRO, 1990, Chap. II.3, 4].

> My own interest in these years was less concerned with the detailed consequences of Planck's results, [...] My major question was: what general conclusions can be drawn from the radiation-formula for what concerns the structure of radiation, and even more generally concerning the electromagnetic foundation of physics? [...] Reflections of this type made it clear to me as long ago as shortly after 1900, i.e. shortly after Planck's trailblazing work, that neither mechanics nor electrodynamics (except in limiting cases) claim exact validity. By and by I despaired of the possibility of discovering the true laws by means of constructive efforts based on known facts. [EINSTEIN, 1949, pp. 46-47, 50-53]

As Abiko describes it [ABIKO, 2005 *b*]: «Being unsatisfied with Planck's theory, Einstein's motive for composing the statistical trio [the three papers on statistical thermodynamics, 1902-1904] must have been somehow to construct a general thermodynamics, on which the theory, not only of fluids and solids, but also of thermal radiation could be based. [...] The thread of his thought seems to have been the following. After reading Planck's 1900 paper, Einstein thought that, in order to derive Planck's formula, the resonator energy should be restricted to discrete values. But this means, from the viewpoint of energy conservation, that the energy of thermal radiation itself should also take only a discrete set of values. Therefore, he needed a more direct way somehow to corroborate this inference. This requirement subsequently led him to turn to the Brownian movement of a suspended mirror [in a cavity radiation], that was what he meant by 'a relatively direct method [...] to learn something concerning the constitution of radiation from Planck's formula' [EINSTEIN, 1949, p. 48]». This line of thought was to lead Einstein to his 1907 paper on the specific heat of solids [EINSTEIN, 1907], and that 1909 on wave particle duality [EINSTEIN, 1909].

Let us then analyse the paper of 1905 on light quanta [CASSIDY, 2005]. Einstein did not start from the presumed existence of a threshold in the photoelectric effect, as is commonly reported in the textbooks of physics, but rather he translated his line of thought in a general (he says «formal») requirement, that was based on a radical criticism towards the reductionist attitude: as we have seen, the hypothesis of a corpuscular structure of the radiation field stemmed from the whole range of his considerations made in the previous years, and the threshold in the photoelectric effect was a precise prediction aimed at an experimental confirmation, which was to wait for another 10 years [MILLIKAN, 1916], as Millikan recalled later on

> I spent ten years of my life testing that 1905 equation of Einstein's, and, contrary to all my expectations I was compelled in 1915 to assert its unambiguous experimental verification, in spite of its unreasonableness, since it seemed to violate everything that we knew about the interference of light. [MILLIKAN, 1949]

How did Einstein therefore really proceed? The 1905 paper on light quanta begins expressing one more general requirement of uniformity and generality of the physical description on matter and of the field (the italics are mine):

> A *formal difference* of great importance exists among the theoretical concepts that the physicists have worked out with respect to gases and the other ponderable bodies, and Maxwell's theory of electromagnetic processes in the so-called vacuum. While we can consider that the state of a body is completely determined by the positions and velocities of a very large, although finite, number of atoms and electrons, we make use of continuous spatial functions in order to define the electromagnetic state of a given volume, so that a finite number of parameters cannot be considered sufficient for the complete determination of a state of this nature.

[...] The wave theory of light, which operates with continuous spatial functions, has worked well at the level of purely optical phenomena, and seems really irreplaceable in this field. Nevertheless, it should be taken into account that optical observations refer to time averages more than to instantaneous values; in spite of the total experimental confirmation of the theory of diffraction, reflection, refraction, dispersion, and so on, it still results conceivable that the theory of light, based upon continuous spatial functions, can lead to contradictions against experience when is applied to phenomena of emission and transformation of light.

> In fact, it seems to me that the observations connected to black body radiation, photoluminescence, the emission of cathode rays by ultraviolet light, and other

groups of phenomena connected with the emission and transformation of light, will be much more understandable if we consider them on the basis of the hypothesis that the energy of light is distributed in space in a discontinuous manner. Along with the hypothesis that I want to propose in this paper, when a ray of light expands coming from a point, energy is not continually distributed in a growing space, but it consists in a finite number of energy quanta that are localised in points of space, which move without dividing, and cannot be partially absorbed or emitted. [EINSTEIN, 1905 *a*, p. 132]

Einstein, therefore, did not start from any direct experimental evidence, but from requirements of a very general nature, if compared with those that inspired the majority of the physicists at that time: the «evidence» to which he makes reference emerges instead for him from the line of research that we have discussed. But in the end the very legitimacy of such an hypothesis stemmed from its compatibility with the laws of thermodynamics, to which every development has to conform.

In the 1905 paper not only did Einstein not make reference to Planck' paper, but he did not even consider the full expression of the spectrum of the radiation field, but only Wien's expression (7) for it. Should one speak of luck, or of the numerous successful intuitions on the part of Einstein, since, as we have seen, Wien's expression correctly reproduces only the high-frequency portion of the spectrum, which is exactly the one that properly shows corpuscular behaviour? It seems that he actually realised this just a few years later, just when he acknowledged the simultaneous presence of a wave behaviour beside the corpuscular one! For the moment, it was just on the basis of Wien's law (and for electromagnetic radiation of low density) that Einstein established a common thermodynamic basis for the radiation field and the ideal gas, since in an isothermal transformation

«... the entropy of monochromatic radiation of sufficiently low density varies with the volume in the same form as the entropy of an ideal gas, or a dilute solution.» [EINSTEIN, 1905 *a*]

$$\Delta S_{gas} = Nk_B \cdot \ln \frac{V_2}{V_1} \quad (12)$$

$$\Delta S_{rad} = \frac{E(\nu,T)}{\gamma\nu} \cdot \ln \frac{V_2}{V_1}, \quad (13)$$

that is:

The electromagnetic radiation of low density (in the range of validity of Wien's formula for radiation) behaves thermodynamically as if it were composed of energy quanta, mutually independent, of value $\gamma\, k_B \nu\, N$ [EINSTEIN, 1905 *a*]

It is worth remarking that, since Einstein did not make any reference to Planck's 1900 paper [CASSIDY, 2005], in the above expressions he did not use the constant h: but his conclusion is equivalent to that of Planck's, with $h=gk_B$, as he acknowledged a year later

> [Last year] it seemed to me that Planck's theory of radiation was from a certain point of view opposed to my work. Nevertheless, new considerations … have proved to me that the theoretical foundation on which Planck's theory is based diverges from the principles that would result from Maxwell's theory and the theory of electrons, and really diverges exactly since Planck *implicitly* makes use of the hypothesis of the light quantum … (the italics are mine) [EINSTEIN, 1906 *b*]

Einstein therefore does not acknowledge the introduction of the quantum by Planck! The complete originality of Einstein's procedure and results is generally acknowledged by the historians:

> Anyone who still thinks that Einstein's use of light quanta in 1905 was a generalisation or extension of Planck's theory need only read this paper of 1906 to be disabused of that idea [KLEIN, 1980, p. 171]

> What brought Einstein to the blackbody problem in 1904 and to Planck in 1906 was the coherent development of a research program begun in 1902 [or even before, as we have argued: note is mine], a program so nearly independent of Planck's that it would almost certainly have led to the blackbody law even if Planck had never lived [KUHN, 1978, p. 170-171]

The relative independence and the final convergence of the lines of thought of Planck and Einstein, and the unitary view that inspired mainly the latter in the whole of his research, confirm therefore our interpretation, that at the beginning of the 20th century a deep methodological and practical renovation of scientific practice was introduced into physics, which at the same time made a distinct break with the 19th century attitude, and brought to an end the change that had been carried out with the introduction of models. Obviously, such a renovation concerned only «the new generation» among the physicists, and not without some residual difficulty, given the early stage in the development of the quantum concepts. Einstein's paper received less attention than Planck's, probably given the authority of the latter, and the fact that his assumption apparently dealt only with the exchanges of energy with the material oscillators, and did not seem to imply a radical revision of Maxwell's electromagnetic theory [NAVARRO, 1990, Chap. II.4]. Millikan insisted on the groundlessness of the quantum hypothesis, in spite of his experimental confirmation of Einstein's predictions. Einstein himself met some difficulties in reconciling the light quantum hypothesis with the wave theory of light, as he acknowledged with some caution at the 1911 Solvay Conference and on other occasions:

> I insist on the provisional character of such a concept, which does not seem reconcilable with the experimentally verified consequences of the wave theory. [EINSTEIN, 1911, p. 443]

The point is that the methodological and practical renovation had been fulfilled at that stage, as seems obvious, only in a partial way: the new breaking off, in fact, stripping the physical models of the residual and unjustified ideological limitations, and legitimising complete freedom in the kind of assumptions and procedures, allowed exploitation of the full potentiality of the new method. Such an innovation implied also a further jump in formalisation and abstraction. Such an evolution went on, contradicting in the end even Einstein's methodological criteria, parallel with the further changes of the social and economic situation, and of the related role of science.

9. Specific heats, third principle of thermodynamics and the wave-particle duality

After this detailed analysis of the early introduction of the quantum as a physical entity, we will review, only briefly, however, some of the further steps of the old quantum theory.

9.1. *Einstein's paper on the specific heat of solids*

The treatment that Einstein proposed in 1907 for the specific heat of solids was a further step forward in his program of research [HERMANN, 1967]. What was in fact the real reason for such a treatment? Once more it was not an experimental reason. At that time there was no evidence that specific heats decreased at low temperatures: the physics of low temperatures had not yet been developed, and in the range of temperatures in which one worked, specific heats seemed to be more or less constant: we will see that it was precisely on the basis of Einstein and Nernst's research that the behaviour of specific heats at decreasing temperatures was investigated, and low temperature physics began to be developed.

We have remarked that Einstein's program dealt with the whole range of problems regarding both material bodies and the electromagnetic field. His previous results concerning the latter indicated that the average energy of the oscillators is not kT, but is given instead by eq. (11). This fact left an «asymmetry» with respect to the procedure adopted in statistical thermodynamics for calculating the specific heats of material bodies: Einstein in fact supplied a different proof of eq. (11), «that clarifies its relationship with molecular mechanics» [EINSTEIN, 1907].

> If the elementary oscillators that are used in the theory of the exchange of energy between radiation and matter cannot be interpreted in the sense of current

> molecular kinetic theory, should we not probably modify also the theory for the other oscillators that are used in the molecular theory of heat? In my opinion, there is no doubt about the answer. [EINSTEIN, 1907]

To this end, Einstein considered a homogeneous solid, composed of identical atoms, and assumed that the latter all have the same frequency of oscillation: applying eq. (11), he got the well-known expression for its specific heat, that shows a decrease at decreasing temperatures, vanishing (*exponentially*) at $T = 0$. As we said, at that time no experimental result was available to confirm such behaviour. From now on, the development of the quantum theory was interlaced with that of the third principle of thermodynamics.

It is however interesting to remark that Einstein drew other interesting consequences from this result, that confirmed his criticism toward the classical theories. The lightest atoms should vibrate with higher frequencies than the heavier ones at the same temperature: this would justify the lower value of the molar heat of the light elements, in contrast with the results obtained from the theorem of equipartition of energy. Moreover, supposing that the vibrations that contribute to the specific heat include also the frequencies that are measured in optical absorption by solids, he estimated that the contribution of vibrations to the specific heat starts only when the wavelength for optical absorption surpasses some micron, and only above 50 micron (in full infra-red) the value of equipartition holds: the estimates of the absorption frequencies he obtained in this way, were in agreement with the results available at that time.

9.2. *The third principle of thermodynamics*

We will not discuss in detail the scientific trajectory that led Nernst to the third principles of thermodynamics [HIEBERT, 1978; BARACCA, RUFFO and RUSSO, 1979, Chap. IX-4]: what we wish to point out is that it concretely represented the confluence of the method introduced at the end of the 19th century by chemists (see Par. 5) with the new approach just inaugurated by physicists. In fact Nernst, as we have recalled, was a chemist, engaged in the problem of the determination of electrochemical equilibrium (besides German chemical warfare), with relevant industrial implications: the production of sodium, phosphorus, aluminium [JOHNSON, 1990, pp. 31-33, 44-47]. As already mentioned, he was also concerned with the problem of ammonia synthesis.

> … by 1905 Fischer, Ostwald, and Nernst wished to improve Germany's competitive position in science and industry, particularly by promoting research in increasingly significant areas outside classical organic chemistry. [JOHNSON, 1990, pp. 39-40]

Apart from details about his research [NERNST, 1907, 1969; BARACCA, RUFFO and RUSSO, 1979, pp. 225-236], Nernst realised [NERNST, 1906] that the *arbitrary additive constant* in free energy was reflected by an *arbitrary multiplicative constant* appearing in the expression of the equilibrium constant [Appendix, *1*, eq. (a)], and this prevents the determination of its absolute value starting from thermological data: this conclusion convinced him that *space was left in thermodynamics for a third principle which univocally determined the values of the chemical equilibrium constants* (that is, in principle, since the calculations are quite complicated). Later on he wrote:

> The full content of thermodynamics is exhausted by the new principle, which eliminates the indeterminacy resulting from the presence of an indeterminate additive constant in every particular case of application of the second principle. [NERNST, 1923, Vol. 2, p. 356]

Nernst realised that the most direct consequence of the third principle was that specific heats should vanish at absolute zero temperature, and so started taking out measurements at decreasing temperatures, that confirmed at least the decreasing of the specific heats (although he was very far from absolute zero). At the same time he realised that Einstein had proposed a physical model predicting precisely such behaviour (moreover, we could probably add, with an approach that was homogeneous to the one chemists had adopted). He thus turned into an advocate of the new quantum theory, so that he inspired and organised the 1911 first Solvay Conference in Brussels. On that occasion, Jeans and Rayleigh (though the latter was not able to participate) were the only ones who supported the old classical theories and approach. That «new generation convinced of the new ideas» had come into being, accepting and applying full freedom in working out physical hypotheses and formal developments, beyond any restriction, such as those set by mechanism and reductionism, and was really opening new fields, phenomena, and physical frameworks.

9.3. *The wave-particle duality*

In 1909 Einstein's scientific program, started around 1901, led him [EINSTEIN, 1909] to the calculation of the energy fluctuations of the electromagnetic field, *considering the entire spectrum of cavity radiation*, and to the conclusion that they were composed of two terms, corresponding respectively to fluctuations in a *system of particles*, and in a *system of waves* [KLEIN, 1964]. It seems interesting, from our point of view, to remark that this result, i.e. the wave-particle duality for the electromagnetic field, was formally implicit in the parametrisation (10) used in the first of Planck's papers of 1900, since *the thermodynamic function (8) corresponds just to the mean square average fluctuation of energy* (Appendix, *6*).

10. Outline of the path followed, up to «orthodox» quantum mechanics

Our conclusion is that Planck introduced in 1900 the first non mechanistic approach in physics, although with considerable uncertainty: but it was Einstein who took the decisive step that turned the superseding of the reductionist attitude into a real, new method, capable of reaching completely new physical results, up to the novelties in the natural processes that technical progress was showing.

We will no longer follow in detail the subsequent path that led to the formulation of quantum mechanics (QM), but we will add some comments in order to compare these further developments with the early steps we have thoroughly examined, and to assess the further changes that it implied [BARACCA, LIVI and RUFFO, 1979-80; DONINI, 1982]. Einstein's opposition against the «orthodox» formulation of QM is well known: but from what precisely did it stem?

10.1. *Industry and science in the «melting-pot» of the Weimar Republic*

The process of abstraction and formalisation was further intensified in the following decades. Without denying the peculiarity of the scientific process, there were quite evident connections with social and economic evolution. The transformations brought about by the Second Industrial Revolution were in full development, with dramatic events, and the world was far from reaching a stable and well-balanced structure: the economic, social and cultural landscape was changing [ROHRLICH, 1992; VON MEYENN, 1992]. The conclusion of the First World War opened in effect a phase of deep instability that was to lead to the 1929 Depression. Germany, still maintaining the leadership in the scientific field, went through an extremely tormented period. The Weimar Republic, with its contradictory and dramatic history, and its tragic final outcome, was a real «melting pot», in which advanced and innovative solutions were proposed and experimented, while at the same time it sowed the seeds of future dictatorship. There were strong enlightened and progressive trends, both in politics and in economy (as well as in the arts, such as the experience of the *Bauhaus*), that attempted a *rationalisation* of the whole system, anticipating paths that were to be developed in subsequent decades. Yet, German society was crossed by deep contradictions, and was characterised also by strong *irrational attitudes*, that were exasperated by the defeat of the country in the First World War and the further frustration for the humiliating conditions imposed on Germany by the peace treaty. Arnold Sommerfeld in 1927 in one of the most prestigious of the South German monthlies:

> The belief in a rational world order was shaken by the way the war ended and the peace dictated; consequently one seeks salvation in an irrational world order. [SOMMERFELD, 1927]

In such a situation, the excellence of German science became an even stronger factor of pride and national redemption. We have already noticed the peculiar relevance that industry and science had played during the formation of the German empire, as substitutes for power and national identity: the new dramatic events reinforced such an ideology. Already, on October 3 of 1914, an «Appeal to the Civilised World» from German intellectuals, exponents of the Arts and Sciences, had been thrown out, proudly denying German responsibilities in the war (among the total of 93 signatories were the physicists Philip Lenard, Walther Nernst, Max Planck, Wilhelm Roentgen, Wilhelm Wien; the chemists Adolf Baeyer, Carl Engler, Emil Fischer, Fritz Haber; the mathematician Felix Klein; the zoologist Ernest Haeckel). After the war Planck wrote (many more similar authoritative declarations can be found):

> If the enemy has taken away every defence and power from our mother-country, if the heavy internal crisis has fallen upon us and perhaps even heavier crises are awaiting us, there is one thing no external or internal enemy has yet taken away: the position that German science holds in the world. [PLANCK, 1918]

While Fritz Haber (who tried to extract gold from sea water with the purpose of relieving the burden of war reparations) asserted:

> The collapse of the country as a big political power will remind us imperiously for today and tomorrow, that our existence as a nation depends on the state of great scientific power, which is inseparable from our scientific activity and organisation [HABER, 1921]

The old regime was blamed for losing the war by not listening to its industrialists and scientists. The Weimar Republic actively promoted science; the scientists constituted scientific committees with the aim of resuming and promoting research activity. Scientific development was supported also for material reasons, since, in actual fact, German industrialists had made very good bargains during the war, and they needed to invest their capital: the Weimar Republic lowered taxes and made investments in the scientific field easier. An important feature of the financing of scientific research in the Weimar Republic was that it was no longer directly finalised towards productive purposes, but granted the privilege to long term research programs, which dealt with general, far-reaching problems with sharper ideological implications.

Atomic physics was particularly boosted. Internal competition among scientific institutions also developed. Berlin was denounced as the centre of the betrayal of national pride, and of the Jews (Einstein was the director of the Kaiser Wilhelm Institute in Berlin). In the peripheral seats a nationalistic, chauvinist, and anti-Jewish spirit developed. In fact, the heart of the development of «orthodox» QM was Göttingen, alongside Copenhagen. Two different scientific organisations were established in the early twenties, the *Helmholtz-Gesellschaft* (HG), and the *Notgemeinschaft der deutschen Wissenschaft* (NGW), in response to different, and sometimes conflicting interests [SCHROEDER-GUDEHUS, 1972; FORMAN, 1973, 1974 *a*]. The NGW was created in environments close to the government, and was suspected of supporting the scientific milieux of Berlin: Carl Duisberg and especially Fritz Haber played important roles, but the chief source of funding came from the federal government. The HG gave the bulk of its financial support to the experimentalists and non-Berliners, and was strongly influenced by the anti-Berliner and anti-semitic positions of Lenard and Stark (both Nobel laureates). Funds were directly assigned with preference to research programs of single investigators, within a policy of self-government of the sciences.

10.2. *The formulation of «Orthodox Q.M.» as a turning point*

It was in such a tormented social and cultural environment that so radical a choice as the «Orthodox» (or «Copenhagen») formulation of QM ripened and materialised, carrying the process of formalisation and abstraction to its furthermost consequences. Detailed studies have established a direct connection between such an evolution and the irrational intellectual and cultural climate in Germany, opposed to both materialism and positivism, going beyond the determinist approach in science, and interpreting the introduction of an a-causal attitude as an adaptation of the physicists to this ideology [FORMAN, 1971, 1973, 1974 *a* and *b*]. Thus, for instance, Hoffding, one of Bohr's university professors, was a disciple of the philosopher Kirkegaard [ROSENFELD, 1963; JAMMER, 1966, pp. 166-180]. The influence of the idealistic and anti-deterministic philosophy has been shown on the young Heisenberg. As a sort of counterbalance, the same author has shown [FORMAN, 1978] that in Britain, on the contrary, irrational positions were not at all widespread until the end of the 1920s, whereas a strongly positive evaluation of physics and an increased confidence in, and respect for science as a practical and ethical discipline predominated: such an anti-irrational spirit, in which anti-determinism and aversion to causality were not characteristic of the intellectual milieu, explains for the author the disinclination of British theoretical physicists to alter the epistemological bases of their discipline in a radical way, and abandon causality as a cardinal feature of the new physics.

Without doubt, the turning point constituted by QM cannot be reduced only to social, economic, or cultural influences: nevertheless, it can hardly be explained as a purely scientific choice. An indirect confirmation is given, in some sense, by the influence that QM in turn played on culture and art [ROHRLICH, 1992]: in 1932 Schrödinger delivered at the Prussian Academy of Science, in Berlin, a speech entitled «Is nature conditioned by the environment?», in which he asserted [VON MEYENN, 1992, pp. 214-215]:

> … we all form a part of this cultural environment. Since the planning of our interest plays a role in something, the cultural environment, the spirit of time, or whatever one wants to call it, will exert an influence. In every aspect of a culture common ideological features are found, or, with even more abundance, common stylistic features, in politics, as in art and in science. If one succeeds in finding them also in exact science, one will have a sort of proof of evidence of its subjectivity and its dependence on the cultural environment.

Schrödinger went on to give concrete examples, such as the relationships between the philosophy of the observable and the elimination of the classical description and the «new functionalism» in art; the abandonment of classical causality and the tendencies towards subversion and anarchy in his epoch; the renouncing of detailed spatial-temporal knowledge and the diffusion of statistics in public administration; the synthesis of abbreviated symbolic formalism and the search for suitable ways of managing large masses, both in terms of human beings and in industrial production.

Generally speaking, the problem of controlling the increasing instability, both economic and social, of such a complex reality, which seemed to contradict the inexhaustible pace of economic and technological growth, posed the need of more flexible and effective control tools. In effect, everything seemed to be getting out of control causing instability, from monetary chaos and inflation, to economic and social disorder (in 1920 the Red Army reached the gates of Warsaw, and the spectrum of communist revolution reappeared), as well as labour unrest and growth itself, which generated an overproduction crisis. *The shift from a rigid organisation of labour towards productive rationalisation, based on the statistical correlation of an increasing flux of money, products and goods (including the labour force), was a general trend and a real need.* The adoption of the Scientific Organisation of Labour, embodying methods of psychology and psychological techniques, tended to establish a form of «social technology», aimed at the coordination, correlation and control of multiple factors [DEVINAT, 1927].

The most exact among natural sciences was the most suitable for subsuming such goals, and incorporating them into a formal structure. Actually, it can be noted that this process went on in parallel with the crisis of the «Hilbert program» of a self-consistent formulation of mathematics, caused by Goedel's theorem.

The further shift of QM, from the point of view of our analysis, can be synthetically characterised as follows. Planck, and in a most deep and systematic way Einstein, had broken away from the Eighteenth century mechanistic and reductionist approach: the latter, nevertheless, *maintained the requisite that physical processes had to be described in their continuous evolution in space and time*. Einstein developed his point of view in the decades that followed, in search of a unitary, spatial-temporal physical description, together with Hopf, Stern, Nernst [BERGIA, LUGLI, ZAMBONI, 1979, 1980; BERGIA, 1988 *a*; BERGIA, NAVARRO, 1988; BERGIA, FERRARO, MONZONI, 1985]. The fundamental contributions of Schrödinger [FORMAN and RAMAN, 1969; DE MARIA and LA TEANA, 1982 *a*, *b*; JIMÉNEZ, 1993] and de Broglie enriched this line of research: in particular, Schrödinger's equation was originally developed by its author with the purpose of describing the wave properties of matter, and the ÔYÔ? in his original interpretation represented the «density of matter», and not probability. In this philosophy, there were not «quantum jumps», but the transition, for instance of an electron, had to be described as a continuous evolution in space-time, although not in the old mechanical way.

The next «generation» of physicists, who worked out the «orthodox formulation» of QM, felt instead such a requirement, albeit a concrete and somehow intuitive physical one, to be a further limitation, and got rid of it, explicitly abandoning every continuous description in space and time: *the exponents of this new generation conceived in fact the physical description of the atomic systems as a mere correlation among the possible states of a system, which could not be further specified*. Even the previous reference to thermodynamics and statistics was abandoned as the basic guide, in order to reach even more general and abstract frameworks and a larger freedom of formulation. *The rejection of any kind of physical, spatial-temporal representations, and the limitation of the structure and purpose of the theory to the establishment of correlations between experimental facts,* (*i.e. results of measurements*, the philosophy of *observables*), *constituted the basic choice in the «orthodox formulation» of QM*: a probabilistic basis for such a correlation appeared to be a more flexible and effective structure than the quest for an evolution in spatial-temporal terms. Such a turn started early with the Bohr model of the hydrogen atom[16] [BOHR, 1913], in which he explicitly declared:

> It is evident that I am not in any way trying to provide what is commonly defined as an explanation: in fact, nothing has been said as to how and why radiation is emitted. [BOHR, 1913]

In 1927 and 1929 respectively he explicitly stated [BOHR, 1961, p. 337] (statements of the same content grew in subsequent years; in Heisenberg, statements of even more subjective content are found):

> … no exact description of the spatial-temporal behaviour of the processes is required.
>
> We are here so far from a causal description, that we should attribute in general to an atom in a stationary state the possibility of free election among different transitions to other stationary states.

Einstein's reaction in a letter to Max Born in 1924 sounds openly sarcastic:

> Bohr's opinion about radiation is of great interest. But I should not want to be forced into abandoning strict causality without defending it more strongly than I have so far. I find the idea quite intolerable that an electron exposed to radiation should choose *of its own free will*, not only its moment to jump off, but also its direction. In that case, I would rather be a cobbler, or even an employee in a gaming-house, than a physicist. (Einstein's italics) [EINSTEIN, 1924]

The divergence appeared as radical and incurable, as it was based on *a priori* election on what has, or has not to be a scientific explanation, rather than on objective scientific elements. O. Klein remembers that Bohr, in turn, «could not resign himself to Einstein's concept of the light-quantum»[17] [ROZENTAL, 1967, p. 77]. On the other hand, Schrödinger attributed a reality only to waves, that he interpreted as matter waves [DE MARIA and LA TEANA, 1982 *a*, *b*], and, as late as 1952, denied the existence of quantum jumps. In 1925 Bohr invited him to give a seminar in Copenhagen, and subjected him to a real «brainwashing» in order to «convert» him, so much so that the poor Schrödinger fell sick (reported by Heisenberg, in ROZENTAL [1967], pp. 103-104). Much later Bohr asserted that «Schrödinger has remained completely isolated».

We can conclude therefore that the final formulation of QM matured over a deep divergence, and created incurable contradictions. For many years the two points of view coexisted, and brought fundamental contributions: so that it seems to me that, from a purely physical point of view, the final outcome was not foreseeable *a priori*. In this respect, it could be sufficient to recall as examples some fundamental papers by Einstein in 1916-17 in which, in order to analyse the nature of radiation on the basis of general requirements, he introduced new and fundamental aspects of the interaction between radiation and matter (see for instance: BERGIA [1988 *b*], NAVARRO [1988 *b*]): his reasoning was still based on *statistical thermodynamics*, namely, on the need to make the laws of radiation compatible with Boltzmann's distribution law for matter. Essentially, if one takes into account ordinary processes of absorption and (spontaneous) emission, one falls back on Wien's law (7): in order to make Planck's law compatible with Bohr's absorption and emission mechanisms and the statistical distribution of the energetic levels of atoms, it is necessary to introduce a new process of *stimulated emission of radiation*, which has since become the basis for the laser (Appendix, *7*).

It is important to remark that this contribution by Einstein opened the way for solving a problem that had been left open in Bohr's model, namely the calculation of the intensity of spectral lines. Einstein indicated the magnitudes that had to be evaluated, i.e. his coefficients A_{12} and B_{12}, and —treating the numbers N_1 and N_2 on a statistical basis (Appendix *7*)— the latter were the amplitudes of the *transition probabilities*. So that, quite ironically, it was Einstein who introduced probabilistic considerations! However, *he considered such a hypothesis as temporary, while, on the contrary, it was converted into the basic tool for the «orthodox» school*. It is worth remarking, on the other hand, that the corpuscular concepts of radiation remained alien for the majority of physicists until 1923, when Compton interpreted in corpuscular terms the dispersion of X rays by atoms.

The «spatial-temporal philosophy» achieved more fundamental results. In 1924 L. de Broglie proposed the idea that «any body in motion can be accompanied by a wave, and that it is impossible to separate the motion of the corpuscle and the propagation of the wave». It is well known that the stationary condition for a wave on an «orbit» is equivalent to the Bohr-Sommerfeld quantisation condition. It was the ideas of de Broglie and Einstein that inspired in Schrödinger the complete formulation of *wave mechanics for material particles*: it was a classical equation for the wave properties of matter, in which the stationary states of the atom are proper values associated with a partial derivatives differential equation, whose solutions determine the *density distribution of the electron charge* as the square modulus of the wave function. Along with Schrödinger, therefore, his equation would directly treat the *spatial-temporal evolution* of matter, while in the «orthodox» formulation the interpretation is indirect, since the wave function becomes an abstract entity, merely related to a probability. The divergences of Schrödinger with respect to the Göttingen-Copenhagen school may be synthesised in three points [DE MARIA and LA TEANA, 1982 *a*]: *i*) quantum discontinuities versus continuum; *ii*) probabilistic interpretation versus «realistic» interpretation of the wave function; and *iii*) mathematical «equivalence» and physical «inequivalence» of matrix and wave mechanics. Schrödinger's theory was completely satisfactory to the physicists of Berlin, since it always worked with continuous functions, instead of the disagreeable matrix mechanics and Bohr's philosophy. Einstein, the creator of the light-quantum hypothesis, had written to Max Born:

> I myself do not believe that the solution to the quanta has to be found by giving up the continuum. […] I believe now, as before, that one has to look for redundancy in determination by using differential equations so that the *solutions* themselves no longer have the character of a continuum. But how? (the italics are of Einstein) [EINSTEIN, 1920]

As a confirmation of the fact, already cited, that the ideological climate in post-war Britain was different, it has been shown [DE MARIA and LA TEANA, 1982 *b*] that «Dirac was much less disposed than his German colleagues to abandon a spatial-temporal description of microscopic phenomena and that he struggled to construct the new QM as a *generalisation* of (and not a *break* with) classical physics, through a systematic utilisation of the classical Hamiltonian formalism [...] Dirac always remained fairly indifferent —when not actually hostile— to the epistemological pillars of the 'orthodox' interpretation (to begin with the 'correspondence principle' and subsequently the 'uncertainty principle' and 'complementarity'). He began to utilise Schrödinger's wave formalism without any problems; and in doing so he initially departed from Born's probabilistic interpretation, as an unavoidable and necessary one for the new QM, maintaining that it was not the 'ultimate description' of the world [DIRAC, 1927]. [...] even when, in October 1927, at the 5th Solvay Conference, Dirac was converted to the probabilistic interpretation, he still deviated significantly from the Göttingen-Copenhagen physicists regarding metaphysical foundations of that interpretation.»

In spite of the successes of the old school of thought, in those same years the situation was reversed. We will not carry further here the analysis of the birth and development of the «orthodox interpretation» of QM, in terms of probability amplitudes.

Later on Heisenberg wrote (the italics are mine):

> Propagation, absorption and emission of light are *experimental facts* which have to be posed at the basis of any attempt of clarification, and *not explained* ... Waves have a probabilistic nature, *they do not represent reality in the classic sense, but rather the «possibility» of such a reality.* Waves define probability in every point that an atom emits or absorbs: energy is not conserved in the elementary processes, and is valid for statistical averages.

Actually, QM *has rejected any reference to the spatial-temporal evolution of the state of the system, and limits itself to establishing correlations, in probabilistic terms, between experimental events and observable quantities (frequencies, transition probabilities), based on non-commutative algebra.* The two points of view turned out to be incompatible, in the first place for the incompatible positions of their respective authors, who held opposite concepts about what reality is, and what science describes. Heisenberg wrote in a letter to Pauli: «The more I weigh up the physical part of Schrödinger's theory, the more horrible it appears to me»; while to Schrödinger Heisenberg's theory «Made me depressed, not to say that I was repulsed by a rather difficult method of transcendental algebra, that defied any visualization».

It would be interesting to investigate and discuss the way in which QM —born in a society full of tensions and contradictions, which were to explode into the crisis of 1929 and a totalitarian regime— has constituted the basis for subsequent scientific developments. In fact, the contradictory tendencies of Weimar society were to develop subsequently, on the one hand into Nazi totalitarianism (current trends have identified «modern tendencies in Nazism, such as the increasing intervention and control of the State in the economy), on the other into American society (where the most qualified exponents of German culture and science had fled). The response to the 1929 crisis and to the subsequent depression began with Roosvelt's *New Deal*, but was fully developed later on, after the Second World War. In order to prevent the recurrent «deadly vocation» of capitalism, a mechanism of growth was to develop, in which the innovation and creation of new branches were so rapid and continuous as to satisfy a rate of consumption such that any overproduction crisis was avoided.

With such dynamics, the role of scientific theory deeply changed: it no longer consisted in providing general representations of the world, but rather, and more simply, the most flexible frame of reference, such that it did not limit at all, but rather stimulated the most free of developments and the search for the most practical and direct solution, being applicable to whatever problem. In the framework of the late 19th century, mechanism had constituted in some sense the concrete ground for the control of the conceptual and practical development of scientific branches: nevertheless, with the change of social conditions, it was transformed into a framework of unacceptable limitation for scientific investigation. The first step was, therefore, the debunking of mechanicism, and resorting to more general frameworks, in which more general and free scientific hypotheses could be elaborated. At the end of the process, parallel to the outcomes of the social crisis, QM has provided the ideal basis: its absolute flexibility, related to its level of abstraction, offered a common, formal basis both for extreme formal developments, and for the proliferation of specialised branches, that characterised scientific development beginning from the 1930s, and especially after the Second World War (nuclear physics, , solid state physics, electronics, quantum electronics, astrophysics, cosmology, biophysics). It may be useful, in this sense, to remark the methodological analogy between the planning of QM and Norbert Wiener's information theory: information too is considered and formalised disregarding its specific content and meaning, with respect to the sender and receiver. This is shown, for instance, by the convergence of Wiener's and Von Neumann's ideas [MONTAGNINI, 1999-2000, 2002]. The increasing need to control a growing flow of data of different nature can be considered as the concrete factor that may have led to the common choice of an extremely flexible treatment, establishing a merely formal connection between them, regardless of their intrinsic meaning and function.

Such developments went far beyond Einstein's philosophy, so much so that they strongly contradicted his realistic attitude, and received his firm opposition: nevertheless, they took root in the step that he took just one century ago. The methodological and practical break that he brought about, actually opened a new frontier in the development of science, in the canons of its elaboration and practice, that, with the further evolution of the complexity of the social and economic situation, could not be contained within the boundaries traced by Einstein. Every true revolution goes far beyond the ends and the conception of its authors.

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NOTES

1. Unlike the majority of his contemporaries, Sommerfeld saw Boltzmann as the nimble bull-fighter.
2. One may remark that actually scientists made use of hypotheses all the same, though they were not considered as such, but as something «natural», since they expressed common concepts, largely acknowledged paradigms, or in general the mentality of that time: some examples are Sadi Carnot's «hydraulic analogy» [BARACCA, 2002], imponderable fluids, action-at-a-distance *vs.* action-by-contact. See for instance: SCHOFIELD [1970], ROSSI [1973, 1974].
3. Actually, two physicists had previously proposed the kinetic model, but times were not ripe: Herapath and Waterston submitted two papers for publication in the *Philosophical Transactions of the Royal Society*, but Davy rejected both [BRUSH, 1965-1972, *1*, 14-19]. Herapath resorted to publishing his paper on a journal of philosophy [HERAPATH, 1821], but it received little notice until 35 years later, after the papers by Joule, Krönig, Clausius and Maxwell. Waterston's paper was read to the Royal Society in 1946, and an abstract was printed, but the paper was not published, and remained in the Society's archives and was generally unknown until 1892, when Lord Rayleigh discovered and published it [WATERSTONE, 1893] .
4. S. G. Brush has published important contributions on the history of the kinetic theory. The first one [BRUSH, 1966] contains the English translation of many original fundamental papers on the subject. The second one [BRUSH, 1976] contains a detailed historical reconstruction of the development of the theory.

5. A thorough historical and critical reconstruction of Boltzmann life, scientific production and methodological positions is given by CERCIGNANI [1998].
6. «It was Mach who, in his *History of Mechanics*, shook off this dogmatic trust [that mechanics is the basis of physics]: his book, when I was young, exerted a deep influence on me» [EINSTEIN, 1958].
7. The advantage of the US consisted mainly at that time in its enormous natural and human resources, although the country had started a marked industrial development after the War of Secession (1861-65): the true technological take off of the country was prompted by the First World War. Germany stayed weaker with respect to England in the aspects of the financial resources, the colonial empire, as well as in the sea trade, as it turned out during the First World War.
8. The main reference for the analysis we are developing is, as we have said, the work of LANDES (1965, 1969).
9. For instance, at 600º C the reaction proceeds through a chain of binary collisions leading to partial dissociations and associations
   $H_2 \rightarrow H+H$, $H+O_2 \rightarrow OH+O$, $O+H_2 \rightarrow OH+H$, $OH+H_2 \rightarrow H_2O+H$.
10. Carnot's theorem already states that the efficiency of the ideal engine does not depend on the fluid on which it works. Carnot had obtained this result in 1824 on the basis of the theory of caloric fluid [BARACCA, 2002]: after Joule's results in 1842-48, Kelvin remarked the apparent contradiction with Carnot's assumption, and in a series of papers in 1849-51 he and Clausius concluded that Carnot's results were in fact independent from such an assumption (the latter is in fact equivalent to an entropic reasoning, see the cited paper by Baracca), and arrived at the second principle of thermodynamics.
11. I must mention a relevant aspect, that could seem to be in contradiction with my analysis, that is to say the role on Einstein's scientific path of Mach's ideas, which we have qualified as an exponent of the resistance against the new method. Einstein writes in fact in his autobiography: «It was Mach who, in his *History of Mechanics*, shocked this dogmatic faith [in mechanics as the basis of physics]: his book, when I was young, had a deep influence in me» [SCHILLP, 1970, p. 12]. Later on, in his research on gravitation, Einstein developed deep reservations about Mach's ideas.
12. As in other cases, Einstein proposed the random motion of such particles in an original form, without reference to Brownian motion, a connection that he acknowledged later [EINSTEIN, 1906 *a*; NAVARRO, 1990, Cap. I (6-8); RENN, 2005, *a*].
13. KUHN [1978] provides an extremely accurate internal reconstruction, even if at the end he comes to recuperate a substantially continuist and evolutionary view, that, quite surprisingly, seems in contradiction with his previous thesis on «scientific revolutions», deferring at the end the introduction of quantisation to 1906.
14. The reconstruction of the genesis of the Bose-Einstein statistics is among the most complicated and controversial. For a detailed analysis, we refer you to BERGIA, FERRARO and MONZONI [1985], and BERGIA [1987].
    We cite also a quite formal but interesting paper by BACH [1990], in which the surprising thesis is developed «that what we now call Bose-Einstein statistics actually had

been introduced by Boltzmann in 1977 in the context of establishing the entropy-probability relationship […] but that two circumstances prevented a clear distinction between Bose-Einstein and Maxwell-Boltzmann statistics. […] Boltzmann clearly stresses that he changes the physical quantity he assumes to be uniformly distributed, but he does not indicate that with this step he implicitly changes the levels of his description …, and in this way he switches from Bose-Einstein to Maxwell-Boltzmann statistics.» [BACH, 1990, 2-3].

Other papers identify the Bose-Einstein statistics in papers by LORENTZ [1910], and NATANSON [1911]. I also recall a paper by DEBYE [1910], in which he deduced Planck's law by a procedure similar to that used at present in textbooks.

From this point of view, it seems interesting to compare the different context of the same single problem in different authors: In Planck *energy elements* $e = hn$ (clearly indistinguishable) are distributed among *material oscillators*; in Debye *energy quanta* are distributed among the *normal modes* of the radiation field (material oscillators do not even appear); in Bose *real particles* are distributed among *cells* in the physical space. Neither in Bose, nor in Einstein considerations about *indistinguishability* appear before 1925 [BERGIA, 1987].

15. The dependence of (11) on frequency is essential in order for total energy not to diverge, as it happens with the «classical» calculation based on equipartition of energy: in fact, with growing frequency, for $h\nu>kT$, the probability $exp(-E/kT)$ that there is only one quantum becomes extremely small, «killing» the divergence of the density of normal modes. On the contrary, for $h\nu<kT$ the average energy (11) tends to the classical value. See for instance the detailed discussion in the textbook of TOMONAGA [1962].
16. It is interesting however to recall that the three Bohr's papers of 1913 had been preceded by an unpublished *memorandum* (translated in BOHR [1963]), in which the problem of spectra was not yet considered, only the fundamental level of the atom was quantised, and *the aspect of chemical bond played a more important role* than it did in the trilogy of the subsequent year. The relevance of the chemical problems in Bohr's reasoning have been remarked by HIROSIGE and NISIO [1964]. Moreover, a physicist could wonder that until the end of the decade the chemists proposed and worked out *statical models* of atoms and molecules (such as the «cubic atom»), that had the great merit of clarifying the concept of the covalent bond [LEWIS, 1916, 1917; LANGMUIR, 1919; KOHLER, 1971, 1974, 1975].
17. It seems worth remarking that a radical and generalised prejudice against the concept of the light-quantum persisted even well after Millikan's experimental confirmation of the laws of the photoelectric effect in 1916: see for instance NAVARRO [1990], pp. 111-113.

Appendix

In this Appendix we will summarize some technical aspects useful in order to better understand the main points of our analysis.

1. Thermodynamic functions and chemical equilibrium

The method in which chemical equilibrium is calculated from free energy is easily exemplified for the case of ideal gases. In a chemical reaction among gaseous substances (for simplicity at constant *T* and *V*), the Helmholtz free energy, *F=U-TS*, of each component has the expression

$$F = \left(U - TS_0\right) + nRT \ln P = F_0 + nRT \ln P, \quad \text{where } F_0 = U - TS_0.$$

The variation of this free energy, for instance in the specific reaction , is therefore

$$\Delta F = nRT \ln \frac{P^2_{NH_3}}{P^3_{H_2} P_{N_2}} + \Delta F_o \quad \text{(a)}$$

[where corresponds to the difference of the constant terms in eq. (4) of the text], so that the equilibrium constant results

$$\frac{P^2_{NH_3}}{P^3_{H_2} P_{N_2}} = e^{-\Delta F_0 / nRT} = K_p(T), \quad \text{(b)}$$

that is to say exactly eq. (1) of the text.

2. The change in statistical mechanics with respect to kinetic theory

In the kinetic theory thermodynamic functions are *built up* starting from molecular collisions (reductionism). In statistical mechanics macroscopic properties are defined in a _-space with *2sN* dimensions (being *s* the number of degrees of freedom of the particles composing the system) by an abstract *probability function _(q,p)*, which is directly and univocally related with the thermodynamic function that characterises the specific macroscopic state. For instance, in the *microcanonical ensemble*, which represents an isolated system of energy *U*, *it is assumed* $\rho_{micr}(q,p)=const \neq 0$, and the entropy of the system corresponds to the volume occupied by the state in the _-space, namely

$S(N,U,V) = k_B \ln\Gamma(N,U,V)$, where

$$\Gamma(N,U,V) = \underset{(\text{hipersup.}U)}{\int\ldots\int} d^{sN}q\,d^{sN}p$$

This appears even more evident in the *canonical ensemble*

$\rho_{\mathrm{can}}(q,p) = exp\{[F(T,N,V) - E(q,p)]/k_BT\} \equiv$

$\equiv exp\{F(T,N,V)/k_BT\}\cdot exp\{-E(q,p)/k_BT\}$, (c)

which corresponds to a state of fixed temperature T of the system, whose free energy simply corresponds to the normalization of probability

$$F(T,N,V) = ln\{\int exp[E(q,p)/k_BT]\cdot d^{sN}q\ d^{sN}p\}.$$

Generalisation to quantum statistical mechanics. Such a direct relationship with thermodynamics implies that the generalization of the formalism to quantum statistical mechanics retains the same functional dependence, changin the classical functions for the corresponding quantum operators

$$\hat{\rho}_{\mathrm{can}} = \exp\{[F(T,N,V) - \hat{H}]/k_BT\} \Rightarrow F(T,N,V) = U - TS = -k_BT\cdot\ln\sum_n(-E_n/k_BT)$$

3. Planck's first thermodynamic calculation in 1900

Planck had already associated Wien's formula (7) with the lowest-order parametrization of function (8),

$$\left(\frac{\partial^2 s}{\partial\varepsilon^2}\right)^{-1} = -\alpha\varepsilon\ :$$

in fact, from the first principle $\partial s/\partial\varepsilon=1/T$, whence $\partial s/\partial\varepsilon=-1/\alpha\cdot 1n(\varepsilon/\beta)$ gives the energy of the resonator $\varepsilon=\beta\cdot\exp(-\alpha/T)$, and the density of radiant energy

$$u(\nu,T)\cdot d\nu = 8\pi\beta/c^3\cdot\nu^3\cdot e^{-\alpha(\nu/T)}\cdot d\nu\quad .$$

Wien's formula reproduces only the high-frequency region of the spectrum of radiation: Planck studied therefore the higher order parametrization

$$\frac{\partial^2 s}{\partial\varepsilon^2} = \frac{-\alpha}{\varepsilon^2+\gamma\varepsilon}\quad \text{(d)}$$

By integrating one obtains

$$1/T \equiv \partial s/\partial\varepsilon = (\alpha/\gamma)\cdot\ln[(\gamma+\varepsilon)/\varepsilon],\quad \text{(e)}$$

That is

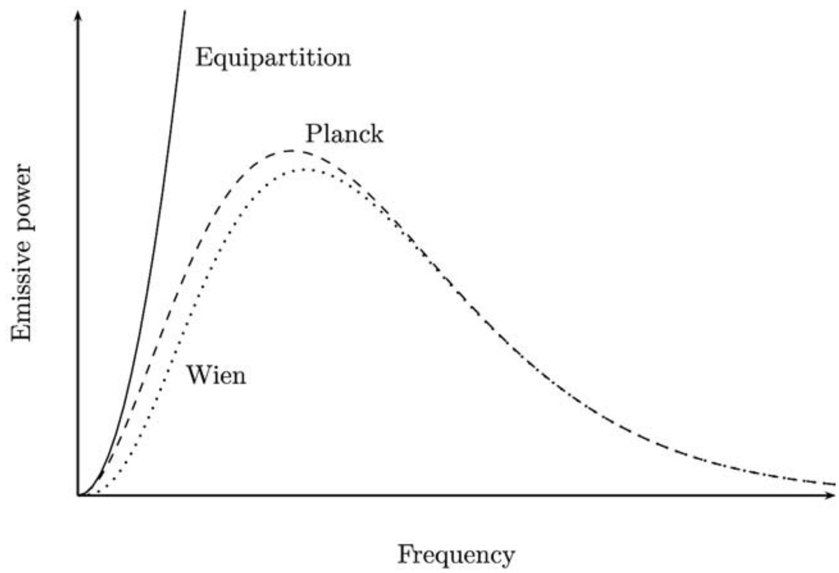
$$\varepsilon = \frac{\gamma}{\exp(\alpha / \gamma T) \pm 1}$$

And finally, since the general Wien's theorem requires that $\gamma = A\nu$, y $\alpha/\gamma = B\nu$, Planck's formula

$$u(\nu, T) = \frac{A\nu^3}{e^{B\nu/T} - 1}$$

4. Planck's formula as interpolation beween Wien's and Rayleigh's

It is immediate to see that only the quadratic term, $\partial^2 s/\partial\varepsilon^2 = -1/c\varepsilon^2$, gives $1/T \equiv \partial s/\partial\varepsilon = c\cdot\varepsilon^{-1}$, that is $\varepsilon = c^{-1}\cdot T$, which would correspond to Rayleigh's formula, since for the general law of Wien c^{-1} must be proportional to the frequency ν : in this sense Planck's formula can be seen as an interpolation between Wien's and Rayleigh's (fig. 1).



5. The second of Planck's 1900 calculations

The energy E of the oscillators of frequency ν can be expressed in terms of the number z_ν of states of average energy $\bar{\varepsilon}$, or of the number n_ν of energy quanta ε_0:$E=z_\nu\cdot\bar{\varepsilon}=n_\nu\cdot\varepsilon_0$. The probability (10) *assumed* by Planck leads to the entropy of an oscillator, using Stirling approximation for the factorial

$$s_\nu = \frac{S_\nu}{z_\nu} = \frac{k_B \ln W\nu}{z_\nu} = \frac{k_B}{z_\nu}\ln\frac{(z_\nu+n_\nu)^{(z_\nu+n_\nu)}}{z_\nu^{z_\nu}\cdot n_\nu^{n_\nu}} = k_B\left[\left(\frac{n_\nu}{z_\nu}+1\right)\cdot\ln\left(\frac{n_\nu}{z_\nu}+1\right)-\frac{n_\nu}{z_\nu}\cdot\ln\frac{n_\nu}{z_\nu}\right]$$

$$= k_B\left[\left(\frac{\bar{\varepsilon}}{\varepsilon_0}+1\right)\cdot\ln\left(\frac{\bar{\varepsilon}}{\varepsilon_0}+1\right)-\frac{\bar{\varepsilon}}{\varepsilon_0}\cdot\ln\frac{\bar{\varepsilon}}{\varepsilon_0}\right]$$

The thermodynamic relation leads finally to

$$\frac{1}{T}=\frac{\partial s_\nu}{\partial\varepsilon}=\frac{k_B}{\varepsilon_0}\cdot\ln\left(1+\frac{\varepsilon_0}{\bar{\varepsilon}}\right) \ .$$

This expression coincides with eq. (c), that Planck intended to justify, so that the average energy of a resonator of frequency ν results

$$\bar{\varepsilon}(\nu,T)=\frac{\varepsilon_0}{e^{\varepsilon_0/k_BT}-1}$$

And for the general law of Wien it must be $\varepsilon = h\nu$.

6. The physical meaning of the function $\left(\frac{\partial^2 s}{\partial\varepsilon^2}\right)^{-1}$ and the wave-particle duality

Expressing the probability as $W=\exp(S/k_B)$, at equilibrium (S maximum) it must be $\partial s/\partial\varepsilon=0$, and the second-order development come out to be:

$$s(\varepsilon)=s(\bar{\varepsilon})+\tfrac{1}{2}(\varepsilon-\bar{\varepsilon})^2\cdot\partial^2 s/\partial\varepsilon^2 \ .$$

One has therefore

$$\overline{(\varepsilon-\bar{\varepsilon})^2}=\frac{\int_0^\infty(\varepsilon-\bar{\varepsilon})^2\cdot W(\varepsilon)}{\int_0^\infty W(\varepsilon)}=\frac{\int_0^\infty(\varepsilon-\bar{\varepsilon})^2\cdot e^{\frac{1}{2}k_B(\partial^2 s/\partial\varepsilon^2)(\varepsilon-\bar{\varepsilon})^2}\cdot d\varepsilon}{\int_0^\infty e^{\frac{1}{2}k_B(\partial^2 s/\partial\varepsilon^2)(\varepsilon-\bar{\varepsilon})^2}\cdot d\varepsilon}=\frac{2\left[\frac{1}{2}k_B(\partial^2 s/\partial\varepsilon^2)\right]}{4\left[\frac{1}{2}k_B(\partial^2 s/\partial\varepsilon^2)\right]^3}=-k_B\left(\frac{\partial^2 s}{\partial\varepsilon^2}\right)^{-1}$$

using the gaussian integrals $\int_0^\infty x \cdot \exp(-ax^2)dx = \frac{\sqrt{\pi}}{4a^3}$,

and $\int_0^\infty \exp(-ax^2)dx = \frac{\sqrt{\pi}}{2a}$.

Planck's parametrization (d) implies (Einstein, 1909)

$$\overline{(\varepsilon - \bar{\varepsilon})^2} = -A\varepsilon - B\varepsilon^2 \ ,$$

That is, two independent contributions to fluctuations, respectively of a particle and a wave nature.

7. Stimulated emission of radiation and Planck's law

Consider in the first place only the two traditional processes of *absorption* and *spontaneous emission*. The number N_{abs} of photons absorbed per unit time and volume is proportional to the number N_1 of atoms in the fundamental state E_1 and the density u_v of photons

$$N_{abs} = B_{12}(\nu) \cdot u_\nu \cdot N_1 \ .$$

Spontaneous emission by an atom in the excited state E_2 does not require the presence of radiation: the number of emitted photons is therefore proportional to

$$N_{em,esp} = A_{21}(\nu) \cdot N_2 \ .$$

In thermal equilibrium $N_{abs}=N_{em,esp}$, and for eq. (c) $N_2 / N_1 = \exp-(h\nu / k_B T)$, so that it results

$$u_\nu = \frac{A_{21} \cdot N_2}{B_{12} / N_1} = \frac{A_{21}(\nu)}{B_{12}(\nu)} \cdot e^{-h\nu/k_B T} \ ,$$

That is Wien's law (7), with $A_{21}/B_{12}=8\pi h\nu^3/c^3$.

If one takes into account *stimulated emission*, it must be instead $N_{em,est}=B_{21}(\nu)\cdot u_\nu . N_2$. In thermal equilibrium between absorption and emission it must be

$$B_{12}(\nu) \cdot u_\nu \cdot N_1 = A_{21}(\nu) \cdot N_2 + B_{21}(\nu) \cdot u_\nu \cdot N_2$$

whence

$$u_\nu = \frac{A_{21}}{B_{12}} \cdot \frac{1}{\frac{B_{12}}{B_{21}} \cdot \frac{N_1}{N_2} - 1} = \frac{A_{21}}{B_{12}} \cdot \frac{1}{\frac{B_{12}}{B_{21}} \cdot e^{h\nu/k_BT} - 1}$$

which is Planck's formula, with $B_{12}=B_{21}$, y $A_{21}/B_{21}=8\pi h\nu^3/c^3$.

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