Physics Before and After Einstein
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Chapter 3

Mechanistic Science, Thermodynamics, and Industry at the End of the Nineteenth Century

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1. Introduction

The physical theories developed during the first decades of the twentieth century have introduced a radical new way of considering both natural phenomena and the structure and tasks of scientific explanation. Albert Einstein can be considered as the father of this revolution in physics, having introduced some of the most innovative concepts and theories: although, at the end, he strongly opposed the extreme formal drift of the “orthodox” formulation of quantum mechanics by the Copenhagen school.

The level of abstraction and mathematical treatment reached by the latter theory makes it not only extremely difficult for lay people to understand, but also problematic to teach to students in scientific fields that do not require deep mathematical bases and strong abstraction capacities. This last difficulty implies a serious contradiction with respect to the growing diffusion and pace of technological advancement, since the quantum theory is a century old, is a fundamental tool in this field, and should therefore have a deeper diffusion.

It does not help, in this respect, to point out, as most physicists do, that the structure of quantum mechanics is one that corresponds to the properties of the atomic world. We do not question the success of the quantum theory, but we hold that in the path that led to its formulation, specific choices were made, related to the social and cultural environment and currents, and to the spread, growth and evolution of the Industrial Revolution in Western Europe [25]. Scientific activity obviously has its own specificity, but scientists studying the laws of nature are not insulated from the world outside, they are instead men of their time, involved with its social problems, mentality, cultural paradigms and philosophical currents. A rational reconstruction of this environment and these choices could then help in the difficult task of making the final structure and concepts of quantum mechanics more acceptable.

This chapter presents a historical analysis, discussing how the twentieth-century revolution in physics was the result of a long and complex evolution, from an initial empirical and phenomenological formulation based on experimental evidence and data, towards increasingly complex and formal structures based on models [1]: mathematical models in physics, models of molecules and reactions in chemistry, other hypothetical structures in other branches. This evolution overturned the relationship between science and technology, and transformed the first into a powerful productive force: the drift towards formalisation made science a flexible tool, applicable to every field, while production was growing into a complex system of increasingly specialised branches. At the same time, the organisation of scientific research changed from one of individual scientists investigating on the basis of their personal resources and interests, to a complex structure financed by the State or corporations; its material means and instruments became increasingly convoluted, reaching the dimensions of huge laboratories with an international status. In the course of such a process, the understanding of, and control over, natural phenomena have deepened astonishingly, just as in the field of technical applications and innovation. This evolution was neither linear nor completely understandable on a purely "internal" basis, in the sense that the changes and choices involved are hardly reducible to purely scientific requirements.

2. Limitations of the Early Phenomenological Scientific Approach

The first phase of industrialisation, starting with the eighteenth-century Industrial Revolution in England, was essentially based on empirical inventions. Technical innovations (like the steam engine, or many elementary chemical processes) could not rely on previous scientific knowledge and instead derived from individual inventiveness and creativity. During the first half of the nineteenth century, scientific development remained substantially dependent on technical innovation, and functioned as a tool to provide understanding and sounder bases for the underlying principles, in order to allow further improvement. Scientific knowledge undoubtedly became increasingly systematic, as the specific scientific branches acquired greater autonomy and rigorous foundations. The prevailing scientific attitude was however still 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.

This prescription was rarely fully implemented in practice, due to the unavoidable presence of common sense, or ideological concepts, like the "hydraulic analogy" adopted by Sadi Carnot in 1824, or the explanation of interactions in terms of forces acting at a distance. However, it was a wholesome reaction to the indiscriminate use of metaphysical speculations in the past, although it severely limited the possibility of unfolding or foreseeing really new properties or phenomena, and could hardly lead to completely new technological devices. One of the most explicit examples was the general rejection of the atomic model, although Dalton had already formulated the atomic concepts at the beginning of the nineteenth century, and Avogadro (1811) and Ampère (1814) had introduced the molecular hypothesis. Such a rejection delayed, for instance, the development of thermodynamics and of the energetic concepts (which had been introduced by John Smeaton on an empirical basis in the second half of the eighteenth century): thermodynamics was born mainly as the science of the steam engine, and its further development did not overcome this horizon until the second half of the nineteenth century. Chemistry, on the other hand, although its quantitative settlement had definitely overcome the limits of alchemy, maintained an empirical and phenomenological attitude, which was to prove a substantial obstacle to the understanding of the nature of chemical substances and of the mechanisms of chemical processes. This is particularly evident in the case of organic chemistry: once the idea of a non-physical vital force was overcome, Gerhardt proposed (in 1844) a classification based on "structural types", "without the need of turning to hypotheses, but strictly keeping inside the limits of experience" [18]. Gerhardt's classification turned out to be substantially misleading, due to the absence of models of molecular structures.

3. The Mid-Century New Breath (1850–1870): From Empiricism to Theoretical Models

This scientific attitude changed around mid-century, when the approach of early nineteenth-century science showed its inadequacy in the face of the changes of the social and cultural situation and of the productive structure.

Joule had already referred to models of matter and atoms in his fundamental investigations on the "mechanical theory" of heat (1842–48), although he limited himself to qualitative considerations in order to support the new concept. The following decade saw a true upsetting of the previous methodological foundations, with the introduction of models both, and almost simultaneously, in physics and in chemistry, in order to reach a deeper understanding of the processes that were studied, and to get new results: these models were formulated in quantitative, mathematical terms.

On the social and economic front, in the second half of the century the middle class established its power in central Europe; and in the first two decades of this period the new social situation began to influence every aspect of life – social, cultural and practical. The defeat of the old aristocratic class and the establishment of a capitalistic economy and an industrial system posed the need, before the possibility, for a big step forward in every field. In the previous century, the accomplishment of an industrial system had been limited to Great Britain, which had developed an impressive industrial power; early industrialisation began to develop in France after the 1789 revolution, but was almost stopped by the Restoration. When the contracting middle class reached the conditions for developing its economic and entrepreneurial activity in the countries of central Europe (essentially the German-speaking area), the problem of competing with the overwhelming British industrial and economic power posed problems and challenges that were overcome through innovations in every field: practical, cultural and ideological. Protectionism began to decline, and an international area of free trade was established. This free enterprise was encouraged and enhanced by the setting up of new forms of credit and by new developments in banking systems.

These changes were accompanied by considerable technical innovation. The technological model of the first Industrial Revolution proved to be increasingly restrictive for the new requirements: a number of bottlenecks had to be overcome by means of a technological jump. In the two decades after 1850 there was a spectacular increase in the rate of inventions and innovations, although they still remained essentially independent of scientific advances.

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 developed in the course of the previous century into a massive, rather rigid structure, that proved to be quite difficult to reorganise – the German steel industry was essentially developed on the basis of these new processes: at the beginning of the twentieth century the average German steelworks was about four times the size of a British one, while German production overtook British production.

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 process as far as possible. The emerging German industry, on the other hand, used 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. Another important instance of innovation was the invention of the internal combustion engine.

Along with these processes, however, an awareness grew in leading technological fields that leaving the process of innovation to almost haphazard activity or to the ingenuity of inventors was inadequate. Some kind of guide to technical and industrial innovation was now needed, and such a guide could only be provided by scientific research, if it could overcome the substantially empirical approach that strongly limited the possibility of new results or discovering new processes. It is worth noting here that this change did not result from a conscious decision: instead it was a response to a new spirit of inquiry and investigation into natural phenomena that broke with the old, traditional methods, and reflected the participation of science and technology in the new society and economy. It was a process of general maturation which reflected itself in all aspects of the activity of members of the emerging class.

This new attitude induced a deep methodological renovation in the investigation and explanation of natural phenomena that turned the scientific practice of the previous half-century upside down. Thus models based on non-observable entities began to be adopted as useful tools to lead to the prediction of new properties or 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. A new theoretical physics was thus born, based on a hypothetical-deductive approach. The new 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 any case, insights and advances were made in the understanding and practical control of processes or phenomena, or new phenomena were predicted. One of the most astonishing examples, as we will see in more detail, was Maxwell's prediction of electromagnetic waves, made possible by the mathematical representation of the electromagnetic field in terms of fluids.

It is emblematic that this change occurred almost simultaneously in physics and chemistry during the 1850s, starting with the adoption of the atomic molecular theory.

a) Physics. In physics, this started with an explanation of thermodynamic properties in terms of the *atomic structure of matter*. Krönig in 1856 and Clausius in 1857 derived the expression of pressure in an ideal gas through a mathematical treatment of the average effect of the elastic shocks of gas atoms on the walls of a container, thus providing a justification of the fundamental equation of state of the ideal gas. It is worth noting that similar calculations had been previously performed by Herapath in 1820 and by Waterson in 1843, but their papers had not been accepted for publication. In the following years, Maxwell and Boltzmann formulated, in a more compact and rigorous mathematical form, the kinetic model of gases, deducing in a systematic way its consequences (Appendix, *1*). They found unexpected connections between properties that appeared independent on an empirical basis (e.g. the relationship between transport coefficients, based on the concept of the mean free path of atoms), and laws that could not have been established by pure experimentation (such as the independence of viscosity on pressure). Boltzmann reached a general formulation of kinetic theory (*Boltzmann equation*, 1872) [6], providing an interpretation of entropy and the irreversible character of thermodynamic processes in a gas in terms of collisions between atoms. In particular, he 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). As we will see in more detail, Botzmann believed he had found a mechanical explanation for the thermodynamic properties of gases.

At the same time, 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 "optical ether". 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 which used forces acting at a distance, introduced by Newton, but adopted mainly by the French school [34].

Maxwell explicitly theorised the resort to "physical analogies", namely "the partial similarity between the laws of one science and those of another one, which allow that one of them illustrate the other" [28]: like the analogy of a gas with a system of elastic spheres, or of the electromagnetic field with a mechanical fluid, called the "electromagnetic ether". Mathematical theory developed on these grounds, identifying electric and magnetic actions with the states of pressure, stress or torque inside the hypothetical fluid, and came to extremely important results. First, Maxwell formulated the general laws of the electromagnetic field (*Maxwell equations*) [27], fulfilling the unification between electric and magnetic phenomena. Second, he predicted the existence of electromagnetic waves, on the basis of the physical properties of the ether which, in order to reproduce experimental properties, had to be a highly elastic fluid. Finally, he predicted the electromagnetic nature of light, on the basis of the identity of the properties of his "electromagnetic ether" with those of Stokes' "optical ether". The existence of electromagnetic waves was experimentally confirmed by Hertz in 1888.

These results strikingly confirmed the superiority of the new theoretical approach based on models, since it would have been difficult, if not impossible, to reach such conclusions through a purely empirical approach: electromagnetic waves constitute one of the discoveries that have transformed and renewed technology, production and social relations.

It is worth noting that these advances in theoretical physics were accompanied by progress in experimental physics, with a widening of fields of research, an improvement in equipment and a growing accuracy in experimental procedures.

b) Chemistry. The changes in chemistry proceeded along similar lines. In 1859, at an international meeting held in Karlsruhe, Stanislao Cannizzaro reproposed Avogadro's hypothesis of the distinction between atoms and molecules [7]: contrary to what had happened half a century before, now the atomic–molecular model of matter was not only immediately accepted in the German-speaking countries (in France, for instance, this theory still met with opposition, showing the scientific and technological lag accumulated by this country after the splendour of the first half of the century), but it became the basis of a kind of "molecular engineering" that promoted chemical technology and production, giving Germany a clear superiority in this field. Models of the internal structure of complex molecules were systematically developed, connecting the macroscopic properties to such structures, or to specific atomic groups: this allowed the design of, on the one hand, new molecules with specific chemical properties, starting from known atomic groups, and, on the other hand, more efficient industrial processes of synthesis. One of the most astounding results was Kekulé's hexagonal model of the benzene molecule [23] (1865; Appendix, *7*), which became the basis for the modern classification of organic compounds. Although these chemical models were not mathematical in the strictest sense, the new level of abstraction and formal reasoning are evident.

Another fundamental advance made possible by the new conception was the concept of chemical equilibrium. Previously, only the simplest processes up to the exhaustion of reactants had been developed, but the development of organic compounds involved more complex reactions that often do not even occur in normal thermodynamic conditions and require exceptional pressure and temperature values. The concept of chemical equilibrium was introduced for the first time in 1864 by Guldberg and Waage, by considering a combination of activities of reactants and reaction products: it is worth emphasising that their treatment, although formulated in rather obscure terms, presented a strong analogy with Boltzmann's formulation of gas theory (see Appendix, *6*).

To sum up, the main feature of the new scientific approach introduced after 1850 was that all the properties of the phenomena, and their characteristic parameters and functions were mathematically or formally deduced on the basis of models of their microscopic structure and interactions between the elementary, unobservable components of the system (atoms and molecules in matter, fluids in wave and electromagnetic phenomena). This new approach allowed a big jump in the understanding and treatment of physical and chemical systems, strengthening the belief that a mechanical interpretation of all natural processes could be provided.

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 (Darwin, 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 [9].

4. Triumph and Contradictions of Mechanism

The developments connected with the new method obtained the most remarkable scientific results in the last decades of the nineteenth century. These advances opened new perspectives in science and technology, leading to the overturning of the previous relationship of dependence of the former on the latter. This took place at the turn of the century, when a new phase of industrialisation, centred in Germany, took off. science became an effective guide for technical innovation and productive development, i.e. a real productive force.

It is important to note however, that the routes followed by physics and chemistry diverged: while physics went on developing and refining the theories introduced during the 1850s and 1860s, chemistry, as we will discuss in the next section, took a different approach, which anticipated the revolution in physics of the beginning of the twentieth century. Let us begin with physics.

The impressive advances in physics led to an intensive construction of fundamental theories which gave the impression that almost all the fundamental phenomena of nature had been essentially understood and explained. Field and matter were the two basic aspects (a dichotomy whose criticism was the basis of Einstein's 1905 paper on "light quanta"). On one hand, Maxwell's electromagnetic theory, based on the electromagnetic ether, fulfilled the unification of the electric and magnetic fields, providing a basis for the treatment of every aspect of these phenomena (Appendix, *8*). On the other hand, Boltzmann's kinetic theory provided a general basis for calculation of the thermodynamic properties of gases, and an explanation of irreversibility and the second principle: it seemed therefore to open the way to a generalisation including every aspect of matter.

This impressive theoretical construction was, however, undermined by an intrinsic contradiction. It appeared in fact as the triumph of mechanics, providing a mechanical explanation of all known natural phenomena. But this underlying mechanical philosophy severely limited its potentialities, and led at the same time to deep and unexpected paradoxes. The end of the nineteenth century thus marked a time of triumph and of crisis for mechanistic philosophy.

The full development of the kinetic theory of gases, accomplished by Boltzmann [8], seemed to fulfil the ideal of a complete reduction of thermodynamics to mechanics, successfully explaining and calculating all the properties of gases in terms of the interactions and collisions of their constituent atoms and molecules. Boltzmann maintained such an attitude in spite of the further advance he himself had made in 1877 with the introduction of the probabilistic interpretation [4].

A first criticism had been made the previous year by Loschmidt (although with a positive intention), with the remark that mechanical processes are reversible, while the Boltzmann equation predicted irreversible behaviour, corresponding to the second principle of thermodynamics (*reversibility paradox*). In order to overcome this criticism, Boltzmann introduced a new fundamental concept, showing that entropy can be given a probabilistic interpretation, and the final state of the thermodynamic evolution, i.e. the equilibrium state of the gas, can be obtained as the most probable state (see Appendix, *3*). However, it seems that Boltzmann did not fully perceive the fundamental overturn of the relationship between mechanics and thermodynamics implied by the introduction of probability, in spite of the further, and fundamental, developments he brought to this concept in subsequent years.

But the contradictions and paradoxical consequences raised by the kinetic theory did not end here. In the last decades of the nineteenth century, kinetic theory was subject to a hail of criticisms and attacks that led Boltzmann to declare in 1896: "I am conscious to be only an individual feebly fighting against the current of time" [5]. In fact, the year before Zermelo had pointed out a second paradox of the kinetic theory, known as the *recurrence* *paradox*. In order to appreciate the relevance of this criticism, it must be recalled that Zermelo was an 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. The paradox derived from a theorem proven by Poincaré for a (bounded) mechanical system, according to which such a system has to return to a state arbitrarily near the initial one over a sufficiently long period of time: this behaviour seemed to imply that entropy could not go on growing until it becomes a constant, but that sooner or later it has to 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 was tremendously long, much more than the life of the universe. In spite of the relevance of such considerations and calculations, he seemed to miss the fundamental point, which was that Poincaré's theorem concerned the "microscopic state" of the system, but had nothing to do with the "macroscopic" one, since the latter is defined in terms of an ensemble of microscopic states, compatible with the macroscopic one. Such a consideration would have opened the way to a wider perspective, in which dynamic properties such as recurrence could be viewed as manifestations of thermodynamic fluctuations, but one had to wait for Einstein in order to attain a full awareness of this.

There were even more problems raised by the kinetic theory, such as those relating to the specific heats of gases, whose values were correctly predicted, on the basis of the theorem of equipartition of energy (Appendix, *1*), by taking into account only the translational and rotational degrees of freedom of atoms and molecules. But an internal structure of these components was slowly being discovered, and it seemed a fatal contradiction that their inclusion in the kinetic formalism would have led to unacceptable values for specific heats. Such a contradiction was to be solved only when quantum theory showed that the internal degrees of freedom are "frozen" (i.e. they cannot be excited by thermal motions) at ordinary temperatures (see Appendix, *2*).

It is however important to remark here that the criticisms of and attacks on kinetic theory did not derive only from such contradictions, but were rooted in a more general philosophical and methodological attitude. The cultural milieus in central Europe were dominated by currents of thought that rejected the new insights into natural phenomena and the very legitimacy of using models based on non-observable entities. They critically re-examined the positivistic philosophy, supporting a scientific approach restricted to observable phenomena and data. The most profound, authoritative and influential current was critical empiricism, formulated by Ernst Mach and Avenarius, who denied the reality of anything beyond direct empirical evidence, which was in turn reduced to sensations. This viewpoint – although it also produced important results, such as studies on the connections between sensations and perceptions, and the development of psychophysics – led to the rejection of the reality of atoms, considered as "economical" tools, and to idealistic positions denying matter itself. Nevertheless the anti-mechanistic polemic reached a deep level of critical awareness; so much so that Einstein acknowledged his debt towards Mach in retrenching the role of mechanics [11]. Conclusions not much different from Mach's were reached by a different, much rougher theory named "Energetics", formulated by the chemist Ostwald, who pretended to reduce every phenomenon to manifestations of energy. Planck himself strongly criticised these conceptions, but recalled in his memoirs that it was practically impossible to be heard against Mach's and Ostwald's authority. Boltzmann accused Mach's philosophy of reaching sterile solipsistic conclusions, and had direct and harsh disputes with Ostwald, who denied the possibility of providing a mechanical explanation of irreversibility.

One can see how the theme of mechanical interpretation was at the core of the cultural and scientific debate at the end of the nineteenth century, and was really the weak side of the most advanced physical theories.

In a similar context, one may also discuss the difficulties that arose in electromagnetic theory, as it was formulated on the basis of the electromagnetic ether or, more precisely, a certain kind of "mechanical" ether, conceived as a classical fluid. The most generally known was the paradox known as the "ether wind" (Appendix, *9*). It may be described as conceiving of the ether as a kind of absolute frame of reference: an interpretation corresponding to the formulation of Newtonian mechanics, the one that Einstein was to criticise in his formulation of the theory of special relativity in 1905. At the end of the nineteenth century it seemed obvious (besides being mathematically demonstrated using the Galilean transformation laws for uniform translations) that the behaviour of the electromagnetic phenomena was to change with the motion of the experimental apparatus (or the Earth) with respect to the ether, just as we experience wind when moving through the atmosphere. In these years 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). Here again the contradiction was not inherent in Maxwell's electromagnetic theory, but in its mechanical interpretation, as Einstein showed in 1905. In fact Maxwell's theory met with much opposition, in spite of its successes and aplications to electromagnetic devices. After all, one common feature of the spectacular advance in physics at the end of the nineteenth century was its mechanical and reductionist foundation, which is essential in order to understand the basis of the twentieth-century revolution in physics, and the formal and abstract turn it introduced. At the end of the nineteenth century the mechanical philosophy succeeded in the construction of a massive building that seemed to demonstrate the triumph of mechanics: the latter provided the common basis for the increasing proliferation and specialisation of branches of natural sciences. Such developments brought about an increase in mathematical complexity: models and theories however, based on clear mechanical concepts, 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).

With respect to the contradictions raised by end-of-century reductionist physics, it is important to emphasise that the latter contained possibilities for their solution – however involved they may appear – which would have constituted different routes from the one that eventually prevailed. These routes were interrupted by the start of the twentieth-century revolution in physics, but it is important to state that the evolution of science implies choices that are not merely of a scientific nature, but involve more general factors.

In the realm of thermodynamics Boltzmann, as we have seen, reacted to the criticisms introducing new fundamental developments of kinetic theory, namely probabilistic considerations, that enormously enriched the mechanical foundation of the theory. His considerations on the "recurrence time" and its dependence on how close should the initial state recur, could have been kinetically interpreted in terms of fluctuations, with frequencies inverse to their amplitudes: irreversibility is a probabilistic trend, and the recurrence of the microscopic molecular configuration of initial state is not impossible, only extremely improbable (in the same sense as a monkey randomly typing would compose, although it would take an incredibly long time, the sequence of letters of the *Divina Commedia*). In order for a chair to rise spontaneously, all the molecules in the air should move upward together, an extremely improbable, but not impossible event: if it were impossible, Brownian motion would not exist. Many of Boltzmann's points of view are in agreement with modern developments in the dynamics of complex systems.

Boltzmann was a dramatic figure, since he introduced new approaches and concepts that have remained cornerstones in natural science, but he remained substantially locked into a reductionist position that prevented him from fully utilising the novelty of the new hypotheses at the beginning of the twentieth century, even those directly connected with his own proposals. He was deeply upset by the attacks on his work, and this seems to have been one of the reasons that led him to commit suicide in 1906.

For electromagnetism and the problem of the ether, the situation developed even further. Lorentz worked out the "electron theory" [26], in which matter was conceived as composed of elementary electric charges of a corpuscular nature (This an hypothesis that preceded the discovery of the electron by J.J. Thomson in 1897; Appendix, *9*). 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 electron theory are in fact Maxwell's equations together with Lorentz's equation for the motion of a charged particle in an electromagnetic field. Such a theory thus had a reductionist structure, being based on interactions between the elementary components of the system: in a sense it was an electromagnetic version of mechanical theories. Lorentz's theory, which embodied the concept of ether, was quite successful: it predicted, from the electromagnetic nature of the interacting forces in matter, a contraction of bodies in the direction of their motion through the ether (*Lorentz contraction*), that exactly offset the "aether wind". This Lorentz contraction was not (as it is sometimes presented) an ad hoc hypothesis, but rigorously followed from electromagnetic theory: it is the same as predicted from Einstein's theory of special relativity, which retains electromagnetism while rejects Newtonian mechanics and Galileo transformations [3]. At the time, all experiments confirming the electron theory were also in agreement with special relativity, and vice versa. How could it happen, then, that the latter superseded Lorentz's electron theory? This question will be answered below.

Apart from the physical difficulties raised by the mechanistic philosophy, it is worth remarking that such an attitude suffered from an internal contradiction, and a crucial limitation of its own potentialities: in fact, once the recourse to models had been adopted as a powerful way to investigate and forecast new properties and phenomena, the limitation to mechanical models constituted an unjustified limitation of their full potential. We will analyse this aspect in more detail in the next sections.

Moreover, while physicists were making such an effort to complete this mechanical building, to try and reach the final explanation of natural phenomena, a series of completely new processes were being discovered. The discovery of X-rays, of radioactivity, of cathode rays and of the electron (which were only later recognized as the same thing), of the internal structure of atoms, and the determination of the complete spectrum of electromagnetic radiation created a need for new physical concepts and theoretical frames. This meant that 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, signalling the first break with the mechanistic philosophy.

5. The Second Industrial Revolution and the anti-Mechanistic turn of the German Chemists

German chemists were the first to break with the mechanical foundation of science at the end of the nineteenth century. This happened with no dramatic discussions, and appeared to be a logical choice faced with problems that would have been too difficult, if not impossible, to solve using a mechanical approach.

In order to understand this evolution, one has to put it in the context of the economic and social changes taking place at the end of the nineteenth century. The end of the Civil War in the United States and the unification of the German Empire in 1871, followed by the economic crisis and the great depression of 1873–96, opened the door to the development of an industrialisation process so new and so rapid that it really was a revolution. The order of the most advanced industrial powers was completely upset 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 overtaken by Germany and the US, when several of the leading productive sectors in Britain almost collapsed, faced with increasing German technical leadership and competition. Also, the material and technical bases of production radically changed during these decades: from coal, wood, some of the simplest chemical products, iron and some empirically produced steel, to electricity, industrially produced steel, an increasing quantity of complex chemical products and oil. The power of the newly unified German Empire (following the Austrian–Prussian war of 1866) immediately manifested itself by routing the imperial French army in the French–Prussian war (1870–71), when the recently founded Krupp ironworks provided the German army with 300 new guns.

Scientific development took quite different courses in different countries, as a consequence of variations in the respective socio-economic situations. German science acquired world leadership for half a century, in physics, chemistry and mathematics (until the "brain drain" under the Nazi regime). The US, on the other hand, thanks to its enormous natural resources, lagged behind in science until the first decades of the twentieth century, and developed a technicistic and pragmatic attitude, disregarding general theoretical frameworks and systematic investigation [31]. The eclipse of British science and technology in the second half of the nineteenth century was clearly perceived, denounced and analysed in Britain: several Parliamentary Commissions were appointed in these decades, to investigate the reasons for this worrying decline and to suggest solutions. A German chemist, A.W. Hoffmann, was appointed as director of the Royal College of Chemistry in London. Meanwhile, British physics remained tied to mechanical models. France also lost the leading scientific position it had enjoyed in the first half of the nineteenth century: there were some eminent French personalities (Poincaré for example), but in general French science lagged behind; in particular, for a long time French chemists did not accept the atomic theory, under the authority of M. Berthelot.

The German economy was characterised by the rapid growth of a modern industrial system, based on continually renewing processes, on intensive and programmed technological progress, and on scientific investigation, both fundamental and applied. The chemical industry (especially organic chemistry, and in particular the dye industry, which accounted for 85–90% of world output at the end of the nineteenth century) and the electric industry were the leading sectors. The recently established modern chemical firms (BASF, Hoechst, Geigy) grew very rapidly in these decades [22], built up huge laboratories and developed intensive scientific investigation. It was here that industry assumed its modern structure, based on programmes of team investigation, and gradually shifted direction towards the research laboratory. Modern research laboratories were shaped in these science-based industries. 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). Very close contacts and collaborations were established by these firms with leading university investigators. Major technical scientific programmes were undertaken, such as BASF's seventeen-year investigation, costing one million pounds, into the industrial synthesis of indigo, and the "fixation of nitrogen" (or ammonia synthesis) carried out in 1913 by the academic chemist Fritz Haber and BASF chemist C. Bosch. The latter process allowed Germany, while completely surrounded, to continue to resist for years during the First World War, since it could synthesise explosives and fertilisers (the only other source being guano from Chile, which was subject to the British control of the seas, and was moreover subject to exhaustion: this had been in fact the main motivation behind the Germans developing the new methods of synthesis). When the Allies inspected the Oppau plant for ammonia production in 1919, they discovered the great technical progress that had been made. In this connection, it is worth recalling Haber's direct involvement in war research, as the organiser, and the real father (violating international laws) of the German manufacture and use of chemical weapons (at Ypres in 1915): a role that he claimed in his Nobel Lecture (1918).

Much research was also taking place within the German electrical industry. In Berlin in 1884 the large and very advanced *Physicalische Technische Reichsanstalt* was founded, at which the fundamental measures on the spectrum of electromagnetic radiation were obtained in 1900.

One main factor supported all these developments: Germany took advantage of its very advanced educational system, which could satisfy the growing need for 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 the above-mentioned collaboration with the main firms guaranteed close contact of the academic milieus with the concrete problems of production and technical innovation. The German schools of chemistry became the most advanced in the world, and almost all chemists who wanted a thorough training went to study in Germany.

Many crucial branches of physics arose from the dynamics of technical innovation in chemistry. The problem of radiant electromagnetic energy and of black-body radiation (Appendix, *10*) – which was to be at the basis of the quantum revolution at the beginning of the next century – derived directly from the spectroscopic method of chemical analysis introduced by Bunsen and Kirchhoff in 1860 (which led to the discovery of some chemical elements). The study of the thermodynamic properties of physical systems at high temperatures and pressures was encouraged by the discovery of complex chemical reactions (such as the synthesis of ammonia) that do not occur under normal conditions. The problem of catalysis stimulated the production of new alloys (such as the chromium–nickel alloys supplied by Krupp), and a better understanding of metallurgy. Research into the physics of very low temperatures was in turn pushed forward by problems in the liquefaction of gases and the fractional distillation of air, in order to obtain cheap oxygen and nitrogen for the chemical industry.

The main consequence of this situation in fundamental science was a change in the foundations of chemistry and thermodynamics. The search for increasingly refined compounds was becoming relentless: more complex molecules had to be synthesised through increasingly sophisticated operations of "molecular engineering" which involved more complex reactions under increasingly difficult conditions of chemical equilibrium, leading to unusual conditions of pressure and temperature, very far from the normal ones.

This situation inevitably affected not only the practical attitude of chemists, but also their way of shaping the scientific treatment of these processes. Chemists were confronting new problems of unprecedented difficulty, and were subject to increasing pressure and urgency. The mechanical approach, i.e. the construction of thermodynamic properties starting from the interactions of microscopic components of matter, revealed itself as inadequate to cope with both the complexity of these processes and the new rate of innovation and development of the chemical industry. In other words, mechanics had provided a natural reference frame as long as the technical basis of production and the organisation of labour had maintained a mechanical structure, but the development of the production cycle of the modern chemical (mainly organic) industry presented a complex, systemic structure, showing the limitations of the scientific elaboration that could be based on mechanics, and indicating the need for a new, more compact approach.

An example of this is the calculation of conditions for chemical equilibrium in complex reactions. The approach introduced by Guldberg and Waage could in principle be developed in terms of collisions between the molecules; however, the process was too cumbersome to achieve concrete results, especially since even the simplest reactions proceed through a sequence of partial decomposition and recombination stages, strongly dependent on thermodynamic conditions: this would lead to incredible complexity in the dynamics of molecular activation collisions.

In this situation, chemists were the first to abandon the mechanical approach, and turn instead towards thermodynamics, since it was more flexible. Thermodynamic laws are largely model-independent (recall how Sadi Carnot adopted a "hydraulic analogy" for heat, while Joule had referred to mechanical considerations: the analysis of this apparent contradiction led Kelvin and Clausius to the formulation of the second principle around 1850). They allow one not to be concerned with the specific course of the reactions, since a treatment in terms of state functions depends only on the initial and the final states. In the last decades of the nineteenth century the theory of the free energy state functions was developed (the term "thermodynamic potentials" coined for them was emblematic) in order to treat equilibrium conditions in heterogeneous systems, whose most typical applications were to chemical reactions. After partial contributions by Van't Hoff, Le Chatelier and others, the general theory was formulated in 1876 by Willard Gibbs [19], the same man who later formulated statistical mechanics.

The atomic and molecular constitution was obviously not rejected, and often there was the need to resort to microscopic considerations (for instance, to compute reaction speeds): this however was no longer done on mechanical grounds, but only after the general features of the processes had been established using a thermodynamic treatment. In some sense, thermodynamics took the place of mechanics as a guide and reference frame to work out the properties and laws of the processes: the way was open for conceiving a different, more general and flexible class of models and theories than the mechanical-reductionist ones. An explicit acknowledgement of this shift may be perceived, for instance, in Van't Hoff's approach to reaction kinetics, a dynamic property that cannot be deduced from thermodynamics:

> Within the limits of our knowledge of theoretical laws, reaction velocity may be approached from two different points of view. First of all, we find support from thermodynamics, since the laws governing the speed must be in agreement with the equilibrium laws which are established at the end. Secondly, one may, on the ground of simple kinetic concepts, foresee laws that have always had up to date a good experimental confirmation. We will develop successively: (a) the reaction speed and equilibrium; (b) the reaction kinetics [35].

6. The Take-off of the Twentieth-Century Revolution in Physics: Planck, Gibbs, Einstein and Nernst

This section analyses developments in physics at the beginning of the twentieth century. According to our analysis, the essence (or at least the pre-condition) of this revolution consisted of the superseding of the mechanical and reductionist methods. Martin J. Klein has discussed the role played by thermodynamics in Planck's and Einstein's method and concepts [24]; Navarro correctly adds that, as we will see, it was, more precisely, the statistical formulation of thermodynamics that was important to Einstein's work [30].

This revolution produced three physical theories: statistical mechanics, the special theory of relativity and quantum theory. Einstein played a crucial role in all three, both as a pioneer and as the author of some of the main ideas. We will not follow a strictly chronological order.

The new ideas derived from the acquisition of an anti-mechanistic and anti-reductionist attitude. The new principles, rather than being built up in a reductionist way, were extracted from phenomenological data by selecting some general property to be raised at the level of a fundamental principle. Often the same big problems that, as we have seen, were bothering physicists were turned upside down and simply eliminated by assuming them to be principles of general validity, confirmed by overall experimental evidence: agreement with traditional theoretical frameworks was thus thought to be unnecessary.

The most evident example of this are the two principles that in 1905 Einstein held at the basis of the special theory of relativity [16], i.e. that the velocity of light is independent from the velocity of the source, and that physical laws retain the same form for observers in relative uniform motion (Appendix, *9*): in this way, the problems related to the hypothesis of the ether simply disappeared, this concept being inessential in the theory from the beginning. Thus special relativity simply gave up the ether. The anti-mechanistic stand is particularly evident in this theory, since Maxwell's electromagnetic theory is retained for its covariant character, while Newtonian mechanics is rejected and deeply modified. Special relativity, moreover, presents quite a different structure from Lorentz's electron theory: apart from the substantial equivalence of the results, the same problems are solved here in a much simpler way. After strong initial opposition, Einstein's theory was finally accepted by the scientific community [21], for its non-mechanistic character and its greater flexibility and simplicity, although Lorentz's theory concretely represents an alternative framework.

Einstein's scientific attitude changed the methodological criteria of a scientific explanation. One of his constant concerns and guiding criteria was with symmetry requirements of the physical laws and the physical aspect of nature. This was the starting point of both his 1905 papers on special relativity ("It is known that Maxwell's electrodynamics [...] when applied to moving bodies leads to asymmetries that do not appear to be inherent in the phenomena") and one on the light quantum [15] ("A formal difference of great importance exists between the conceptions that physicists support with respect to gases and the other material bodies, and Maxwell's theory concerning electromagnetic processes in the so called vacuum").

The basic methodological features in the formulation of the theory of special relativity had been anticipated some years before in the formulation of statistical mechanics, by Gibbs [20] in 1902, and by Einstein himself in a series of independent papers published in 1902–1904 [17]. In this case the basic role of thermodynamics was evident. The general laws of thermodynamics for heterogeneous systems had already been established, and had shown their usefulness in the treatment of complex systems, as compared with the reductionist approach, which remained essentially limited to rarefied gases. The time was thus ripe for a general theoretical advance, providing a deeper foundation for thermodynamics. Gibbs' and Einstein's substantially equivalent formulations of statistical mechanics overturned the mechanical approach to thermodynamics: the fundamental thermodynamic state functions and their properties (unifying the First and Second Principles) are retained as the basic relations, introduced in a compact form through the appropriate definition of a general probability function in an abstract space, having a number of dimensions of the order of the Avogadro's number. The expression of this probability is precisely what defines the characteristic thermodynamic function (see Appendix, *4*), which is therefore introduced and calculated in a purely formal way, instead of being "built up" from the interactions of the elementary components, or "reduced" to them.

With the formulation of statistical mechanics, the contradiction between thermodynamics (in its kinetic formulation) and mechanics simply disappears, and they become two independent and complementary theories. When a system composed of a number of smaller particles is considered, only one of two complementary descriptions can be adopted:

- *either* one determines its *microscopic*, or *mechanical state*, defined by the exact values of the positions and velocities of all the particles: such a state obeys the laws of mechanics, is *reversible*, and exhibits Poincaré's recurrence property; or
- one defines its *macroscopic*, *or thermodynamic state*, in terms of the probabilities that the particles fall into small but finite intervals (cells) of the coordinates: in such a case, the microscopic state is no longer determined, the laws of mechanics are therefore no longer applicable, the evolution of the macroscopic state is *irreversible* and obeys the laws of thermodynamics.

One may observe how this concept was anticipated by Boltzmann who, however, maintained an ambiguous position on it: in fact, he did not seem to appreciate the introduction of statistical mechanics (so he never acknowledged Planck's formula for blackbody radiation, although he had actively worked on it, deriving the so-called Stefan–Boltzmann law for total emission power).

As for Einstein, it is important to remark that, although his formulation of statistical mechanics is equivalent to that of Gibbs, he developed a much deeper appreciation of the probabilistic aspects of thermodynamics [29]. In fact, while Gibbs was satisfied with proof that fluctuations are negligible when systems are made up of a large number of particles, Einstein, on the other hand, was interested in singling out physical situations (characterised by a relatively small number of particles) in which fluctuations were no longer negligible, in order to trace them back to the atomic structure of the system. This led him to the treatment of Brownian motion (Appendix, *5*) in his third 1905 memoir [14], and provided the basis for methods to determine Avogadro's number.

Einstein's contributions to quantum theory are discussed in Chapters 8 and 9, so we will end here with an appreciation of his originality. Planck is generally praised for the early introduction of the quantum hypothesis in his famous paper of 1900, but it seems difficult to maintain this thesis: while it must be acknowledged that he introduced the first non-mechanistic approach in the study of a physical problem. From the end of the nineteenth century, disagreeing with Boltzmann's probabilistic interpretation, Planck had developed an approach based on pure thermodynamics, and he had mastered the thermodynamic theory of the radiant field. In 1900, as soon as new experimental results on the full spectrum of cavity radiation had been presented, he derived his fundamental radiation formula in two successive papers [33]: in the first (by now completely forgotten) through pure parametrisation of a thermodynamic function of the radiation field (Appendix, *11*). Searching then for an explanation of his formula (not because of the failure of Rayleigh's approach, which he never quoted), he resorted in the second paper to Boltzmann formalism, used in a heterodox, non-reductionist way. He later called this "an act of despair" – assuming an exotic expression for probability (that a quarter of a century later became Einstein–Bose statistics [2], but in 1900 it did not make sense). Here, in order to reckon the different distributions of a continuum energy on discrete material oscillators, he used a discretisation procedure that was quite common at that time [10]: as for the "small parts" of energy – proportional to frequency for mere thermodynamic reasons, $\varepsilon_0 = h\nu$, the value of "Planck's constant" h being determined by a fit to the experimental curve – when the ratio $E_\nu/h\nu$ "is not an integer, one takes the nearest integer number". As he later wrote:

> "Since the creator of an hypothesis has *a priori* full freedom in its formulation, he has the faculty of choosing as he likes the concepts and propositions, provided that they do not contain logical contradictions" [32].

Einstein's 1905 hypothesis of the "quantum of light" was by no means a development of Planck's idea (which "seemed to me even opposite to mine", as he wrote the following year [13]), and should be acknowledged as the true introduction of the quantum as a fundamental physical entity.

The analogy we have drawn between the break with mechanism in chemistry and in physics is confirmed by Nernst's 1906 formulation of the third principle of thermodynamics: he was actually a chemist, but realising that the vanishing of specific heats at low temperatures, which follows from his principle, had been foreseen by Einstein in 1907 [12], he turned into a supporter of the new quantum theory, and went on to publish several important works with Einstein.

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Appendix

In this Appendix we will summarise some aspects of the phenomena, scientific problems and theories we have discussed in this chapter: we will follow a logical instead of a historical order, grouping the arguments in different scientific fields.

Thermodynamics, Kinetic Theory and Statistical Mechanics

1. Kinetic theory. The starting point of the kinetic model was the interpretation of the pressure exerted by gas as the average force impressed per unit surface and time by the elastic collisions of the molecules on the walls. The model interprets the absolute temperature T as proportional to the average kinetic energy of the molecules $\langle\varepsilon\rangle \equiv \frac{1}{2}m\langle v^2\rangle$: for a monatomic gas $\langle\varepsilon\rangle = 3/2 \cdot k_B T$, where $k_B = R/N_A$ is the Boltzmann's constant ($R = 8.31$ J/K·mol is the ideal gas constant, and $N_A = 6 \cdot 10^{23}$ the Avogadro number, i.e. the number of molecules per mole). Another fundamental consequence is the *theorem of equipartition of energy*: the average energy $1/2 \cdot k_B T$ is associated with each *degree of freedom* of the molecules (the number of independent movements: three translational ones for monatomic molecules, two additional rotational movements for diatomic molecules: when they are considered respectively as a rigid sphere and a rigid dumbbell, see point *2*). Note that the average molecular energy grows linearly with the (absolute) temperature.

2. Specific heats, quantisation and "frozen" degrees of freedom. The application of the theorem of equipartition of energy gives the right results for the specific heats of monatomic and diatomic gases, provided that their molecules are treated respectively as rigid spheres or dumbbells. But atoms have an internal structure, and chemical bonds are far from rigid: this introduced further (internal) degrees of freedom, whose contribution on the basis of equipartition modify such results. This difficulty was resolved by quantum theory, according to which the energy states of a (bounded) physical system are quantised, and the separation between the quantised states depends on the specific system. Recalling that the average molecular energy $\langle\varepsilon\rangle$ grows linearly with temperature, the energy gap between the rotational states of a molecule is lower than $\langle\varepsilon\rangle$ at room temperatures, so that they may be excited by thermal motion. The electronic states of atoms and molecules and the vibrational states of a diatomic molecule are separated by energy gaps higher than $\langle\varepsilon\rangle$ at room temperatures, so that they cannot be excited, and appear to be "frozen": they may be excited at higher temperatures (sodium placed on a flame shows the yellow colour, or characteristic spectral line, due to excitation of its electron state; in the nucleus of a star, reaching millions of degrees, atoms are completely ionised, and the nuclear states are excited).

3. Boltzmann's probabilistic foundation of thermodynamics. Boltzmann's reaction to criticism led him to the introduction of probabilistic concepts in kinetic theory: in 1877 he associated a probability W with the "thermodynamic" state of the gas, defined as the number of the corresponding, distinct "microscopic" states. He defined entropy as $S = k_B \cdot \ln W$, interpreted irreversibility as an evolution towards more probable states (entropy growth), and derived the thermodynamic state of equilibrium as the most probable one.

4. Thermodynamics and statistical thermodynamics (mechanics). In order to appreciate the development in statistical thermodynamics (1902–04) with respect to the reductionist approach of kinetic theory, consider for example the *canonical ensemble*, which describes a macroscopic system in thermal equilibrium with a thermostat, whose corresponding thermodynamic function is Helmholtz's free energy, $F = U - T \cdot S$, where the state functions F, U, S depend on the state variables V, T, N. Let $E(q, p)$ be the total energy of the system in terms of the set $\{q, p\}$ of canonical coordinates of the N microscopic constituent particles (a number sN is given for each of the canonical coordinates, s being the number of degrees of freedom of the particles: $s = 3$ for a monatomic gas): $q_1, q_2, \ldots, q_{sN}$; $p_1, p_2, \ldots, p_{sN}$. The fundamental *probability function* in the $2sN$-dimensional abstract space (Γ-space) subtended by this set of coordinates is *assumed* to have the expression

$$\begin{aligned}\rho(q, p) &= \exp\left\{\frac{F(V, T, N) - E(q, p)}{k_B T}\right\}\\ &\equiv \exp\left\{\frac{F(V, T, N)}{k_B T}\right\} \cdot \exp\left\{\frac{-E(q, p)}{k_B T}\right\},\end{aligned}$$

in which the free energy F is directly inserted as a normalisation constant (the probability being normalised by prescribing $\int \rho(q, p) \cdot d^{sN}q\, d^{sN}p = 1$) and is therefore *directly linked* to (rather than "deduced from") this canonical probability through integration in the abstract Γ-space

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

The expression of the abstract probability $\rho(q, p)$ is therefore such as to correspond to free energy: notice that ρ is a function of the microscopic coordinates, while F depends on the macroscopic state variables (V, T, N), and is therefore "constant" in the Γ-space. $\rho(q, p)$ is the generalisation of Boltzmann's probability W, and is most conveniently described in terms of an *ensemble* of identical systems in the same macroscopic state, exhausting all the distinct microscopic states; such a treatment can be extended to other macroscopic states (*microcanonical ensemble*, *gran-canonical ensemble*). In this approach, the atomic constitution of the system is clearly assumed, but its thermodynamic properties are no longer built up from the dynamics of the interactions between these microscopic constituents: mechanics plays no role in thermodynamic behaviour. This direct correspondence of probability with the thermodynamic functions implies that the former retains the same functional expression in quantum statistical thermodynamics.

5. Brownian motion. While a *solution* contains molecules dispersed amid molecules, in a *suspension* (*colloid*) the dispersed particles are aggregates of microscopic dimensions but are composed of a considerable number of molecules (*Brownian particles*, from the name of their discoverer Brown, 1836). Such particles show disordered zigzag motions. In 1905 Einstein correctly described their behaviour as a random process, deriving from the casual, asymmetrical collisions of the surrounding molecules on such particles (interpreted as deviations, i.e. fluctuations, from the statistically isotropic distribution).

Chemistry

6. Analogy between kinetic theory and the concept of chemical equilibrium. The basic tool in Boltzmann's gas theory is the function $f(\boldsymbol{r}, \boldsymbol{v}, t)$, specifying the number (or the probability) of molecules with position $\boldsymbol{r}$ and velocity $\boldsymbol{v}$, and the basic hypothesis is that the rate of collisions between molecules with velocities $\boldsymbol{v}$ and $\boldsymbol{u}$ is simply proportional to the product of individual probabilities $f(\boldsymbol{r}, \boldsymbol{v}, t) \cdot f(\boldsymbol{r}, \boldsymbol{u}, t)$ (*molecular chaos* hypothesis: we have discussed the limitations and the problems raised by such hypothesis). Guldberg and Waage assumed that in a chemical reaction such as $A + B \leftrightarrow C + D$ the velocities of the direct and inverse reactions are respectively proportional to the products of concentrations (i.e. the numbers of molecules) $[A][B]$, and $[C][D]$ – the analogy with Boltzmann's assumption is evident – resulting in an equilibrium constant given by the ratio $[C][D]/[A][B]$. We will see that both formulations had to reveal the common limitation consisting in their substantially mechanical nature.

7. Kekulé's hexagonal model and organic chemistry. Organic chemistry deals with carbon compounds. The classification of such substances is based on the internal structure of their molecules. The basic distinction is between the *acyclic* (or *aliphatic*) *series* – such as methane or ethane, which have open-chain molecules – and the *cyclic* (or *aromatic*) *series* (besides two minor ones, the *alicyclic* and the *heterocyclic series*). *Cyclic* compounds are particularly stable, owing to the closed structure of their molecules, derived by the simplest one, i.e. the hexagonal structure of benzene, C_6H_6, which is a hexagon of six carbon atoms, each linked to an outer hydrogen atom.

Electromagnetism, Ether and Special Relativity

8. Maxwell's equations and electromagnetic waves. Maxwell's equations establish the fundamental laws of the electromagnetic field: they represent the first *unified theory* in physics, since they unify electrical and magnetic phenomena. It follows from them, for instance, that a variable electric (magnetic) field generates a variable magnetic (electric) field (Faraday's law, and its symmetrical). This is the principle of the generation of alternating electric currents and *electromagnetic waves*, consisting of an electric and a magnetic field oscillating in phase, reciprocally and continuously generating each other, perpendicular between them and to the direction of propagation, with velocity c.

9. "Ether wind", Lorentz's electron theory and Einstein's special relativity. Maxwell established his equations on the basis of a model, in which the electric and magnetic fields were identified with the states of a fluid (ether). However, the interpretation of Maxwell's theory in the context of mechanical philosophy generated several problems, the most generally known being so-called "ether wind": as a wind is experienced when moving through still air, one would expect the behaviour of the electromagnetic phenomena to be affected by a motion relative to ether. This, however, is not observed (Michelson–Morley experiments). In Lorentz's electron theory, the electromagnetic nature of the interactions inside matter results in a contraction in the direction of the uniform motion ("Lorentz contraction") which exactly counterbalances the "ether wind": in these investigations he obtained the so-called "Lorentz transformations", although he did not ascribe them a fundamental meaning.

On the contrary, Einstein's 1905 theory of special relativity *assumed* that the ether wind does not exist, and he based this belief on two principles: the principle of relativity, stating that no experiment performed inside a system can reveal a uniform motion; and the constancy of the velocity of light c, which is the maximum velocity attainable in nature. On this basis Einstein rejected Newton's concepts of absolute space and time, concluding that a uniform motion is described by Lorentz's instead of Galileo's transformations: contraction of distances (and dilatation of time intervals) in the direction of the motion follow, as well as the mass-energy equivalence $E = mc^2$. Maxwell's equations turn out to be correctly Lorentz covariant, while Newtonian dynamics has to be replaced by relativistic dynamics, which it approaches for small velocities compared to that of light c.

Radiant Energy and Planck's 1900 Papers

10. Radiant energy consists of electromagnetic waves, which also propagate in a vacuum. Every surface emits radiant energy, whose characteristic frequency spectrum in thermal equilibrium starts from zero and extends to higher frequencies as its absolute temperature T increases (the total energy emitted per unit surface and time being proportional to T^4; the Stefan–Boltzmann law): at room temperature it is limited to the infrared region, and only at thousands of degrees does it reach the visible band (we cannot see objects at night). The shape of this spectrum was determined experimentally in 1900, was heuristically explained by Planck, and was studied by Einstein, who introduced the "light quantum" (1905) and wave-particle dualism (1909).

11. Planck's 1900 first paper. Planck treated the radiation field on the basis of a thermodynamic function, the second derivative of the entropy s of an oscillator coupled with the field, with respect to its energy ε: $(\partial^2 S/\partial\varepsilon^2)^{-1}$. This expression may be shown to represent the mean square fluctuation of the oscillator energy. Planck had already identified Wien's commonly accepted expression for the spectrum, $E(\upsilon, T) = a\upsilon^3 \cdot \exp(-b(\upsilon/T))$, with the simplest parametrisation, posing this function as simply proportional to the oscillator energy ε (integrate once, and identify the first derivative of entropy with the inverse of the absolute temperature T). When new experimental results disproved Wien's formula, in 1900, Planck simply tried the subsequent parametrisation, i.e. a linear combination of ε and ε^2, and got his formula: $E(\upsilon, T) = \frac{a\upsilon^3}{e^{b\upsilon/T}-1}$, a and b being two constants that in his second paper he related to Planck's constant $h = 6\cdot 10^{-34}$ J·s, and Boltzmann's constant k_B. It is interesting to note that this parametrisation can be interpreted *a posteriori* as an interpolation between Wien's and Rayleigh's formulas for the two extremes of the spectrum, the term in ε^2 giving just the second one: but Planck did not even mention Rayleigh's formula. Planck's parametrisation also implies wave–particle duality, as evidenced by Einstein in 1909.

12. Planck's 1900 second paper. The success of his formula led Planck to search for an explanation, resorting to Boltzmann's statistical approach (which he had previously not accepted), but he did not use Boltzmann's expression for the number of distinct partitions of N particles in k cells, $W = N! \cdot \prod_{i=1}^{k} \frac{1}{n_i!}$. Instead he assumed, without an explicit justification, the radically different expression: $W = \prod_{i=1}^{k} \frac{(n_i+z_i)!}{n_i!z_i!}$, z_i being the number of material oscillators in cell i, in which n_i quanta are distributed.

References

[1] A much more detailed analysis along these lines may be found in: A. Baracca, S. Ruffo and A. Russo, *Scienza e Industria 1848–1915*, Bari, Laterza, 1979.

[2] S. Bergia, C. Ferraro and V. Monzoni, "Planck's heritage and the Bose statistics", *Annales de la Fondation Louis de Broglie*, **10** (1985), 161; S. Bergia, "Who discovered the Bose-Einstein statistics?", in *Symmetries in Physics (1600–1980)*, edited by M.G. Doncel, A. Hermann, L. Michel, A. Pais, Servei de Publicacions UAB, Barcelona, 1987.

[3] For these aspects see for instance S. Bergia: "Einstein and the birth of special relativity", in: *Einstein, A Centenary Volume*, ed. by A.P. French, Heinemann, London, 1979; *Einstein: Quanti e Relatività, una Svolta nella Fisica Teorica*; series "I Grandi della Scienza", I, **6**, December 1988; R. McCormmach, "Einstein, Lorentz and the electron theory", *Hist. Stud. Physical Sciences*, **2** (1970), pp. 41–87.

[4] L. Boltzmann, "Bemerkungen über einige Probleme der mechanischen Wärmyheorie", *Wien Ber.*, **75** (1877), pp. 62–100; "Über die Beziehung zwischen dem Zwiten Hauptsatze der mechanischen Wärmtheorie und der Wahrscheinlichkeitsrechnung resp. den Sätzen über Wärmegleichgewicht", *Wien. Ber.*, **76** (1877), pp. 373–435.

[5] L. Boltzmann, *Vorlesungen über Gastheorie*, 2 vols., J.A. Barth, Leipzig, 1896–1898: foreword to the second volume (English translation with an introduction by Stephen G. Brush, *Lectures on Gas Theory*, University of California Press, 1964).

[6] L. Boltzmann, "Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen", *Sitzsungsberichte Akad. Wiss.*, Wien, II, **66** (1872), pp. 275–370.

[7] S. Cannizzaro, "Sunto di un corso di filosofia chimica, fatto nella R. Università di Genova", *Il Nuovo Cimento*, **VII** (1858), pp. 321–66.

[8] For a deep survey of Boltzmann's figure see C. Cercignani, *Ludwig Boltzmann, e la Meccanica Statistica*, La Goliardica Pavese, 1997 and *Ludwig Boltzmann, the Man who Turned Atoms*, Oxford University Press, 1998.

[9] F. Darwin, *More Letters of Charles Darwin*, London, 1903, Vol. 1, pp. 126, 139.

[10] Boltzmann had a "finitist" concept of mathematics: see R. Dugas, *La Théorie Physique au Sens de Boltzmann*, Griffon, Neuchâtel, 1959, pp. 25–29.

[11] "It was Mach who, in his *History of Mechanics*, shook this dogmatic faith [in mechanics "as the final basis of all physical thinking"]; this book exercised a profound influence upon me in this regard while I was a student" (A. Einstein, "Autobiographical notes", in P.A. Schilpp (ed.), *Albert Einstein: Philosopher–Scientist*, La Salle, Open Court, p. 21).

[12] A. Einstein, "Die Plancksche Theorie der Strahlung und die Theorie der spezifischen Wärme", *Annalen der Physik*, **22** (1907), pp. 180–90, 800 (Berichtigung).

[13] A. Einstein, "Theorie der Lichterzeugung und Lichtabsorption", *Ann. Phys.*, **20** (1906), pp. 199–206.

[14] A. Einstein, "Über die von molekularkinetischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen", *Annalen der Physik*, **17** (1905), pp. 549–60. In a subsequent paper Einstein acknowledged the relationship of his theory with the Brownian motion: A. Einstein, "Zur Theorie der Brownschen Bewegung", *Annalen der Physik*, **19** (1906), pp. 371–81. See e.g. L. Navarro Verguillas, *Einstein Profeta y Hereje*, *cit.*, Chap. I (6–8).

[15] A. Einstein, "Über einen die Erzeugung und Verwandlung des Lichtes betreffenden hueristischen Gesichtspunkt", *Annalen der Physik*, **17** (1905), pp. 132–48: Einstein refers respectively to the atomic model, that implies a finite number of co-ordinates, and to the field description, in terms of continuous functions.

[16] A. Einstein, "Zur Elektrodynamik bewegter Körper", *Annalen der Physik*, **17** (1905), pp. 891–921. See S. Bergia, "Einstein and the birth of special relativity", in *Einstein, A Centenary Volume*, edited by A.P. French, Heinemann, 1979, pp. 65–90; T. Hirosige, "The ether problem, the mechanistic worldview, and the origins of the Theory of Relativity", *Hist. Stud. Physical Sciences*, **7** (1976), pp. 3–82.

[17] A. Einstein: "Kinetische Theorie des Wärmegleichgewichtes und des zweiten Hauptsatzes der Thermodynamik", *Annalen der Physik*, **9** (1902), pp. 417–33; "Eine Theorie der Grunlagen der Thermodynamik", *Annalen der Physik*, **11** (1903), pp. 170–87; "Zur Allgemeinen molekularen Theorie der Wärme", *Annalen der Physik*, **14** (1904), pp. 354–62.

[18] M.C. Gerhardt, *Précis de Chimie Organique*, Paris, 1844–45.

[19] J.W. Gibbs, "On the equilibrium of heterogeneous substances", *Trans. Connecticut Acad.*, **3**, 108, 343 (1875–1878); in *The Scientific Papers of J.W. Gibbs*, Longmans Green and Co., London, 1906, I, 55–349.

[20] W. Gibbs, *Elementary Principles in Statistical Mechanics, Developed with Special Reference to the Rational Foundations of Thermodynamics*, Yale University Press, 1902; reprinted by Dover, New York, 1960.

[21] See for instance: S. Goldberg, "In defence of ether: the British response to Einstein's special theory of relativity, 1905–1911", *Hist. Stud. Physical Sciences*, **2** (1970), pp. 89–125. As a matter of fact, opposition and criticisms against the special theory of relativity has never appeased, up to now; apart from the furious attacks the Einstein and his theory received by the nazi regime and scientific community.

[22] The annual compared rates of growth of the German chemical industry were (P.M. Hohenberg, *Chemicals in Western Europe 1850–1914*, Rand McNally & Co., Chicago, 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%

[23] A. Kekulé, *Bulletin de la Société Chimique*, t. III (1865), 98; *Annalen der Chemie und Pharmacie*, **137** (1866), 129.

[24] M.J. Klein: "Thermodynamics and quanta in Planck's work", *Physics Today*, **19**, 27 (Nov. 1966); "Einstein's first paper on quanta", *The Natural Philosopher*, **2** (1963), pp. 59–86; "Einstein, specific heats and early quantum theory", *Science*, **148** (1965), pp. 173–80; "Thermodynamics in Einstein's thought", *Science*, **157** (1967), pp. 509–516.

[25] Our natural reference is to D.S. Landes, *Unbound Prometheus* (Cambridge University Press, 1969), whose analysis of technological changes coincides with our appreciation of the features and periods of scientific changes.

[26] H.A. Lorentz, *The Theory of Electrons* (Reprint) Dover, New York, 1952.

[27] J.C. Maxwell, *A Treatise on Electricity and Magnetism*, 1873 (reprinted by Dover, New York, 1954).

[28] J.C. Maxwell, "On Faraday's lines of force", *Transactions of the Cambridge Philosophical Society*, **10** (1856), 27, reprinted in *The Scientific Papers of J.C. Maxwell*, Paris, 1927, Vol. I, pp. 155–229.

[29] J. Mehra, "Einstein and the Foundation of Statistical Mechanics", *Physica*, **79A** (1975), pp. 447–477; A. Baracca and R. Rechtman, "Einstein's Statistical Mechanics", *Revista Mexicana de Fisica*, **31** (1905), pp. 695–722; L. Navarro Verguillas, *Einstein Profeta y Hereje*, Barcelona, Tusquets, 1990, Chap. 1.

[30] L. Navarro Verguillas, "On Einstein's statistical mechanical approach to early quantum theory", *Historia Scientiarum*, **43** (1991), pp. 39–58; *Arbor*, **CXLVIII, 581** (1994), 109.

[31] See for instance: D. Noble, *America by Design*, New York, Knopf, 1977; M. De Maria and R. W. Seidel, "The scientist and the inventor", *Testi e Contesti*, **4** (1980), pp. 5–32.

[32] M. Planck, *La conoscenza del mondo fisico*, Italian translation Torino, Boringhieri, 1964, p. 231.

[33] M. Planck, "Über eine Verbesserung der Wien'schen Spektralgleichung", *Verhandl. Deutsch. Physik Gesellschaft*, **2** (1900), 202–204; and "Zur Theorie des Gesetzes der Energieverteilung im Normalspektrum", *Verhandl. Deutsch. Physik Gesellschaft*, **2** (1900), pp. 237–245. The procedures of the two Planck's papers, and several aspects of the early quantum theories, are discussed in details in A. Baracca, *Manuale Critico di Meccanica Statistica*, CULC, Catania, 1976.

[34] See for instance A. Rossi, "The two paths of physics", *Scientia*, VII–VIII (1973), pp. 565–84 (first part), and IX-X-XI-XII (1974), pp. 1–26.

[35] Van't Hoff, *Leçons de Chimie-Physique*, Hermann, Paris, 1898, p. 175.