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Malcolm Longair
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PART I

THE DISCOVERY OF QUANTA

1 Physics and theoretical physics in 1895

1.1 The triumph of nineteenth century physics

The nineteenth century was an era of unprecedented advance in the understanding of the laws of physics. In mechanics and dynamics, more and more powerful mathematical tools had been developed to enable complex dynamical problems to be solved. In thermodynamics, the first and second laws were firmly established, through the efforts of Rudolf Clausius and William Thomson (Lord Kelvin), and the full ramifications of the concept of entropy for classical thermodynamics were being elaborated. James Clerk Maxwell had derived the equations of electromagnetism which were convincingly validated by Heinrich Hertz's experiments of 1887 to 1889. Light and electromagnetic waves were the same thing, thus providing a firm theoretical foundation for the wave theory of light which could account for virtually all the known phenomena of optics.

Sometimes the impression is given that experimental and theoretical physicists of the 1890s believed that the combination of thermodynamics, electromagnetism and classical mechanics could account for all known physical phenomena and that all that remained was to work out the consequences of these recently won achievements. As remarked by Brian Pippard in his survey of physics in 1900,[1] Albert Michelson's famous remark that

> 'Our future discoveries must be looked for in the sixth place of decimals.' (Michelson, 1903)

has often been quoted out of context and is better viewed in the light of Maxwell's words in his inaugural lecture as the first Cavendish Professor of Experimental Physics in 1871:

> 'I might bring forward instances gathered from every branch of science, showing how the labour of careful measurement has been rewarded by the discovery of new fields of research, and by the development of new scientific ideas.' (Maxwell, 1890)

Maxwell's prescient words were the battle-cry for the extraordinary events which were to take place over the succeeding decades. In fact, the late nineteenth century was a period of ferment in the physical sciences when many awkward fundamental problems remained to be solved. These exercised the minds of the greatest physicists of the period. Ultimately, the resolution of these problems was to revolutionise the foundations of physics with the discovery of the wholly different world of quantum mechanics. Let us begin by reviewing some of the issues which led to the crisis of early twentieth century physics.[2]

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1.2 Atoms and molecules in the nineteenth century

The origin of the modern concept of atoms and molecules can be traced to the understanding of the laws of chemistry in the early years of the nineteenth century. In the late eighteenth century Antoine-Laurent de Lavoisier established the *law of conservation of mass* in chemical reactions. Then, in the period between 1798 and 1804, Joseph Louis Proust established his *law of definite proportions*, according to which:

> 'A given chemical compound contains the same elements united in the same fixed proportions by mass.'[3]

For example, oxygen makes up 8/9 of the mass of any sample of pure water, while hydrogen makes up the remaining 1/9. In 1803, John Dalton followed up this law with his *law of multiple proportions* according to which:

> 'When two elements combine together to form more than one compound, the weights of one element which unites with a given weight of the other are in simple multiple proportion.'

Next, in 1808 Joseph-Louis Gay-Lussac published his *law of combining volumes of gases*, which states:

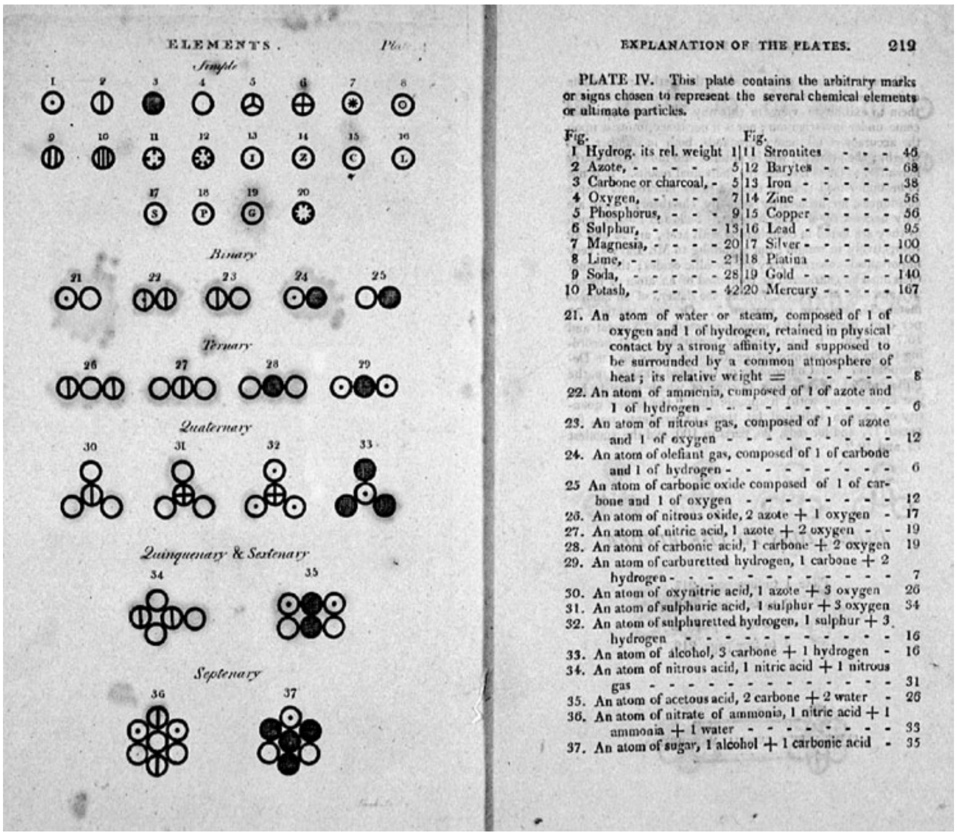
> 'The volumes of gases taking part in a chemical change either as reagents or as products, bear a simple numerical relation to one another if all measurements are made under the same conditions of temperature and pressure.'

For example, two volumes of hydrogen react with one volume of oxygen in forming two volumes of water vapour.

These concepts were synthesised and taken much further by Dalton in his influential treatise *A New System of Chemical Philosophy* (Dalton, 1808). He asserted that the ultimate particles, or atoms, of a chemically homogeneous substance all had the same weight and shape and drew up a table of the relative weights of the atoms of a number of simple substances (Fig. 1.1). According to his hypothesis, the atoms are particles of matter which cannot be subdivided into more primitive forms by chemical processes. Originally, Dalton and Berzelius considered that equal volumes of gases under identical physical conditions contain the same number of atoms, but this concept did not agree with the observed relations of the volumes of different combining gases. The solution was provided by Amadeo Avogadro who in 1811 realised that the physical unit was not a single atom but a cluster of a small number of atoms, which he defined as *molecules*, namely the smallest particle of the gas which moves about as a whole. *Avogardo's hypothesis* then states that:

> 'Equal volumes of all gases under the same conditions of temperature and pressure contain the same numbers of molecules.'

A central role in what follows concerned the molecular, or atomic, weight of a substance. This is defined to be the weight of the particle on a scale in which the oxygen atom has weight 16 units. Correspondingly, the gram-molecular weight was defined as the weight of the particle on a scale in which the weight of oxygen was 16 gram.[4] Consequently,



EXPLANATION OF THE PLATES. 219

PLATE IV. This plate contains the arbitrary marks or signs chosen to represent the several chemical elements or ultimate particles.

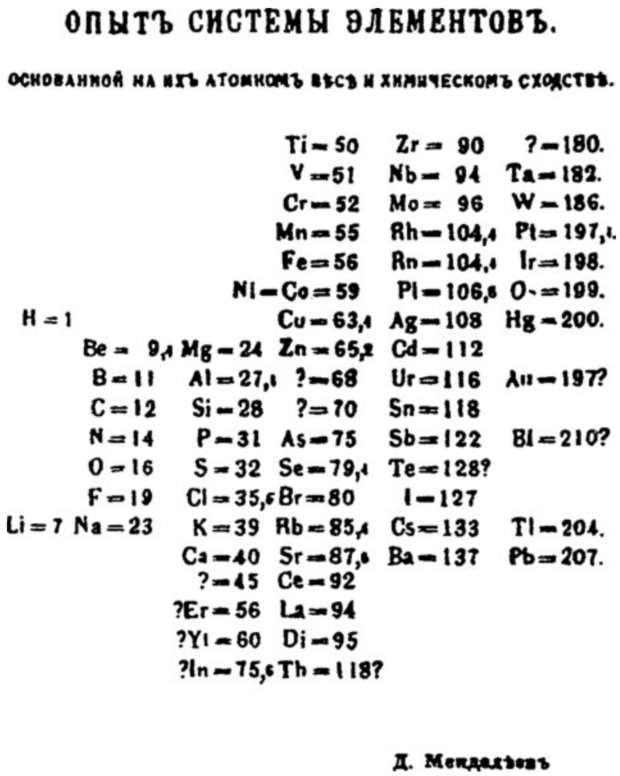
Fig.			Fig.		
1	Hydrog. its rel. weight	1	11	Strontites - - -	46
2	Azote, - - - -	5	12	Barytes - - - -	68
3	Carbone or charcoal, -	5	13	Iron - - - - -	38
4	Oxygen, - - - -	7	14	Zinc - - - - -	56
5	Phosphorus, - - -	9	15	Copper - - - -	56
6	Sulphur, - - - -	13	16	Lead - - - - -	95
7	Magnesia, - - - -	20	17	Silver - - - - -	100
8	Lime, - - - - -	21	18	Platina - - - -	100
9	Soda, - - - - -	28	19	Gold - - - - -	140
10	Potash, - - - -	42	20	Mercury - - - -	167

21. An atom of water or steam, composed of 1 of oxygen and 1 of hydrogen, retained in physical contact by a strong affinity, and supposed to be surrounded by a common atmosphere of heat; its relative weight = - - - - - - 8
22. An atom of ammonia, composed of 1 of azote and 1 of hydrogen - - - - - - - - - - - - 6
23. An atom of nitrous gas, composed of 1 of azote and 1 of oxygen - - - - - - - - - - - 12
24. An atom of olefiant gas, composed of 1 of carbone and 1 of hydrogen - - - - - - - - - - - 6
25 An atom of carbonic oxide composed of 1 of carbone and 1 of oxygen - - - - - - - - - - 12
26. An atom of nitrous oxide, 2 azote + 1 oxygen - 17
27. An atom of nitric acid, 1 azote + 2 oxygen - - 19
28. An atom of carbonic acid, 1 carbone + 2 oxygen 19
29. An atom of carburetted hydrogen, 1 carbone + 2 hydrogen - - - - - - - - - - - - - - 7
30. An atom of oxynitric acid, 1 azote + 3 oxygen 26
31. An atom of sulphuric acid, 1 sulphur + 3 oxygen 34
32. An atom of sulphuretted hydrogen, 1 sulphur + 3 hydrogen - - - - - - - - - - - - - - 16
33. An atom of alcohol, 3 carbone + 1 hydrogen - 16
34. An atom of nitrous acid, 1 nitric acid + 1 nitrous gas - - - - - - - - - - - - - - - - 31
35. An atom of acetous acid, 2 carbone + 2 water - 26
36. An atom of nitrate of ammonia, 1 nitric acid + 1 ammonia + 1 water - - - - - - - - - - 33
37. An atom of sugar, 1 alcohol + 1 carbonic acid - 35

Fig. 1.1 Dalton's symbols for the atoms of various elements and their compounds (Dalton, 1808).

the gram-molecular weights of all substances contain the same numbers of molecules. Avogadro's hypothesis was disregarded by chemists for almost 50 years until 1858 when Stanislao Cannizzaro convinced the leading chemists of the truth of the hypothesis.

A major preoccupation was putting some order into the properties of the chemical elements. In 1789, Lavoisier published a list of 33 chemical elements and grouped them into gases, metals, non-metals and earths. The search was on for a more precise classification scheme. It was known that certain groups of elements had similar chemical properties – for example, the alkali metals sodium, potassium and rubidium and the halogens, chlorine, bromine and iodine. Dmitri Mendeleyev in 1869 and Julius Meyer in 1870 independently published what became known as the *periodic table* of the elements. The tables were constructed by listing the elements in order of increasing atomic weight and then starting a new column when similar classes of elements appeared (Fig. 1.2). Mendeleyev left gaps in the table if an appropriate element had not yet been discovered and then used the trends to predict the properties of the missing elements. Examples included scandium, gallium and germanium. On occasion, he altered the order by atomic weight in order to match similar elements in different rows.



ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ.

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4.
			Fe=56	Rn=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

Д. Менделѣевъ

Fig. 1.2 Mendeleyev's original version of the periodic table of 1869 (Mendeleyev, 1869). The question marks indicate unknown elements inserted so that similar elements would lie along the same row.

The process of filling in the elements in the periodic table continued throughout the nineteenth century. The understanding of the physics of the atoms of different elements was to be a major concern of Niels Bohr as he struggled to incorporate them into the old quantum theory in the early 1920s. The chemists did not really need the atomic hypothesis to make progress, but rather the empirical rules described above were sufficient to enable remarkable progress to be made in the understanding of chemical processes. As the interest of the chemists waned, however, the physicists took up the reins with the need to provide a microscopic interpretation of the laws of thermodynamics.

1.3 The kinetic theory of gases and Boltzmann's statistical mechanics

The discovery of the first and second laws of thermodynamics in the early 1850s placed thermodynamics on a firm theoretical foundation and these laws were to be elucidated by the next generation of theoretical physicists. Among the challenges was the physical interpretation of the law of increase of entropy which exercised the greatest minds of the subsequent period, including Clausius, Maxwell, Boltzmann and Planck.

1.3.1 The kinetic theory of gases

The laws of thermodynamics describe the properties of matter in bulk. In fact, the theory denies that there is any microscopic structure, its great merit being that it provides general relations between the macroscopic properties of material systems. Nonetheless, Clausius and Maxwell had no hesitation in developing the kinetic theory of gases, considering them to consist of vast numbers of particles making continuous elastic collisions with each other and the walls of the containing vessel. Clausius provided the first systematic account of the theory in 1857 in his paper entitled *On the nature of the motion, which we call heat* (Clausius, 1857). He succeeded in deriving the equation of state of a monatomic gas by working in terms of the mean velocities of the particles. Whilst accounting for the perfect gas law admirably, it did not give good agreement with the known values of the ratios of their specific heat capacities, $\gamma = C_p/C_V$ for molecular gases, where C_p and C_V are the specific heat capacities at constant pressure and constant volume respectively. From experiment, γ was found to be 1.4 for molecular gases, whereas the kinetic theory predicted $\gamma = 1.67$. In the last sentence of his paper, Clausius recognised the important point that there must therefore exist other means of storing kinetic energy within molecular gases which can increase their internal energy per molecule.

One feature of Clausius's work was of particular significance for Maxwell. From the kinetic theory, Clausius worked out the mean velocities of air molecules from his formula $RT = \frac{1}{3}NM\overline{u^2}$. For oxygen and nitrogen, he deduced velocities of 461 and 492 m s^{-1} respectively. The Dutch meteorologist Christoph Buys Ballot criticised this aspect of the theory, since it is well known that pungent odours take minutes to permeate a room. Clausius's response was that the air molecules collide with each other and therefore diffuse from one part of a volume to another, rather than propagate in straight lines. In his paper, Clausius introduced the concept of the *mean free path* of the atoms and molecules of gases for the first time (Clausius, 1858). Thus, in the kinetic theory of gases, it must be supposed that there are continually collisions between the molecules.

Both papers by Clausius were known to Maxwell when he turned to the problem of the kinetic theory of gases in 1859 and 1860. His work was published in 1860 in a characteristically novel and profound series of papers entitled *Illustrations of the dynamical theory of gases* (Maxwell, 1860a,b,c). In a few brief paragraphs,[5] he derived the formula for the velocity distribution $f(u)$ of the particles of the gas and introduced statistical concepts into the kinetic theory of gases and thermodynamics,

$$f(u)\,\mathrm{d}u = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} u^2 \exp\left(-\frac{mu^2}{2kT}\right)\mathrm{d}u\,. \tag{1.1}$$

Maxwell immediately noted

> 'that the velocities are distributed among the particles according to the same law as the errors are distributed among the observations in the theory of the *method of least squares*.'

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Francis Everitt has written that this derivation of *Maxwell's velocity distribution* marks the beginning of a new epoch in physics (Everitt, 1975). The statistical nature of the laws of thermodynamics and the modern theory of statistical mechanics follow directly from his analysis.

Maxwell, however, ran up against exactly the same problem as Clausius. If only the translational degrees of freedom are taken into account, the value of γ should be 1.67. Maxwell also considered the case in which the rotational degrees of freedom of non-spherical molecules were taken into account as well as their translational motions, but this calculation resulted in a ratio of specific heat capacities $\gamma = 1.33$, again inconsistent with the value 1.4 observed in the common molecular gases. In the last sentence of his great paper, he makes the discouraging remark:

> 'Finally, by establishing a necessary relation between the motions of translation and rotation of all particles not spherical, we proved that a system of such particles could not possibly satisfy the known relation between the two specific heats of all gases.'

1.3.2 The viscosity of gases

Despite this difficulty, Maxwell immediately applied the kinetic theory of gases to their transport properties – diffusion, thermal conductivity and viscosity. His calculation of the coefficient of viscosity of gases was of special importance.[6] Specifically, he worked out how the coefficient of *dynamic* or *absolute viscosity* η is expected to change with pressure and temperature. He found the result

$$\eta = \tfrac{1}{3}\lambda\overline{u}nm = \tfrac{1}{3}\frac{m\overline{u}}{\sigma}\,, \tag{1.2}$$

where λ is the mean free path of the molecules, $\overline{u}$ is their mean velocity, n their number density and σ the collision cross-section of the molecules – λ and σ are related by $\lambda = 1/n\sigma$. Maxwell was surprised to find that the coefficient of viscosity is *independent of the pressure*, since there is no dependence upon number density n in (1.2). The reason is that, although there are fewer molecules per unit volume as n decreases, the mean free path increases as n^{-1}, enabling the increment of momentum transfer to take place over greater distances. Furthermore, as the temperature of the gas increases, $\overline{u}$ increases as $T^{1/2}$. Therefore, the viscosity of a gas should increase with temperature, unlike the behaviour of liquids. This somewhat counter-intuitive result was the subject of a brilliant set of experiments carried out by Maxwell from 1863 to 1865 (Fig. 1.3). He confirmed the prediction of the kinetic theory that the viscosity of gases is independent of the pressure. He expected to discover the $T^{1/2}$ law as well, but in fact found a stronger dependence, $\eta \propto T$.

In his great paper of 1867, he interpreted this result as indicating that there must be a repulsive force between the molecules which varied with distance r as r^{-5}. This was a profound discovery since it meant that there was no longer any need to consider the molecules to be 'elastic spheres of definite radius' (Maxwell, 1867). The repulsive force,

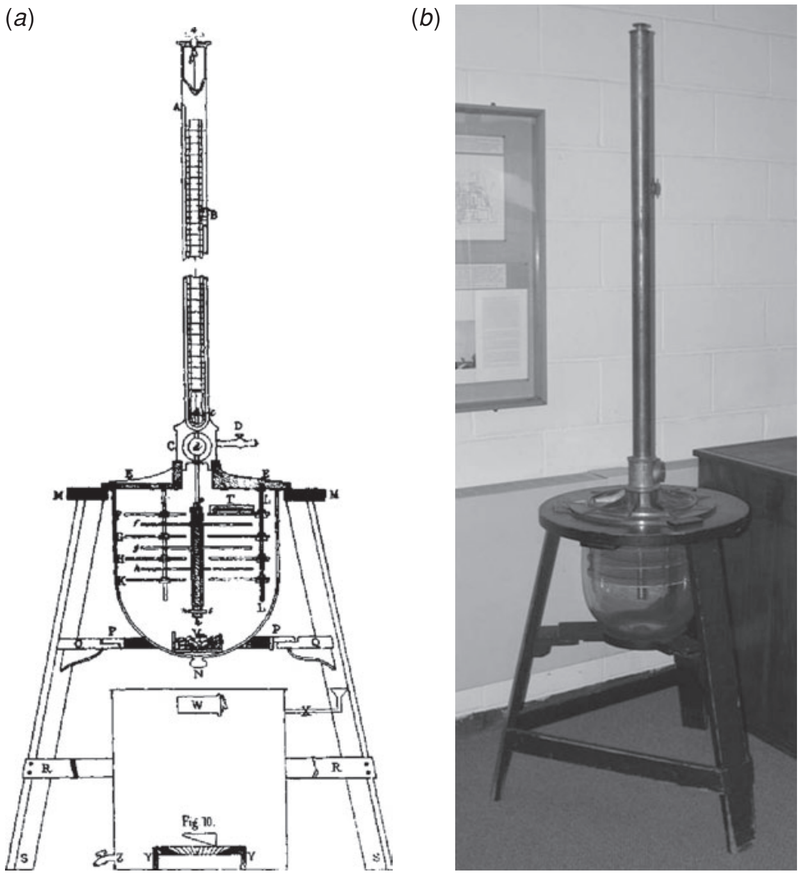

Fig. 1.3 (*a*) Maxwell's apparatus for measuring the viscosity of gases. The gas fills the chamber and the glass discs oscillate as a torsion pendulum. The viscosity of the gas is found by measuring the rate of decay of the oscillations of the torsion balance. The oscillations of the torsion balance were measured by reflecting a light beam from the mirror attached to the suspension. The pressure and temperature of the gas could be varied. The oscillations were started magnetically since the volume of the chamber had to be perfectly sealed. (*b*) Maxwell's apparatus on display in the Cavendish Laboratory.

proportional to r^{-5}, meant that encounters between molecules would take the form of deflections through different angles, depending upon the impact parameter. Maxwell showed that it was more appropriate to think in terms of a *relaxation time*, roughly the time it would take a molecule to be deflected through 90°, as a result of random encounters with other molecules. According to Maxwell's analysis, molecules could be replaced by centres of repulsion, or, in his words, 'mere points, or pure centres of force endowed with inertia' – it was no longer necessary to make any special assumption about molecules as hard, elastic spheres. To express this insight more provocatively, the concept of collisions between particles was replaced by interactions between fields of force.

1.3.3 The kinetic theory of gases and the law of increase of entropy

Another problem concerned the origins of the spectral lines observed in atomic and molecular spectra. If these were associated with internal resonances within molecules, then presumably these provided further means by which energy could be stored in the gas according to the principle of the equipartition of energy, which awards an average of $\frac{1}{2}kT$ of energy to each degree of freedom in equilibrium. Consequently, the number of degrees of freedom N per molecule would increase and the ratio of specific heat capacities,

$$\gamma = \frac{C_p}{C_V} = \frac{\frac{1}{2}NkT + kT}{\frac{1}{2}kT} = \frac{N+2}{N}\,, \tag{1.3}$$

would tend to unity. The fact that the kinetic theory, and specifically the equipartition theorem, could not satisfactorily account for all the properties of gases was a major barrier to the acceptance of the kinetic theory. Furthermore, there was no direct experimental evidence for the existence of atoms and molecules.

The status of atomic and molecular theories of the structure of matter came under attack from a small number of prominent physicists, including Ernst Mach, Wilhelm Ostwald, Pierre Duhem and Georg Helm who rejected the approach of interpreting the laws of macroscopic physics at the microscopic level. Their approach was based on the concept of 'energetics', in which only energy considerations were invoked in understanding physical phenomena, in clear conflict with those who favoured atomic and molecular theories. Most late nineteenth century physicists were, however, of the view that, although the details were not quite right, the atomic and molecular hypothesis was indeed the way ahead.

In 1867, Maxwell first presented his famous argument by which he demonstrated how it is possible to transfer heat from a colder to a hotter body on the basis of the kinetic theory of gases, in violation of the strict application of the law of increase of entropy (Maxwell, 1867). This argument is commonly referred to as involving 'Maxwell's demon'.[7] The Maxwell velocity distribution describes the range of velocities which inevitably must be present in a gas in thermal equilibrium at temperature T. He considered a vessel divided into two halves, A and B, the gas in A being hotter than that in B with a small hole drilled in the partition between them. Whenever a fast molecule moves from B to A, heat is transferred from the colder to the hotter body without the influence of any external agency. It is overwhelmingly more likely that hot molecules move from A to B and in this process heat flows from the hotter to the colder body with the consequence that the entropy of the whole system increases. According to the kinetic theory of gases, however, there is a very small but finite probability that the reverse will happen spontaneously and entropy will decrease in this natural process.

In the late 1860s, Clausius and Boltzmann attempted to derive the second law of thermodynamics from mechanics, an approach known as the *dynamical interpretation of the second law*. The dynamics of individual particles were followed in the hope that they would ultimately lead to an understanding of the origin of the second law. Maxwell rejected this approach as a matter of principle because of the simple but compelling argument that Newton's laws of motion and Maxwell's equations for the electromagnetic field are time