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Rudolph Clausius – A pioneer of the modern theory of heat

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ABSTRACT

Rudolph Clausius (1822–1888) played an important role in advancing the theory of heat during the 19th century. His contributions concerned the development of the two fundamental principles of heat as well as the microscopic approach of kinetic theory where he introduced the new concept of the mean free path. He always strictly separated these two fields. When Clausius took up his studies the idea that heat belonged to the so-called imponderables which were weightless and invisible had not yet disappeared. Carnot had still used that idea for his well-known cycle. Clausius was able to make the Carnot-cycle compatible with the concept of heat as a kind of motion.

His research opened the way for thermodynamics later chiefly advocated by Planck as well as for modern statistical physics mainly connected with the names of Maxwell and Boltzmann. Scientific education and research of Clausius will be discussed here in the context of the development of the theory of heat. As he published most of his important papers on this subject already during the first two decades of his career we confine on this period. Clausius began his studies in Berlin in 1840, habilitated there in 1850 and was appointed at the newly founded Polytechnical School in Zürich in 1855. It will be shown that Clausius remained an outsider in the physics community of his time as he himself did not perform any research experiments.

1. Introduction

Rudolph Clausius (1822–1888) had already published most of his contributions to the theory of heat in the early phase of his career. We shall discuss this period till 1865 when he introduced the concept of entropy.

Clausius was peculiar as a physicist. He did not work experimentally but almost exclusively theoretically. Clausius was one of the very few in this respect in Germany at that time. Up to the end of the 19th century physics education at German universities did not feel the need for such theorists and appointed experimentalists as chair holders usually. Therefore Clausius had a problem concerning his academic career. In his research on the theory of heat Clausius followed the microscopic as well as the macroscopic approach without connecting them. Nothing of his ideas of the behaviour of the molecules should be incorporated in his investigations on the macroscopic phenomena.

The papers of Clausius can be regarded as the starting point of the modern theory of heat. Ludwig Boltzmann (1844–1906) and James Clerk Maxwell (1831–1879) continued on the path of the microscopic approach with more sophisticated statistical methods then. Max Planck (1858–1947) on the other side declined all that as a waste of time and propagated the phenomenological approach with the two fundamental principles as the only useful way for two decades. Already in his dissertation of 1879 Planck had claimed to advance the ideas of Clausius. Till the end of his life Planck always regretted that Clausius had never replied to any of his letters and that it had been impossible to meet him. [1] Subsequently it was just Planck who brought together the two different approaches when he was looking for the entropy function of black radiation in 1900.

2. Concepts and ideas of heat in 19th century

At the time when Clausius took up his studies the controversies about the concept of heat as a kind of substance had not been definitely finished. Up to the mid of 19th century science had used imponderables to describe and explain a variety of phenomena in nature. This meant that besides normal matter further substances existed which were invisible and weightless. They were elementary, i.e. they could not be decomposed any more, and worked as carrier substances of the corresponding phenomena. So there was the assumption of substances of light and heat as well as that of fluids of electricity and magnetism. This concept was deeply shattered for the first time when the phenomena of diffraction were discovered in 1818. Diffraction could be explained by a wave theory of light. This had not only meaning for the field of optics. One

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member of the family of imponderables disappeared and so the common approach to all phenomena in nature had been lost. Furthermore the connection between electricity and magnetism showed that one of the fluids was not necessary [2].

In the 1830s analogies between light and radiation of heat were found. The latter showed all the well-known features of light like refraction, reflexion or polarisation. This stimulated the idea of a wave or vibration theory of heat. In this sense oscillations of matter and ether, the medium of the propagation of light, should be responsible for the transport of heat also. However, this was only a qualitative discussion without any empirical consequences. So the vibration theory of heat remained an alternative in a waiting position.

There were several phenomena of heat which could still be interpreted just with a substance rather easily. Since the end of 18th century it was known that supplying of heat did not increase the temperature of melting ice. Such a kind of heat could not be measured by a thermometer; therefore it was called latent heat [3].

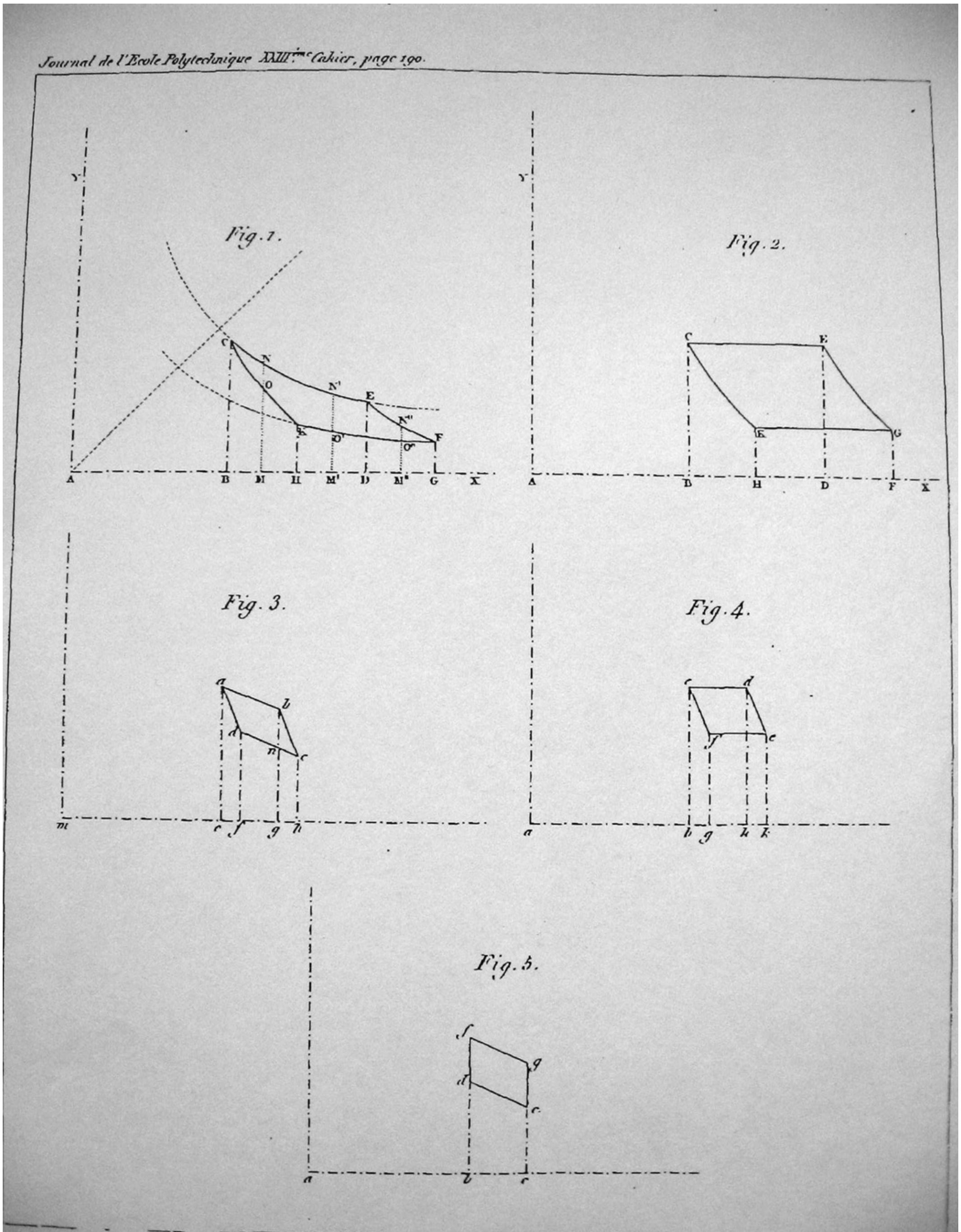


Fig. 1. Clapeyron had illustrated the Carnot cycle for the first time; here we have his sketches from his original paper, following the last text page, reprinted also in Annalen der Physik Vol 59, 1843, appendix Taf.II.

This was characteristic for all phase transitions and the amount was specific for the kind of matter. Since then we speak of specific heats. Such behaviour was very similar to that of chemical bonds with their definite proportions. So heat resembled a chemical element in this respect. Heat as a kind of motion appeared impossible in this context as this would have meant "freezing" a motion for an arbitrarily long time. For that reason several ideas and concepts of heat could coexist in the first half of 19th century. The friction experiments of Benjamin Thompson [Count Rumford] (1753–1814) at the beginning of the century have been classified as a falsification of the idea of heat as a substance only in retrospective [4].

3. Study years of Clausius (1840–1844) the concept of Carnot

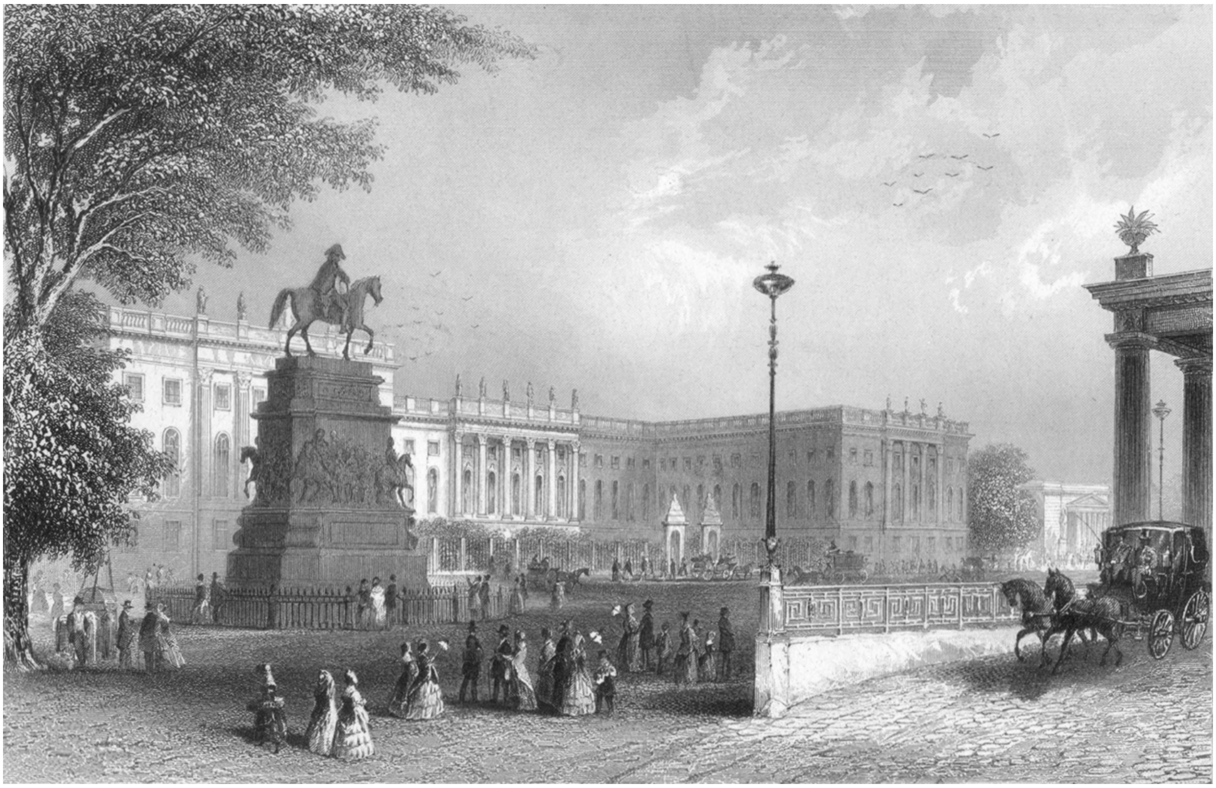
Rudolph Clausius was born in Cöslin, a town in Pomerania in 1822. After finishing Gymnasium in Stettin he began to study at the University of Berlin in 1840. The university had been founded 30 years ago and in the meantime had emerged as one of the largest in the German-speaking territories. At that time more than 1600 students were enrolled there [5].

As we know from Clausius manuscripts he learned about the different concepts of heat in a lecture he attended in winter term 1842/43. His professor told that physics of heat was still in a "phase of transition" but expected that a wave or vibration theory of heat would subsequently make its way. [6]. During his studies Clausius at least once dealt with physics of heat more intensively. He belonged to the participants of the new colloquium of Gustav Magnus (1802–1870) where students came together to give seminar papers of recent publications. In this way current research could be discussed.

Clausius presented Clapeyron's treatise, which analysed how heat could generate mechanical work [7]. It had been published in French already in 1834 but because of its importance appeared in "Annalen der Physik" in German language again in 1843 [8]. Benoît Paul Émile Clapeyron (1799–1864) had transformed Carnot's fundamental paper of 1824 in a mathematical language illustrating his cycle process in the diagram well-known until today (Fig. 1).

Carnot's publication itself was not available any more and his ideas were spread and became known by Clapeyron's work solely [9].

Sadi Carnot (1796–1832) - educated as an engineer - had published only this single paper during his short life of 36 years but influenced the direction of research on the phenomena of heat decisively. He investigated the general question how heat, still regarded as a substance, could be used for the generation of mechanical work most efficiently. Carnot assumed that the transfer of heat to a lower temperature level was quite analogous to falling matter and therefore produced mechanical work. He explicitly used the term "drop height". Carnot developed a thought experiment, the reversible cycle process, where the kind of the applied engine did not play any role. This abstraction made it possible to transform a subject of technique into a subject of physics. Carnot showed that the maximum of the generated work was not dependent of the agents employed but of the two reference temperatures only. He could confirm this with a proof by contradiction: If an engine exists that is more efficient and therefore able to exceed that maximum it would be possible to construct a perpetual motion machine. But in the words of Carnot: "Such a creation of mechanical work is a contradiction to all present ideas, to the laws of mechanics and to a healthy physics. Therefore it is inadmissible." [10].



Berlin University about 1850, from Albert Henry Payne, Berlin und seine Kunstschätze, Leipzig and Dresden, 1850.

4. From teachers exam to a call to Zürich (1844–1855) the idea of a second principle of heat

After passing exam for teachers in 1844 Clausius taught a few hours a week at the Friedrich-Werder-Gymnasium in Berlin for the next six years. It was one of the renowned educational institutions in Prussia of that time. His research focused on subjects of the then so-called meteorological optics. That comprised the phenomena of light in the atmosphere as dawn and afterglow, rainbow or northern lights. Clausius especially investigated the reflexion of sunlight and had already published two papers when he finished his dissertation concerning this subject in June 1848. The regulations of Berlin University required a dissertation written in Latin. But Clausius wanted to avoid the fruitless labour of translation and looked for a university where he could receive the doctoral degree with his German version. A corresponding letter of inquiry was answered positively by the Philosophical faculty of the University of Halle on June 27. Clausius then submitted not only his dissertation but also two of his recent publications, which were reviewed as well. The rather quick procedure did not permit a really deep analysis of Clausius' achievements. But the referees wrote in their report that they had the impression of "expertise" and "apparent emerging skill" which was sufficient for the admission to the oral exam which took place already on July 15, 1848. Clausius got the evaluation "passed very honourable" and received the doctoral degree directly afterwards [11].

In meteorological optics Clausius had found a suitable subject for his mathematical-theoretical inclinations. There had not been much theoretical research before. Clausius took up an assumption that not air itself but small floating steam bubbles reflect sunlight. That enabled him to explain the blue colour of the sky as well as dawn and afterglow. It is important that he used probability considerations here. They provided a justification for his approach to reduce the reflexions of a large number of arbitrarily formed masses to the same number of spheres [12].

In a more than 50 pages long publication of 1850 Clausius dealt with the conversion of heat into mechanical work. He started with the approach of Carnot or Clapeyron but abolished the idea that heat was an indestructible substance which both of them had still used. He substituted this by the concept that heat and mechanical work can be converted into each other in a fixed proportion. It is a special case of the principle of the conservation of energy which was still not generally accepted. The mutual connections and conversions between different phenomena in nature had been the background for developing such a common concept like energy. The knowledge of such conservation began to establish only gradually around 1850. In this context Clausius mentioned explicitly the experiments of James Prescott Joule (1818-1889) and was one of the very few who quoted the calculation of the mechanical equivalent of heat performed by Julius Robert Mayer (1814–1878) in 1842.

So the old investigation of Carnot and the new concept of the mutual conversion of heat and mechanical work were brought in line by Clausius. He stated expressively: "that heat is no substance but consists of a motion of the smallest parts of the bodies." [13] Therefore the old and well-established conservation principle of mechanics had to be applied. Clausius did not tell anything about the kind of motion. It was sufficient for him to relate the kinetic energy of that motion to the amount of heat. However, there are allusions to the behaviour of the molecules. So he interpreted the latent heat of vaporization as work against the external pressure and work to overcome the attraction between the particles. We are not far from the kinetic theory of gases when he noticed: "that the reciprocal attractions of the particles which are effective in solid and liquid fluid bodies are neutralized in the case of gases." [14] Without a repulsive or attractive force the gas molecules should move in a straight line then. But we cannot find this consequence here explicitly.

Clausius understood that also with the new idea of heat as a form of energy the Carnot cycle would be the most effective way for the conversion into mechanical work. Similar to Carnot he gave a proof by contradiction: He started with the converse assumption and got the result that it could be possible to transfer any quantity of heat from a cold body to a warm one without expenditure of work or any other alteration. But such a conclusion contradicted any experience. Clausius considered the negation of that conclusion a second fundamental principle of heat. He had regarded the equivalence of heat and work as the first principle. Clausius connected both to calculate the so-called Carnot function or the mechanical equivalent of heat. He valued the rather good agreement with the data of Joule's experiments as a confirmation of the "correctness of Carnot's basic principle in the shape which it had taken by the connection to the first principle [equivalence of work and heat]." [15].

These publications were the basis to apply for habilitation in 1850. The procedure gives an impression how Clausius' research was evaluated by his colleagues in Berlin. Habilitation at Berlin University was cumulative at that time, i.e. all published papers were submitted to the faculty. Not a physicist but Franz Encke (1791–1865), an astronomer who as a student of Carl Friedrich Gauβ (1777–1855) had been well educated in mathematics, became the referee of the faculty. He evaluated the achievements of Clausius positively. However, he avoided any definite statements on the results of the papers. So he called the applied hypotheses plausible but added restrictively, that they alone would not give explanations. This concerned the assumption of the existence of small steam bubbles by dealing with the atmospheric light dispersion as well as the modification of Carnot's principle. The methodological approach of Clausius was principally accepted by Encke in this context because of the small "knowledge of the inner constitution of the bodies". As there were no doubts about the ability of Clausius to teach, Encke concluded "that the habilitation of Mr. Clausius at the university of this town can be regarded as an acquisition:" After the usual probation lecture and the subsequent colloquium Clausius became "Privatdozent" for physics on December 12, 1850 [16].

Clausius had made a name of himself in the scientific community in the meantime but was regarded as one-sided. This can be confirmed by a report for the replacement of the physics chair in Heidelberg in 1854. Gustav Kirchhoff (1824–1887) was at the top of the list and got the position subsequently. Clausius had also been considered: "Prof [sic] Clausius has earned well-founded esteem by his ingenious excellent treatises about heat and matters of optics. His papers till here are of pure mathematical physical character; experimental investigations of others serve as starting points. As I do not know Prof Clausius personally and as I have no information what kind of position he has in Berlin, I am not able to give any information whether he is familiar with experimental physics." [17] But the latter was an almost necessary precondition for physics chairs in Germany. The papers of Clausius did not contain references to any experiments which he had performed himself. However, in 1855 the newly founded Polytechnical School in Zürich looked just for a mathematical physicist. Clausius was recommended highly by Johann Christian Poggendorff (1796-1877) and Wilhelm Weber (1804-1891) who counted him among the most outstanding scholars on mathematical physics but nevertheless wrote: "… it is not known to me that he has made experimental physics to a special subject of his activity." [18] Even here we get a hint on the one-sided qualification of Clausius. He received the call to Zürich and began to give lectures in autumn 1855. Clausius became also co-director of the physical cabinet and got some responsibility concerning the purchase of new equipment.

Polytechnikum about 1865, from Samuel Zurlinden: Hundert Jahre: Bilder aus der Geschichte der Stadt Zürich in der Zeit von 1814–1914, Volume 1, Zürich 1914.

5. The kinetic theory of gases (1856–1858)

The first paper of Clausius on the kinetic theory of gases was written as a reaction to an article of August Krönig (1822–1879) with the title “Grundzüge der Gase” which had been published in “Annalen der Physik” in 1856 [19]. Krönig revived some ideas already formulated in England before. But different from those his paper stimulated further research. It used a model gas where the molecules moved straightly with constant velocity and stroke each other as well as the wall of the vessel elastically. This led to the well-known gas laws rather easily.

Did it make any sense to publish another article on this model? Clausius showed that an isolated idea is less important than the incorporation in a broader context. Whereas the molecules of that model had been only treated as mass points without any structure Clausius made them to physical objects in 1857 [20]. He assumed that they could rotate and also believed that the single atoms of a molecule had the freedom to oscillate against each other. Clausius was able to calculate the relation between the translation energy K and the total energy H of a molecule:

$K = \tfrac{1}{2}\,\mathrm{nmv}^2$ (energy of translation); n number, m mass, v velocity of the molecules; $H = c_\mathrm{v}\,\mathrm{nm}\,T$(total energy); c_v the specific heat at constant volume, T absolute temperature;

The change of energy by increasing volume:

$\mathrm{dH} = c_\mathrm{v}\,\mathrm{nm\,dT} + \mathrm{pdV} = c_\mathrm{p}\,\mathrm{nm\,dT}$; p pressure, V volume, c_p the specific heat at constant pressure leads to

$$\frac{K}{H} = {}^3/_2\left(\frac{c_p}{c_v} - 1\right)$$

There are characteristically values for different types of gases. For “simple” gases with the well-known value

$$\frac{c_p}{c_v} = 1,421 \text{ Clausius got } \frac{K}{H} = 0,6315$$

As the translation energy was smaller than the total energy he concluded that, other motions of the constituents of the molecules take place.” [21] In the case of more complex gases, Clausius added, the relation would become even smaller.

Using $\mathrm{pV} = {}^1/_3\mathrm{nmv}^2$ and experimental data of Henri Victor Regnault (1810-1878) [1 kg of atmospheric air fills a volume of 0,7733 cubic metre under pressure of 1 atm at the freezing point of water] Clausius could easily get another quantitative result and calculate the velocities of the molecules. He got rather large values but did not give any comments on that: oxygen 461 m/s, nitrogen 492 m/s and hydrogen 1844 m/s (here m/s means metre per second). He also described the other aggregate states as a consequence of the different mobility of the molecules. That was in agreement with considerations in his paper on the conductivity of electrolytes of the same time [22]. Furthermore he developed a new qualitative idea about vaporization which he described as a state of a dynamical balance.

Several scientists published their objections against the kinetic theory then [23]. The large velocities of the molecules seemed to be incompatible with macroscopic phenomena like the slow escape of gases from any vessel. One of the critics even recognised that there was a potential way out. [24]. The kinetic theory did not make any statement about the length of the way the molecules passed through between two strikes. The problem could be solved when segments of the straight motion were interrupted in short, erratic intervals by the influence of molecular forces. But this idea was rejected by the critic himself because it became necessary to use the calculus of probability which he considered inacceptable for physics.

However, this was no problem for Clausius. As mentioned above he had already used the calculus of probability in his early investigations on optics. So he introduced the new concept of the mean free path in 1858 [25]. For this purpose Clausius defined a sphere of action similar to that in his theory of elasticity of 1849 [26]. The radius of this sphere of action s was chosen in a way that the effective forces were repulsive inside and – decreasing with the distance - attractive outside. The assumption of attractive forces could be justified by the experiments of Joule and William Thomson [later Lord Kelvin] (1824–1907), who in the case of free expanding gases had found decreasing temperatures. Then the mean free path ℓ was the distance which a molecule could move in the average, “before its centre of gravity comes into the sphere of action of another molecule.” [27] Clausius was able to show that W, the probability of the molecules to traverse a certain distance x without a strike decreases exponentially with the length of that distance. This reminds on his considerations on light dispersion:

$$W\left(x\right) = e^{-x/\ell}$$

Taking λ as the average distance between the molecules:

$$\ell = 3/4\frac{\lambda^3}{\pi s^2}$$

This is only a relation between three unknown quantities. But in the form: $\frac{\ell}{s} = \frac{\lambda^3}{{}^4\!/_3\,\pi s^3}$

Clausius was able to give a vivid description: “The mean length of path of a molecule is in the same proportion to the radius of the sphere of action as the entire space occupied by the gas, to that portion of the space which is actually filled up by spheres of action of the molecules.” [28] Using

$$\frac{\ell}{s} = 1000$$

because this represents the relation between density of ice and steam, Clausius got $\ell = 62\ \lambda$. So he could make it plausible that the mean free path was of similar size as the average distance between the molecules. The model of the kinetic theory of gases had become consistent.

Using this model Maxwell found a new phenomenon in 1859. He arrived at the surprising result that the inner friction was independent of the density [29]. In 1865 nearly simultaneously with the German Oskar Emil Meyer (1834–1909) he performed experiments which confirmed this result rather precisely. It was a breakthrough for the kinetic theory of gases [30].

Clausius published only two more papers about this subject after 1860: On heat conduction in 1862 and on the “virial theorem” in 1870 [31]. So he did not participate in the more sophisticated statistical methods of Boltzmann and Maxwell. Clausius had opened the door but later on became more interested in the macroscopic treatment of heat.

Rudolph Clausius, photo Deutsches Museum München, according to a sketch of Bernhard Herfling, 1861.

6. New formulations of the second principle of heat

Clausius had always separated the microscopic and macroscopic approach. So his thermodynamics remained independent of any special assumption about the motion of the molecules. At the same time W. Thomson advanced the formulation of the second principle of heat. According to Thomson it should have consequences for all phenomena in nature as every transformation of energy is accompanied by heat. Therefore the disappearance of all thermal differences would be unavoidable in his view. He called this the dissipation of energy leading to a gradual decrease of the ability of nature to change anything. The result would be the end of everything [32]. Hermann Helmholtz (1821–1894) brought this in a concise form in 1854: All processes in nature will come to a standstill, “shortly the universe will be condemned to eternal quietness.” [33] Since 1854 Clausius worked mathematically on the second principle, also including irreversible processes. He introduced a new physical quantity which he designated at first as “Verwandlung” or “transformation”. In 1865 he substituted it by the Greek word for “Umkehr” or “reversion” which is “entropy”. This enabled him to express the two principles in a very short form which has become famous:

1. The energy of the universe is constant.
2. The entropy of the universe aims to approach a maximum [34].

7. Concluding remarks

Clausius started his career with research on optics and elasticity before he began to investigate the phenomena of heat in 1850. Already his paper of that year on the “moving force of heat” established a new, a second fundamental principle of heat. Clausius had dismissed the concept of heat as a substance and substituted it by the idea that heat was the kinetic energy of elementary particles. We find allusions to the kind of motion of those particles but he still avoided to become definite in this respect. Clausius followed a hypothetical-mathematical approach which at that time was not generally accepted in Germany. The reputation to be a physicist who had never performed experiments himself was a burden for any academic career. But the position at the Polytechnical School in Zürich offered him a kind of niche. There he developed his ideas of the kinetic theory of gases with the concept of the mean free path. This opened the door for further research mainly connected with the names of Maxwell and Boltzmann. In thermodynamics he introduced the important and far-reaching concept of entropy. There is a direct line to the contributions of Planck. Clausius had formulated important fundamentals in the theory of heat and therefore belongs to the most eminent physicists of 19th century.

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