Proceedings of the ASME 2009 Heat Transfer Summer Conference
HT2009
July 19-23, 2009, San Francisco, California USA

HT2009-88060

A BRIEF HISTORY OF THE T^4 RADIATION LAW

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ABSTRACT

Since the 1700s, natural philosophers understood that heat exchange between two bodies was not precisely linearly dependent on the temperature difference, and that at high temperatures the discrepancy became greater. Over the years, many models were developed with varying degrees of success. The lack of success was due to the difficulty obtaining accurate experimental data, and a lack of knowledge of the fundamental mechanisms underlying radiation heat exchange. Josef Stefan, of the University of Vienna, compiled data taken by a number of researchers who used various methods to obtain their data, and in 1879 proposed a unique relation to model the dependence of radiative heat exchange on the temperature: the T^4 law.

Stefan's model was met with some skepticism and was not widely accepted by his colleagues. His former student, Ludwig Boltzmann, who by then had taken a position at the University of Graz in Austria, felt that there was some truth to the empirical model proposed by his mentor. Boltzmann proceeded to show in 1884, treating electromagnetic radiation as the working fluid in a Carnot cycle, that in fact the T^4 law was correct.

By the time that Boltzmann published his thermodynamic derivation of the radiation law, physicists became interested in the fundamental nature of electromagnetic radiation and its relation to energy, specifically determining the frequency distribution of blackbody radiation. Among this group of investigators was Wilhelm Wien, working at Physikalisch-Technische Reichsanstalt in Charlottenburg, Berlin. He proposed a relation stating that the wavelength at which the maximum amount of radiation was emitted occurred when the product of the wavelength and the temperature was equal to a constant. This became known as Wien's Displacement Law, which he deduced this by imagining an expanding and contracting cavity, filled with radiation. Later, he combined his Displacement Law with the T^4 law to give a blackbody spectrum which was accurate over some ranges, but diverged in the far infrared.

Max Planck, at the University of Berlin, built on Wien's model but, as Planck himself stated, "the energy of radiation is distributed in a completely irregular manner among the individual partial vibrations..." This "irregular" or discrete treatment of the radiation became the basis for quantum mechanics and a revolution in physics.

This paper will present brief biographies of the four pillars of the T^4 radiation law, Stefan, Boltzmann, Wien and Planck, and outline the methodologies used to obtain their results.

EARLY RADIATION STUDIES

Heat transfer, as a serious branch of study in physics, began with Sir Isaac Newton, although his contributions to this subject are but a small part of his complete body of work including calculus, mechanics, optics, and of course, gravity. Natural philosophers of the day deduced that the heat transfer rate was some function of the temperature, although they had difficulty distinguishing between the now commonly known modes of heat transfer: conduction, convection and radiation. Early research into geological history motivated Joseph Fourier to study heat conduction in solids, and then extend his work to incompressible fluids, but postponed any kind of work studying heat transfer in atmospheric gases. Early visual studies of convection heat transfer in gases were performed by Rinaldini in 1657. Euler began the first mathematical theories of convection, and Rumford later discovered convection currents in liquids in 1797. At the time, scientists had difficulty separating conduction and convection in a fluid, and it was widely held that fluids did *not* conduct heat.

Early researchers had a rudimentary knowledge of radiation heat transfer, and believed that heat could be transferred by radiation through a vacuum. To separate conduction and convection effects from radiation, it would be necessary to draw a vacuum between two surfaces. It was not fully understood, however, that a sufficiently low pressure had to be achieved and that residual gases could affect the radiation transfer by absorption and reradiation. One observation that became quite clear was that at high temperatures, the heat transfer was no longer simply a function of the temperature difference. What the dependence was, however, was another issue. For a more detailed early history of heat transfer, see Brush [1,2].

After some issues in trying to determine a proper temperature scale, and some fits and starts, Dulong and Petit [3] performed a series of experiments to determine the rate of radiation heat transfer between two bodies. Their paper, which was awarded a prize from the French Académie des Sciences in 1818 proposed a relation for the emissive power of radiation,

$$E = \mu a^T \tag{1}$$

Where a =1.077 and μ was a constant dependent on the material and size of the body. The dependence on the temperature in the exponent helped explain the higher heat transfer rates at higher temperatures, but had a significant disadvantage. There would be heat transfer even at T = 0. Nevertheless, even decades after the T^4 law was discovered, a textbook stated that the Dulong and Petit law, "seems to apply with considerable accuracy through a much wider range of temperature differences than that of Newton," and is based on "one of the most elaborate series of experiments ever conducted."[4] Further experiments were performed by Tyndall [5], Provostaye and Desains [6], Draper [7] and Ericsson [8], all making slight variations to the constants determined by Dulong and Petit, but keeping the basic structure of the model intact. This was the state-of-the-art when Josef Stefan, Professor and Director of the Institute of Physics at the University of Vienna began his own investigation of the problem.

JOSEF STEFAN

Josef Stefan (Fig. 1) was born on March 24th, 1835 in the small village of St. Peter, on the outskirts of Klagenfurt, in modern-day Austria. He was the illegitimate son of ethnic Slovenes. His father Aleš was a miller and baker, and his mother Marija Startinik was a maidservant. He began his studies at the University of Vienna in 1853, studying physics and mathematics, graduating in 1857. The year after his graduation, he passed his doctoral examination at the University of Vienna and accepted a position at the University's Physiological Institute. He was more interested in physics-related work, and was eventually offered a full professorship in mathematics and physics in 1863, becoming the youngest person in the Austro-Hungarian empire to hold that rank. Two years later in 1865, he was appointed the Director of the Institute of Physics at the University of Vienna, a position he held until his death in 1893.[9] Among his students at the Institute were Ludwig Boltzmann and the psychoanalyst Sigmund Freud, who took physics courses as part of his medical studies.

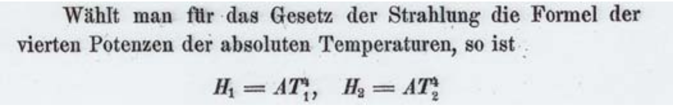
Figure 1. Portrait of Josef Stefan, taken around 1885.

Stefan did not feel comfortable with the Dulong and Petit law, so he began to delve into their work more closely. Drawing on his past experience in conduction heat transfer, he reconstructed their apparatus, shown in Fig. 2. Based on the design, he estimated that a significant portion of the heat was lost by conduction and not by radiation, as had been presumed by Dulong and Petit. By subtracting out the heat lost by conduction and reanalyzing the data, Stefan saw that the heat transfer was proportional to the temperature to the fourth power. Figure 3 below shows the form of the T^4 law as it first appeared in print in 1879.[10] Stefan didn't realize the importance of his proportionality constant, *A*, but noted that it, "depend[ed] on the size and the surface of the body." He also noted that the temperature had to be given in absolute values.

The unusual form of his model forced Stefan to test it on previously published data, and he wanted to see how well it worked at temperatures higher than those used by Dulong and Petit. He first looked at Tyndall's work, which gave heat transfer data on a platinum wire over a wide temperature range. After studying Tyndall's data, Stefan wrote, "From weak red heat (about 525°C) to complete white heat (about 1200°C) the intensity of the radiation increases from 10.4 to 122, thus nearly 12-fold (more precisely 11.7). The ratio of the absolute temperature 273+1200 and 273+525 raised to the fourth power gives 11.6.” [11] This result gave Stefan additional confidence in his model, and he proceeded to test it on the data of Provostaye and Desains, Draper, and Ericsson, and found that the T^4 model fit their data better than the Dulong and Petit model.

Figure 2. Original apparatus which Stefan used to evaluate the amount of heat lost in an experiment by Dulong and Petit.

Although Stefan was an outstanding experimentalist, neither he nor any of his students performed (or at least published) radiation experiments themselves. It is not known why. For this reason, perhaps, Stefan was not completely confident in his model. He wrote that his analysis had a, “hypothetical nature and reasoned support for [it] was impossible, so long as measurements are not made of radiation to surroundings at absolute zero, or at least a very low temperature.”(translation from Dougal [11]) Interestingly, Stefan never computed a value of his proportionality constant, *A*, but from a straightforward analysis from Stefan’s paper, it can be easily determined to be 5.056 x 10^{-8} W/m^2K^4, which is about 11% lower than the currently accepted value of what we now know as the Stefan-Boltzmann constant.



Wählt man für das Gesetz der Strahlung die Formel der vierten Potenzen der absoluten Temperaturen, so ist

$$H_1 = AT_1^4, \quad H_2 = AT_2^4$$

Figure 3. The first appearance in print of the T^4 law.[10]

LUDWIG BOLTZMANN

Ludwig Boltzmann theoretically tackled the radiation problem which his mentor Stefan studied experimentally, long after Boltzmann left Vienna during his second professorship at the University of Graz.

Boltzmann (Fig. 4) was born on February 20, 1844, just outside the medieval protective walls of Vienna, to a middle class family. His father, Ludwig Georg, was a civil servant of the Habsburg empire, working in the taxation office. His mother was Maria Pauernfeind, the daughter of a well-to-do Salzburg merchant.[12] He was a precocious boy who early in life was taught by a private tutor, and then as the family moved to various locations throughout Austria, attended the local *Gymnasium*. He took piano lessons from the famed composer Anton Bruckner. Although the lessons ended abruptly, Boltzmann continued to play the piano for the rest of his life.[13] In 1863, Boltzmann entered the University of Vienna to study mathematics and physics, and after publishing two papers, received his Ph.D. just three years after matriculating. He arrived at the Institute of Physics not long after Stefan assumed the Directorship. Stefan was just nine years older than his student. Also at the Institute was Josef Loschmidt, an older scientist who took Boltzmann under his wing. Loschmidt was the discoverer of the ring structure of the benzene molecule and was the first to accurately determine the size of an air molecule. Loschmidt and Boltzmann hashed out ideas that Boltzmann had on the kinetic theory of gases, which he was developing separately but simultaneously with James Clerk Maxwell of Scotland. After receiving his doctorate and working as an assistant at the Institute, Boltzmann left Vienna in 1869 to become a professor of physics at the University of Graz. He left Graz for Vienna in 1873, then returned to Graz in 1876, where he stayed until 1890. During this second period, Boltzmann set out to prove from thermodynamic principles the experimental model published by Stefan.

Figure 4. Ludwig Boltzmann in Graz, 1887, three years after he derived the T^4 law.

In a deceptively simple analysis, Boltzmann considered a Carnot cycle, using radiation particles as the working fluid. He based his ideas on an earlier paper of Adolfo Bartoli [14] who described some ideas on radiation pressure. Boltzmann combined thermodynamics and Maxwell’s electromagnetic equations with the then novel idea that electromagnetic waves exert a pressure on the walls of an enclosure filled with radiation. In a piston-cylinder system, when the piston moves slowly, the pressure exerted on the piston (from [1,12]) is,

$$p = \frac{e}{3} \tag{2}$$

where e is the energy density. From conservation of energy one can then write,

$$TdS = d\left(eV\right) + pdV = edV + V\frac{de}{dT}dT + \frac{e}{3}dV \tag{3}$$

So,

$$TdS = V\left(\frac{de}{dT}\right)dT + \frac{4}{3}edV \tag{4}$$

The derivatives of the entropy with respect to T and V are respectively,

$$\frac{\partial S}{\partial T} = \frac{V}{T}\frac{de}{dT}, \quad \frac{\partial S}{\partial V} = \frac{4}{3}\frac{e}{T} \tag{5}$$

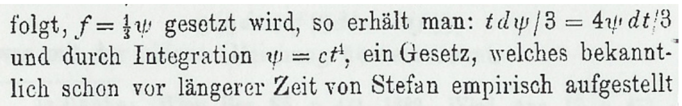
By taking cross-derivatives of the entropy with respect to V and T and equating, one finds,

$$\frac{1}{T}\frac{de}{dT} = \frac{4}{3}\left(T\frac{de}{dT} - e\right)\frac{1}{T^2} \tag{6}$$

Rearranging gives,

$$\frac{de}{dT} = 4\frac{e}{T} \tag{7}$$

Separating and integrating gives the familiar form of the fourth power radiation law, or as Boltzmann originally published it [15], shown below in Fig. 5.



folgt, $f = \frac{1}{3}\psi$ gesetzt wird, so erhält man: $t\,d\psi/3 = 4\psi\,dt/3$ und durch Integration $\psi = ct^4$, ein Gesetz, welches bekanntlich schon vor längerer Zeit von Stefan empirisch aufgestellt

Figure 5. The last step of Boltzmann's derivation of the T^4 law.[15]

Once Boltzmann published his theoretical results confirming Stefan's analysis of experimental data, the T^4 law became more widely accepted. But work on radiation did not cease. Towards the end of his life, Boltzmann spent a large portion of his time and energy defending the kinetic theory of gases, leading the so-called atomistic school of thought, defending the existence of atoms. The opposing school, the energeticists lead by Ernst Mach, held that without visual observation it was impossible to prove that atoms existed. This struggle drained Boltzmann's strength and physics focus. He committed suicide on September 5th, 1906 in his hotel room in Duino, near Trieste, Italy.

WILHELM WIEN

Wilhelm Wien (Fig. 6) was born on January 13th, 1864 in the town of Fischhausen (currently Primorsk), then in East Prussia (now Poland). His father Carl was a well-to-do farmer who married the former Caroline Gertz. He began his advanced studies in 1882, attending the Universities of Göttingen and Berlin, then from 1883-1885 settled in Hermann Helmholtz's laboratory in Berlin, where he earned his Ph.D. in 1886 with a thesis on experimental light diffraction on metal section and the influence of materials on the color of refracted light.[16] He believed strongly that theoretical and experimental physics should not be separated, and was considered an expert in both fields. At the age of 21, Wien befriended Max Planck, who was six years his senior, and they remained lifelong friends and scientific colleagues.

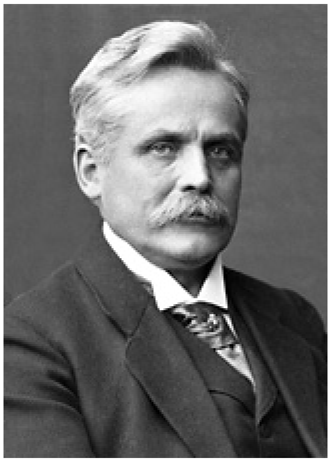


Figure 6. Portrait of Wilhelm Wien

Wien was an ardent Prussian nationalist, who thought that the firing of the Bismarck was the greatest disaster in German history, and that Germany was completely blameless for the first World War.[17] He held a number of academic positions, primarily as professor of Physics, the University of Aachen in 1896, University of Giessen in 1899, and the University of Wurzburg in 1900 where he stayed until 1920, when he accepted a position at the University of Munich, where he spent the rest of his life. He wrote an autobiography, "Aus dem Leben und Wirken eines Physikers," (On the Life and Work of a Physicist), published in posthumously in 1930, which was not published outside of Germany. Wien spent a good portion of his career studying blackbody radiation, but this paper will focus on two of his most well-known contributions.

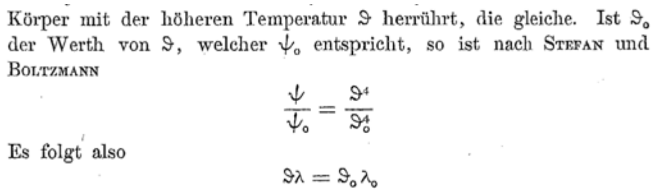
The Displacement Law

Wien felt very strongly that heat radiation could be treated thermodynamically, and began to extend Boltzmann's methods. However, while Boltzmann analyzed the full energy spectrum, Wien concentrated on the energy at a given wavelength.[18] At the time, a thermodynamic approach to radiation was not well-accepted, and both Wien's mentor Helmholtz and Lord Kelvin argued against these methods.

In his 1893 paper[19], Wien argued that two separate processes should give the same energy distribution over the wavelengths if the final temperature of both processes were the same. The first process was the increase in temperature as the energy density increased, and the second the corresponding adiabatic decrease of the volume of the enclosure containing the radiation. By using the Doppler effect, he showed the wavelength λ depended on the velocity of the source, so that the spectral energy densities, ψ, were related to the wavelengths by,

$$\frac{\psi}{\psi_0} = \left(\frac{\lambda_0}{\lambda}\right)^4 \qquad (8)$$

Wien then introduced the Stefan-Boltzmann relation to show, as he did originally below in Fig. 7, what is now known as Wien's Displacement Law,



Körper mit der höheren Temperatur ϑ herrührt, die gleiche. Ist ϑ_0 der Werth von ϑ, welcher ψ_0 entspricht, so ist nach STEFAN und BOLTZMANN

$$\frac{\psi}{\psi_0} = \frac{\vartheta^4}{\vartheta_0^4}$$

Es folgt also

$$\vartheta\lambda = \vartheta_0\lambda_0$$

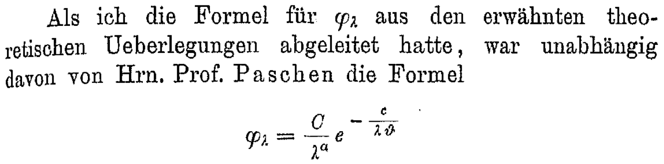
Figure 7: Wien's Displacement law.[19] Here, the θ denotes temperature.

In Wien's description, "In the normal emission spectrum…each wavelength is *displaced* (italics added) on change of temperature, that the product…remains constant."[20] The equation shown in Figure 7 was first referred to as Wien's "Displacement Law" by Lummer and Pringsheim[21,22], who also first calculated the constant to be 0.294 cm·K.

Interestingly, the concept of a "finite quantum of energy," often attributed to Planck, appears in Wien's 1893 paper.

Wien's Distribution Law

Three years later, Wien[23] sought to find a relation to govern the spectral energy distribution of a blackbody. A key hypothesis was that he assumed that blackbody radiation was emitted by molecules which followed Maxwell's velocity distribution.[18] As Wien stated, he used, "Maxwell's law of the distribution of velocities as the basis of the radiation law, but to lessen the number of hypotheses…by drawing upon the results obtained by Boltzmann and myself by pure thermodynamic treatment."[20] This formed the basis of his "molecular hypothesis." By assuming that the wavelength of radiation emitted by a molecule was a function only of its velocity, he found (Fig. 8),



Als ich die Formel für φ_λ aus den erwähnten theoretischen Ueberlegungen abgeleitet hatte, war unabhängig davon von Hrn. Prof. Paschen die Formel

$$\varphi_\lambda = \frac{C}{\lambda^{a}} e^{-\frac{c}{\lambda\vartheta}}$$

Figure 8. Wien's Distribution Law as it originally appeared.[23]

By integrating ϕ_λ over all wavelengths and equating the result with the Stefan-Boltzmann law, he found that the exponent of lambda given in Fig. 8 had to satisfy, $\alpha = 5$,

Wien's distribution law agreed relatively well with experimental data, except that it diverged at large values of the product, λT.

For his work in radiation, Wilhelm Wien won the 1911 Nobel Prize in Physics. In the words of his colleague Max von Laue, "His immortal glory," was that he "led us to the very gates of quantum physics." Wien died on August 30, 1928 in Munich, Germany.

MAX PLANCK

Wien's friend and colleague, Max Planck, studied Wien's results and understood that they modeled experimental results well, but also realized its shortcomings. Planck knew that the thermodynamic arguments were strong, but felt that there were too many hypotheses, and set about a way to minimize them and find a new energy distribution relation.

Max Planck (Fig. 9) was born into a family of scholars on April 23rd, 1858 in Kiel, Germany. His grandparents were theologians who taught at the University of Göttingen, and his father Wilhelm Planck was a professor of jurisprudence at the University of Kiel. His mother, Emma Patzig, descended from a line of pastors. Planck, although a friend and colleague of Wien, did not hold a similar nationalistic view of his homeland. Planck considered himself more liberal politically than the rest of his family. He was a good student who showed talent over a range of subjects beyond science, including history, language and especially music, and he played a number of instruments.[17] By virtue of his amiable personality, he was considered a favorite of his teachers and classmates. He first matriculated at the University of Munich in 1874, then in 1877 studied for a year in Berlin, and in 1879 defended his doctoral dissertation in Munich. In 1885, he was appointed an associate professor of physics at the University of Kiel and in 1889, upon Kirchhoff's death, assumed his position at the University of Berlin. He was held in high esteem for his technical abilities, but was also noted for his leadership and organizational skills. He combined a number of smaller, regional technical societies to form the Deutsche Physikalische Gesellschaft. He became a Dean at the University of Berlin, and after World War I became the highest authority in German physics.

Figure 9. Max Planck in 1901, one year after he published his paper on the quantum of action.

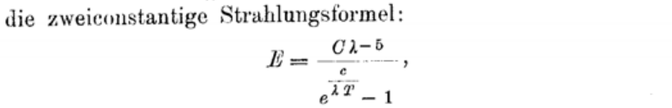
Planck, although a firm believer in Wien's distribution law (Fig. 8), knew very well that it was not valid at large values of λT, and recent experimental results reconfirmed this shortcoming. He realized that at long wavelengths, the entropy had to satisfy the relation,

$$\frac{d^2S}{dU^2} = -\frac{const}{U^2} \tag{9}$$

which followed from the thermodynamic definition of the temperature. After integrating and combining with the relation for the energy in a resonator,

$$U_\nu = \frac{c^3}{8\pi\nu}\rho_\nu \tag{10}$$

Planck derived the relation [24],



und des WIEN'schen „Verschiebungs"gesetzes [1]) erhält man hieraus die zweiconstantige Strahlungsformel:

$$E = \frac{C\lambda^{-5}}{e^{\frac{c}{\lambda T}} - 1},$$

Figure 9. Planck's Distribution Law. [24]

Planck gave these results at a meeting of the Deutsche Physikalische Gesellschaft in 1900 [25]. Days after his presentation, Planck received a note stating that his equation agreed very well with experimental data. It is interesting to note that Planck derived this equation purely on thermodynamic grounds. The entropy that he used to get this result was given by,

$$S_0 = -\alpha\left[\left(\frac{U}{\beta'\nu}+1\right)\ln\left(\frac{U}{\beta'\nu}+1\right) - \frac{U}{\beta'\nu}\ln\frac{U}{\beta'\nu}\right] \tag{11}$$

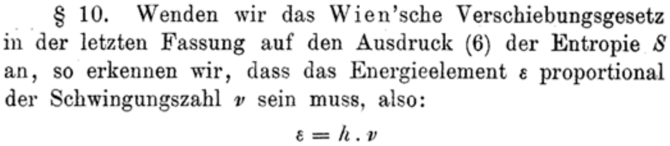
However, he did not feel completely comfortable with the theoretical underpinnings or the physical reasoning behind his distribution law. This motivated him to dig deeper into his results.

Although his distribution was based on an expression for the equilibrium entropy, he understood that thermodynamics alone could not accurately describe blackbody radiation. Wien felt that if his distribution was not valid at all wavelengths, then there was some qualitative difference between short and long wavelength radiation, and therefore there could be no unified theory of electromagnetic radiation. Planck felt strongly that not only was there a unified theory, but that principles of electromagnetism, thermodynamics and physical fields could be combined.[18] He then discussed with Boltzmann the derivation of the velocity distribution of molecules in a gas, specifically the idea of dividing the energy into discrete values.

Boltzmann gave a relation for the number of ways of distributing discrete, equal energy values among a number of molecules. The logarithm of the distribution was,

$$\ln J = n\left[\left(\frac{\lambda}{n}+1\right)\ln\left(\frac{\lambda}{n}+1\right) - \frac{\lambda}{n}\ln\frac{\lambda}{n}\right] \tag{12}$$

Planck saw the similar structure between this and the entropy equation (Eq. 11), and showed that they were equal when as he showed below in Fig. 10 [26],

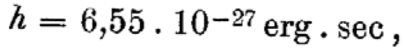


§ 10. Wenden wir das Wien'sche Verschiebungsgesetz in der letzten Fassung auf den Ausdruck (6) der Entropie S an, so erkennen wir, dass das Energieelement ε proportional der Schwingungszahl ν sein muss, also:

$$\varepsilon = h \, . \, \nu$$

Figure 10. The first appearance of the equation E = hν. [26]

along with his calculation of the constant that would bear his name,



$$h = 6{,}55 \, . \, 10^{-27} \, \mathrm{erg} \, . \, \mathrm{sec} \, ,$$

Figure 11. Planck's calculation of the constant shown in Fig. 10 [26].

Hence the quantum of action was born. By integrating Planck's distribution, Fig. 9, over all wavelengths, he got back the Stefan-Boltzmann law.

Planck tried to explain the physical meaning of his discrete energy relation, with little success. Others felt that since Planck didn't fully grasp the implications of his result, he should not get credit for his discovery, but this judgment may be too harsh.[27] As the field of quantum mechanics grew, Planck felt less sure of its veracity. However, for his work, Planck received the Nobel Prize for Physics in 1918. By virtue of his ideas on discretizing the energy of molecules in a velocity distribution, Boltzmann has been considered a grandfather of quantum theory. Planck himself describes the genesis of the T^4 law in his *The Theory of Heat Radiation* [28]. He survived both World Wars, although his son Erwin was killed by the Nazis for participating in a plot to kill Adolf Hitler. Max Planck died on October 4th, 1947 in Göttingen, West Germany.

ACKNOWLEDGMENTS

The author gratefully acknowledges the help of Mrs. Jennifer O'Laughlin of Interlibrary Loans at the University of Idaho for acquiring copies of the original papers.

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