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Lecture Notes for 8.225 / STS.042, "Physics in the 20th Century": Blackbody Radiation & Compton Scattering

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Introduction

These notes discuss two of the main topics for the lecture on "Rethinking Light" in a bit more detail: Max Planck's analysis of blackbody radiation, and Arthur Compton's study of the scattering of high-energy light off of electrons. Reading these notes is *optional*; the notes are meant to fill in some of the gaps in various derivations that we will not cover during our class session.

Blackbody Radiation

In December 1900, Max Planck introduced a formula to describe the specific pattern of light emitted in the form of blackbody radiation. Recall that in the late years of the 19th century, physicists (especially in Berlin's still-new Physikalisch Technische Reichsanstalt, or PTR) were studying the pattern of light emitted from a type of object known as a "blackbody": an object that absorbs (nearly) all the incoming light that might fall upon it (so that it appears black). When a blackbody is heated to a sufficiently high temperature it will glow, emitting a specific pattern of radiation. Above a temperature of about 500° C the glow will include substantial emission in the visible range of the spectrum, which is detectable by the unaided eye. Though the term "blackbody radiation" might sound abstract or esoteric, many people are familiar with the phenomenon: think of the reddish-orange glow of charcoal on a grill or embers in a fireplace.

Thanks to his colleagues at the PTR, Planck had access to some of the most up-to-date and precise measurements of the *spectrum* of blackbody radiation: the amount of energy emitted per frequency ν, per unit volume. Planck's formula took the form

$$u(\nu, T) = \frac{8\pi}{c^3} \frac{h\nu^3}{\left[e^{h\nu/kT} - 1\right]} \,, \tag{1}$$

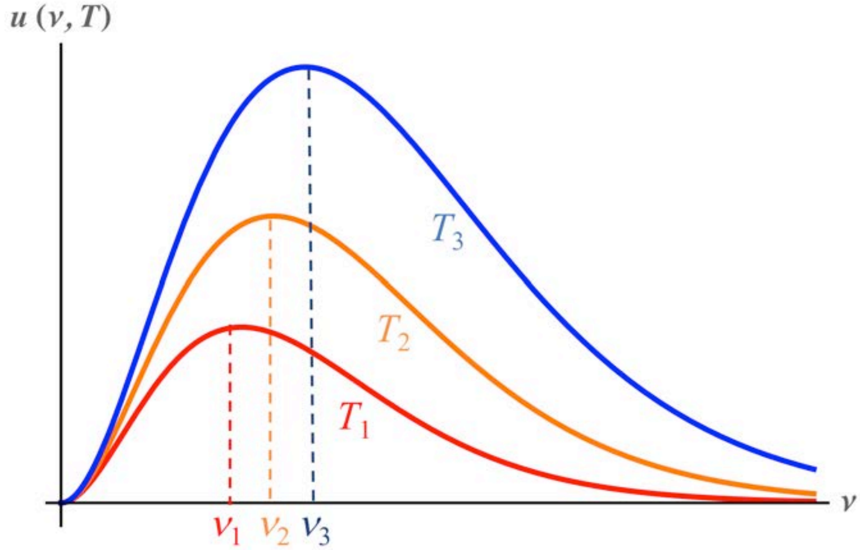

Figure 1: The energy density per unit frequency, $u(\nu, T)$, for blackbody radiation introduced by Max Planck in 1900, as a function of frequency ν, for three temperatures $T_1 < T_2 < T_3$. As the temperature rises, the frequency of peak emission shifts to higher frequencies (toward the blue end of the spectrum), and the total energy output increases.

where k is Boltzmann's constant (familiar from statistical mechanics), and h was a new universal constant, soon dubbed "Planck's constant." Both the peak frequency of emission and the overall amount of energy emitted depend on the temperature T to which the blackbody has been heated. The characteristic shape of the energy density per unit frequency, $u(\nu, T)$, is shown in Fig. 1 for three temperatures $T_1 < T_2 < T_3$.

Physicists and historians continue to debate how Planck arrived at the expression in Eq. (1), and what Planck thought his own equation really meant.[1] In these notes, we will briefly consider a *modern* approach to deriving Planck's expression in Eq. (1), to highlight why physicists *today* consider it to be such a novel break with previous approaches to the interaction between light and matter.

The quantity $u(\nu, T)$ represents the amount of energy emitted by a blackbody per unit frequency per unit volume. To arrive at the expression in Eq. (1), we may proceed in two steps: derive an expression for the number of independent radiation modes within a volume V per frequency ν, and separately derive an expression for the average energy of each mode. In other words, our goal is to find expressions for each quantity on the right side of the

[1]For an indication of the range of debate over Planck's original derivation and interpretation of Eq. (1), compare Thomas S. Kuhn, *Black-Body Theory and the Quantum Discontinuity, 1894 - 1912* (New York: Oxford University Press, 1978) and Kuhn, "Revisiting Planck," *Historical Studies in the Natural Sciences* **14** (1984): 231-252, with the recent discussion in Michael Nauenberg, "Max Planck and the birth of the quantum hypothesis," *American Journal of Physics* **84** (Sept 2016): 709-720.

following expression:

$$u(\nu,T) = \begin{matrix}\text{energy density}\\ \text{per frequency}\end{matrix} = \left(\begin{matrix}\text{number of modes}\\ \text{per frequency per unit volume}\end{matrix}\right) \times \left(\begin{matrix}\text{average energy}\\ \text{per mode}\end{matrix}\right) . \tag{2}$$

Planck calculated the first of these terms in a manner that was totally consistent with the physics of the 19th century. The big change comes with how to evaluate the second term: the average energy per mode.

In the Appendix I describe how to calculate the number of radiation modes per frequency per unit volume within a cavity of fixed size. Planck found

$$\left(\begin{matrix}\text{number of modes}\\ \text{per frequency per unit volume}\end{matrix}\right) = \frac{8\pi\nu^2}{c^3} . \tag{3}$$

As we will see in the Appendix, Planck's approach to deriving this expression made use of Maxwell's treatment of electromagnetic waves. In fact, several of Planck's predecessors had derived this expression during the 1880s and 1890s.

The next step, according to Eq. (2), is to find an expression for the *average energy* per mode, which we may denote $\bar{\epsilon}$. If we were to continue to use (by-then) standard arguments from 19th century physics, we would conclude that in equilibrium at a temperature T, each radiation mode should have an average energy $\bar{\epsilon} = kT$. (This is known as the "equipartition theorem.") This result followed from the pioneering studies of statistical mechanics by figures like Maxwell and Ludwig Boltzmann. The argument is that in equilibrium, the probability that a physical system will be found in a state of energy E is weighted by the "Boltzmann factor" $\exp[-E/kT]$: the greater the energy of the associated state, the less likely it would be to find the system in such a state. If we want to find the *average* value of the energy per mode in equilibrium, we calculate the expectation value

$$\left(\begin{matrix}\text{average energy}\\ \text{per mode}\end{matrix}\right) = \bar{\epsilon}_{\text{classical}} = \frac{\int_0^\infty d\epsilon\, \epsilon\, e^{-\epsilon/kT}}{\int_0^\infty d\epsilon\, e^{-\epsilon/kT}} . \tag{4}$$

Using

$$\begin{aligned}\int_0^\infty dx\, e^{-x/a} &= a \quad \text{for Re}[a] > 0 ,\\ \int_0^\infty dx\, x\, e^{-x/a} &= a^2 \quad \text{for Re}[a] > 0 ,\end{aligned} \tag{5}$$

we find

$$\left(\begin{matrix}\text{average energy}\\ \text{per mode}\end{matrix}\right) = \bar{\epsilon}_{\text{classical}} = kT , \tag{6}$$

consistent with the (classical) equipartition theorem. Combining Eqs. (3) and (6), we then find, for Eq. (2),

$$u(\nu,T) = \frac{8\pi\nu^2}{c^3} kT . \tag{7}$$

This form for the energy density per frequency is known as the "Rayleigh-Jeans" spectrum. Note that according to Eq. (7), the energy of radiation emitted by a blackbody would *grow without limit*; the blackbody would emit more and more energy at higher and higher frequencies. This became known as the "ultraviolet catastrophe." If one took this expression at face value, Maxwell's treatment of radiation, combined with then-standard techniques from statistical physics, suggested that a blackbody should emit an *unlimited* amount of energy per volume — that is, the energy density, $\rho(T) = \int d\nu\, u(\nu, T)$, *diverges* once one integrates $u(\nu, T)$ over all possible frequencies ν. Such an expression *clearly* was not consistent with ordinary experience, let alone the increasingly precise data measured by Planck's colleagues at the PTR.

What Planck did next — and what he thought his next steps actually implied about the nature of radiation — remains a point of controversy among physicists and historians.[2] The standard view among physicists *today* is that quantum theory avoids the ultraviolet catastrophe, and yields an expression for $u(\nu, T)$ that matches high-precision experimental data, by replacing the (classical) equipartition theorem with an entirely new method for accounting for the allowable energies of matter and radiation at the atomic scale. That is, in modern derivations, we arrive at the form of the expression in Eq. (1) by *restricting* the allowable energies per mode to *discrete*, quantized values: in place of the continuum of possible values of ϵ over which we integrated in Eq. (4) to find $\bar{\epsilon}_{\rm classical}$, modern quantum-theoretic treatments *sum* over a set of *discrete* values, $\epsilon_n = nh\nu$, with n a non-negative integer. On this modern view, a radiation mode in the cavity can carry one unit of energy ($h\nu$), or two units ($2h\nu$), or 57 units, but not 1.3 units.

In place of Eq. (4), we write

$$\left(\begin{array}{c} \text{average energy} \\ \text{per mode} \end{array} \right) = \bar{\epsilon}_{\rm quantum} = \frac{\sum_{n=0}^{\infty} nh\nu\, e^{-nh\nu/kT}}{\sum_{n=0}^{\infty} e^{-nh\nu/kT}} \,. \tag{8}$$

To evaluate Eq. (8), we can use some clever tricks, including the usual expression for summing a geometric series:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \quad \text{for } |x| < 1 \,. \tag{9}$$

Then the denominator in Eq. (8) may be evaluated as

$$\sum_{n=0}^{\infty} e^{-nh\nu/kT} = \sum_{n=0}^{\infty} \left(e^{-h\nu/kT} \right)^n = \frac{1}{(1 - e^{-h\nu/kT})} \,. \tag{10}$$

[2]See, e.g., the references by Kuhn and Nauenberg in footnote 1.

For the numerator, let us define $\beta \equiv h\nu/kT$, so that we may write

$$
\begin{aligned}
\sum_{n=0}^{\infty} nh\nu\, e^{-nh\nu/kT} &= h\nu \sum_{n=0}^{\infty} n\, e^{-n\beta} \\
&= h\nu \left[-\frac{d}{d\beta} \sum_{n=0}^{\infty} e^{-n\beta} \right] \\
&= h\nu \left[-\frac{d}{d\beta} \left(\frac{1}{1-e^{-\beta}} \right) \right] \\
&= h\nu \frac{e^{-\beta}}{(1-e^{-\beta})^2}\,.
\end{aligned}
\tag{11}
$$

Combining Eqs. (10) and (11), Eq. (8) then may be written

$$
\begin{aligned}
\begin{pmatrix} \text{average energy} \\ \text{per mode} \end{pmatrix} = \bar{\epsilon}_{\text{quantum}} &= \frac{h\nu\, e^{-h\nu/kT}}{[1-e^{-h\nu/kT}]} \\
&= \frac{h\nu}{[e^{h\nu/kT}-1]}\,.
\end{aligned}
\tag{12}
$$

We now have expressions for each term on the right side of Eq. (2), which yields Planck's expression for the energy density per frequency:

$$
u(\nu, T) = \frac{8\pi}{c^3} \frac{h\nu^3}{[e^{h\nu/kT}-1]}\,, \tag{13}
$$

exactly as in Eq. (1).

Thomas Kuhn contends that Planck himself did not reason this way when he first derived Eq. (13) in 1900. In particular, Kuhn argues that Planck set the *total* energy of the system to be an integer multiple of $h\nu$,

$$
E_{\text{total}} = \sum_n \epsilon_n = Nh\nu\,, \tag{14}
$$

but that Planck did *not* restrict each radiation mode to have a quantized energy $\epsilon_n = nh\nu$. Moreover, Kuhn continues, in Planck's original derivation, he considered energies for sub-systems "in the *range* $(\epsilon_i, \epsilon_i + \Delta\epsilon_i)$"; that Planck used *bins* of size $\epsilon = h\nu$ for his accounting, but then counted how many sub-systems with *continuous* energies fell within bins $[0, \epsilon]$, $[\epsilon, 2\epsilon]$, and so on. In his 1906 lectures, Kuhn notes, Planck still spoke of *continuous* (rather than quantized) energy exchange between the matter of the blackbody and the emitted radiation.[3] Other historians and physicists continue to scrutinize Planck's original derivation as well as Planck's re-derivations during the years after 1900.[4] What all commentators agree upon

[3]See Kuhn, *Black-Body Theory*, and Kuhn, "Revisiting Planck."

[4]For a review of more recent analyses and a comprehensive list of additional references on the topic, see Nauenberg, "Max Planck and the birth of the quantum hypothesis."

is that Planck was highly *reluctant* to break with the statistical arguments (by Maxwell, Boltzmann, and others) that had become standard in his day. Planck wrote to a colleague as late as 1931: "What I did can be described as simply an act of desperation. [... Introducing bins of size $\epsilon = h\nu$] was purely a formal assumption and I really did not give it much thought."[5]

No matter what Planck thought about the *derivation* of his expression in Eq. (13), we do know why he had some confidence about its form. For small frequencies (long wavelengths), Eq. (13) coincides with the Rayleigh-Jeans expression. In particular, for $h\nu \ll kT$, we may expand

$$e^{h\nu/kT} = 1 + \frac{h\nu}{kT} + \mathcal{O}\left[\left(\frac{h\nu}{kT}\right)^2\right] . \tag{15}$$

In that limit, Eq. (13) becomes

$$u(\nu, T) = \frac{8\pi}{c^3}\nu^2\, kT + \mathcal{O}\left[\left(\frac{h\nu}{kT}\right)^2\right] , \tag{16}$$

which exactly matches the Rayleigh-Jeans expression in Eq. (7). *Unlike* the Rayleigh-Jeans form in Eq. (7), however, Planck's expression in Eq. (13) does *not* lead to an "ultraviolet catastrophe." In the limit of large frequencies (short wavelengths), $h\nu \gg kT$, we may expand

$$\frac{1}{[e^{h\nu/kT} - 1]} = \frac{1}{e^{h\nu/kT}\,[1 - e^{-h\nu/kT}]} = e^{-h\nu/kT} + \mathcal{O}\left(\frac{kT}{h\nu}\right) , \tag{17}$$

so that Planck's expression in Eq. (13) takes the form

$$u(\nu, T) = \frac{8\pi}{c^3} h\nu^3\, e^{-h\nu/kT} + \mathcal{O}\left(\frac{kT}{h\nu}\right) . \tag{18}$$

The exponential decay of this function with large ν more than compensates for the factor of ν^3, and the overall energy density per frequency falls gently with increasing frequency, as shown in Fig. 1. Planck had more than only these theoretical features to bolster his confidence. He was also in close contact with experimentalists at the PTR who were refining their own measurements of blackbody spectra in their laboratory. As he lated recalled: "The very next morning [after first presenting his expression at a meeting of the Berlin Physical Society] I received a visit from my colleague [Heinrich] Rubens [an experimental physicist at the PTR]. He came to tell me that after the conclusion of the meeting, he had that very night checked my formula against the results of his measurements and found a satisfactory concordance at every point."[6]

[5]Max Planck to Robert W. Wood, 7 October 1931, as quoted in Nauenberg, "Max Planck and the birth of the quantum hypothesis," p. 715.

[6]Max Planck, *Scientific Autobiography*, trans. F. Gaynor (New York: Philosophical Library, 1949), pp. 39-41, as quoted in Nauenberg, "Max Planck and the birth of the quantum hypothesis," on p. 713.

Compton Scattering

Albert Einstein introduced his "heuristic" notion of a light quantum in 1905, in an article entitled, "On a heuristic point of view concerning the production and transformation of light."[7] About twenty years later, physicists adopted the term "photon" to refer to an individual light quantum, or particle of light. Einstein considered his paper on light quanta to be the most "revolutionary" of the papers he wrote that year.[8] In the paper, he suggested that "in the propagation of a light ray emitted from a point source, the energy is not distributed continuously over ever-increasing volumes of space, but consists of a finite number of energy quanta localized at points of space that move without dividing, and can be absorbed or generated only as complete units."[9]

Although Einstein's suggestion of light quanta offered a particularly economical explanation of puzzling experimental results, such as the photoelectric effect, most physicists remained skeptical of the idea for many years to come. Even after Max Planck had become convinced of the importance of Einstein's work on topics like relativity, for example, he still harbored doubts about Einstein's idea of light quanta. In urging his colleagues to invite Einstein to join the prestigious Prussian Academy of Sciences in 1913, Planck explained, "In sum, one can say that there is hardly one among the great problems in which modern physics is so rich to which Einstein has not made a remarkable contribution. That he may sometimes have missed the target in his speculations, as, for example, in his hypothesis of light quanta, cannot really be held too much against him."[10]

An important step in convincing the broader community to take the idea of light quanta seriously came in the early 1920s, with the experiments by Arthur H. Compton on the scattering of high-energy light off of electrons. In fact, whereas nearly two decades elapsed before Einstein's "heuristic" suggestion of light quanta became broadly accepted within the community, Compton's experimental results were greeted with fanfare almost immediately. He submitted his article on the new results to the *Physical Review* in December 1922; the paper was published in May 1923; and Compton was awarded the Nobel Prize for his efforts in 1927! Physicist Robert Millikan lauded Compton's experiment for "keep[ing] the physicist

[7] Albert Einstein, "Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt," *Annalen der Physik* **17** (1905): 132-148. An English translation is available in John Stachel, *Einstein's Miraculous Year: Five Papers that Changed the Face of Physics* (Princeton: Princeton University Press, 2005 [1998], 177-198.

[8] Albert Einstein to Conrad Habicht, May 1905, as translated in *The Collected Papers of Albert Einstein*, Volume 5, *The Swiss Years: Correspondence, 1902-1914 (English Translation Supplement)* (Princeton: Princeton University Press, 1995), pp. 19-20.

[9] Einstein, "Heuristic point of view," as translated in Stachel, *Einstein's Miraculous Year*, p. 178.

[10] Max Planck, as quoted in Abraham Pais, *Subtle is the Lord: The Science and the Life of Albert Einstein* (New York: Oxford University Press, 1982), on p. 382.

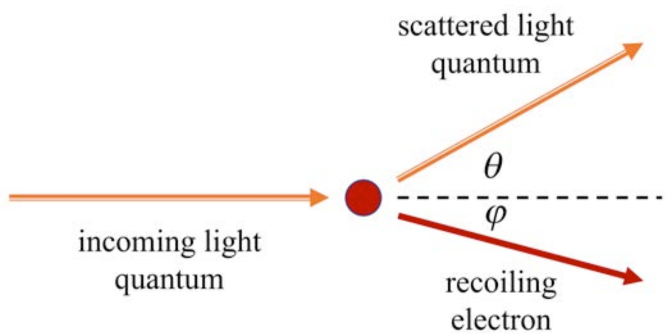

Figure 2: Arthur Compton interpreted his experimental results of the scattering of high-energy X-rays off of electrons in terms of two-body scattering among discrete particles. In this case, the incoming light quantum scattered off an electron at rest; following the collision, the light quantum was scattered at some angle θ from the direction of its original path, while the electron recoiled along some angle φ.

modest and undogmatic."[11]

Compton had not set out to test Einstein's ideas about light quanta; on the contrary, Compton, like most physicists, had been skeptical of Einstein's idea. Instead, Compton was interested in the behavior of high-energy lightwaves, and began conducting a series of experiments on the reflection of X-rays. He measured wave-like properties of the light before and after reflection. In particular, he found a shift in the wavelength of the light following scattering. The amount of the shift in wavelength depended on the angle of scatter:

$$\Delta\lambda \equiv \lambda' - \lambda \propto (1 - \cos\theta) \ , \tag{19}$$

where λ was the wavelength of the incoming lightwave and λ' the wavelength of the scattered lightwave. Compton found he could only make sense of these experimental results if he invoked Einstein's hypothesis about light quanta. Rather than interpreting his light-reflection experiments in terms of continuous waves, Compton analyzed his results as if the incoming light consisted of individual particles, each with a definite energy and momentum, and that individual light quanta scattered off of electrons much as two billiard balls would collide on a pool table. In other words, Compton was only able to make sense of his light-reflection results if he treated the interaction of light with matter in terms of two-body scattering among discrete particles, as in Fig. 2.

Compton analyzed the interaction between high-energy X-rays and electrons by balancing the total energy and momentum of the system, before and after the collision.[12] Prior to the

[11] Arthur H. Compton, "A quantum theory of the scattering of X-rays by light elements," *Physical Review* **21** (1923): 483-502. Robert Millikan's quotation from 1926 may be found in Roger H. Steuwer, *The Compton Effect* (New York: Science History Publications, 1975), p. 288.

[12] In his 1923 article, Compton used the term "light quantum" to describe individual particles of light. For ease of notation in these notes, I will use the term "photon," which entered into common usage a few years after Compton's original publication.

collision, the incoming photon moved along the $\hat{\mathbf{x}}$ axis with energy $E_{\rm photon}$ and momentum $\mathbf{p}_{\rm photon}$ while the electron sat at rest, with energy $E_{\rm electron} = mc^2$ and momentum $\mathbf{p}_{\rm electron} = 0$. Following the collision, the photon scattered at some angle θ from its original direction of motion, with post-collision energy $E'_{\rm photon}$ and momentum $\mathbf{p}'_{\rm photon}$, while the electron recoiled along some angle φ from the incoming photon's path with (relativistic) energy $E'_{\rm electron} = \gamma mc^2$ and momentum $\mathbf{p}'_{\rm electron} = \gamma m\mathbf{v}$. (By the time Compton was conducting his experiments, Einstein's work on special relativity had become fairly well established; given the high energy of the incoming X-rays, Compton readily adopted relativistic kinematics for treating the electron's motion following collision.) To treat the photon's energy and momentum, Compton *reluctantly* adopted Einstein's expressions for individual light quanta:

$$\begin{aligned} E_{\rm photon} &= h\nu = \frac{hc}{\lambda}\,, \\ |\mathbf{p}_{\rm photon}| &= \frac{E_{\rm photon}}{c} = \frac{h\nu}{c} = \frac{h}{\lambda}\,. \end{aligned} \tag{20}$$

Keeping in mind that momentum is a vector quantity — so that each component of the momentum (p_x and p_y) must balance before and after collision — Compton could then write three equations to describe the two-body scattering:

$$\begin{aligned} (\text{conservation of energy :})\ & \frac{hc}{\lambda} + mc^2 = \frac{hc}{\lambda'} + \gamma mc^2 \\ (\text{conservation of } p_x \text{ :})\ & \frac{h}{\lambda} + 0 = \frac{h}{\lambda'}\cos\theta + \gamma mv\cos\varphi \\ (\text{conservation of } p_y \text{ :})\ & 0 + 0 = \frac{h}{\lambda'}\sin\theta - \gamma mv\sin\varphi\,, \end{aligned} \tag{21}$$

where $v = |\mathbf{v}|$ is the magnitude of the electron's recoil velocity. He now had three equations for three unknowns (λ', θ, and φ), so he could solve for the quantity of interest, namely, $\Delta\lambda = \lambda' - \lambda$.

First we may square the expressions that come from p_x and p_y and add them. From the p_x equation, we find

$$\gamma^2 m^2 v^2 \cos^2\varphi = h^2\left[\frac{1}{\lambda^2} - \frac{2}{\lambda\lambda'}\cos\theta + \frac{1}{\lambda'^2}\cos^2\theta\right]\,, \tag{22}$$

and from the p_y equation we may write

$$\gamma^2 m^2 v^2 \sin^2\varphi = h^2\left[\frac{1}{\lambda'^2}\sin^2\theta\right]\,. \tag{23}$$

Adding Eqs. (22) and (23) yields

$$\gamma^2 m^2 v^2 = h^2\left[\frac{1}{\lambda^2} + \frac{1}{\lambda'^2} - \frac{2}{\lambda\lambda'}\cos\theta\right]\,. \tag{24}$$

Squaring the expression that comes from the conservation of energy (after canceling the factor of c that is common to each term), we have

$$\begin{aligned}\gamma^2 m^2 c^2 &= \left[\left(\frac{h}{\lambda} - \frac{h}{\lambda'}\right) + mc\right]^2 \\ &= h^2\left[\frac{1}{\lambda^2} + \frac{1}{\lambda'^2} - \frac{2}{\lambda\lambda'} + \frac{2mc}{h}\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)\right] + m^2c^2\,.\end{aligned} \tag{25}$$

Subtracting Eq. (24) from Eq. (25) yields

$$\gamma^2 m^2 c^2\left(1 - \frac{v^2}{c^2}\right) = h^2\left[-\frac{2}{\lambda\lambda'}\left(1 - \cos\theta\right) + \frac{2mc}{h}\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)\right] + m^2c^2\,. \tag{26}$$

Using the definition of γ, we may rewrite the quantity of the left side of Eq. (26):

$$\begin{aligned}\gamma^2 m^2 c^2\left(1 - \frac{v^2}{c^2}\right) &= \frac{1}{\left(1 - \frac{v^2}{c^2}\right)} m^2c^2\left(1 - \frac{v^2}{c^2}\right) \\ &= m^2c^2\,.\end{aligned} \tag{27}$$

Then the terms m^2c^2 cancel from each side of Eq. (26), leaving

$$\frac{2}{\lambda\lambda'}\left(1 - \cos\theta\right) = \frac{2mc}{h}\left(\frac{1}{\lambda} - \frac{1}{\lambda'}\right)\,, \tag{28}$$

or

$$\lambda' - \lambda = \left(\frac{h}{mc}\right)\left(1 - \cos\theta\right)\,. \tag{29}$$

Not only did this result yield the particular angular dependence that Compton had measured, as in Eq. (19); the coefficient on the right side of Eq. (29), h/mc, yielded a very close fit to Compton's experimental data, once he plugged in the values for Planck's constant (h), the electron's mass (m), and the speed of light (c). Whereas Compton had been skeptical of Einstein's light-quantum hypothesis before embarking on his experiments, he found remarkable agreement with his own data once he applied Einstein's ideas to treat the scattering of light from matter. The coefficient h/mc became known as the "Compton wavelength": it set the *scale* for the observed shift in wavelength for the scattered light.

Note the strange mixing of wave and particle notions throughout: Compton produced light*waves* of known wavelength λ, and measured the shift in their wavelength following scattering; he could only make sense of his empirical results by treating the light as a collection of *individual particles*; and then his result, derived in terms of two-body scattering, yielded a new measure of "wavelength," in terms of the quantity h/mc. This sort of "*wave-particle duality*" became emblematic of more systematic attempts to create a first-principles quantum mechanics during the mid-1920s.

Appendix: Calculating the Number of Radiation Modes in a Cavity

In this Appendix we calculate the number of radiation modes per frequency per unit volume, which is one of the main steps in deriving Planck's expression for the energy density per unit frequency of blackbody radiation. During the 1880s and 1890s, blackbody radiation was often referred to as "cavity radiation," since one of the best ways to produce a blackbody and measure properties of the resulting radiation was to heat a closed cavity — so that inside the cavity there was virtually no incoming light — and then measure the radiation that escaped from the cavity through a tiny window. The properties of the radiation from the cavity would then be independent of any external radiation that might have otherwise reflected off of the cavity itself.[13]

Recall from Maxwell's equation for the propagation of light that the electric field associated with a lightwave satisfies

$$\left[\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right]E(t,x,y,z)=0\,. \tag{30}$$

We are interested in solutions of this wave equation for the case in which the radiation is contained within a cavity, in equilibrium. We may consider a cubic cavity of length L on each side. We want to find *standing-wave* solutions — that is, solutions for E that vanish at the boundaries of the cavity. (If the solutions didn't vanish at the boundaries, then radiation, and hence energy, would leak outside the cavity; but in that case, the system within the cavity would not remain in equilibrium.) If we adopt a separable form for $E(t,x,y,z) = T(t)X(x)Y(y)Z(z)$, then Eq. (30) becomes four separate equations for the four functions:

$$\frac{d^2X}{dx^2}+k_x^2X=0\,,\ \frac{d^2Y}{dy^2}+k_y^2Y=0\,,\ \frac{d^2Z}{dz^2}+k_z^2Z=0\,,\ \frac{d^2T}{dt^2}+\omega^2T=0\,, \tag{31}$$

where

$$\omega^2=c^2\left(k_x^2+k_y^2+k_z^2\right)\,. \tag{32}$$

To satisfy the boundary condition that $E(t,x,y,z)$ vanishes at each edge of the cubic cavity, we may write a solution of the form

$$E(t,x,y,z)=E_0\sin\left(\frac{n_x\pi x}{L}\right)\sin\left(\frac{n_y\pi y}{L}\right)\sin\left(\frac{n_z\pi z}{L}\right)\sin\left(\omega t\right)\,, \tag{33}$$

[13]See, e.g., Nauenberg, "Max Planck and the birth of the quantum hypothesis," p. 710, and Emilio Segrè, "Planck, unwilling revolutionary: The idea of quantization," in Segrè, *From X-Rays to Quarks: Modern Physicists and Their Discoveries* (San Francisco: W. H. Freeman, 1980), 61-77, on pp. 67-68.

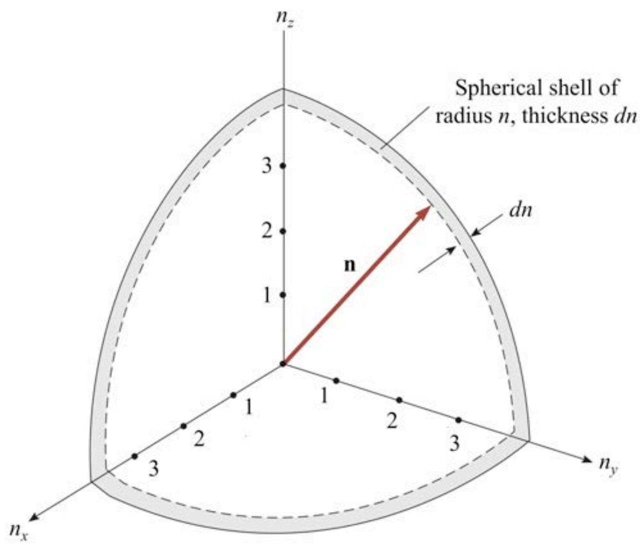

Figure 3: To calculate the number of independent radiation modes that can fit into a cavity of length L, we consider the volume of a thin spherical shell of radius $n = 2L/\lambda$ and thickness dn. Figure adapted from Figure A.1 in Raymond A. Serway, Clement J. Moses, and Curt A. Moyer, *Modern Physics* (New York: Sanders College Publishing, 1989), on p. 464.

where E_0 is the amplitude of the standing wave, and we have parameterized the wavenumbers in each spatial direction as

$$k_x = \frac{n_x \pi}{L}\,,\; k_y = \frac{n_y \pi}{L}\,,\; k_z = \frac{n_z \pi}{L}\,, \tag{34}$$

with n_x, n_y, and n_z each a positive integer. (You can quickly confirm that the solution for E vanishes at each of the edges of the cavity, for example when $x = 0$ and $x = L$, and similarly for the edges in the y and z directions, given that $\sin(n\pi) = 0$ for any integer n.) Using $\omega = 2\pi\nu$ to relate the angular frequency ω to the frequency ν, and the usual relation $\nu\lambda = c$, Eqs. (32) and (34) then yield a relationship between the integers n_i, the cavity length L, and the wavelength λ of the standing wave:

$$n_x^2 + n_y^2 + n_z^2 = \frac{4L^2}{\lambda^2}\,. \tag{35}$$

Eq. (35) indicates that for a fixed cavity size L, combinations of the integers (n_x, n_y, n_z) that yield larger sums $(n_x^2 + n_y^2 + n_z^2)$ correspond to standing waves with *shorter* wavelengths, or (from $\nu\lambda = c$) *higher* frequencies.

Next we want to count the number of independent radiation modes within the cavity that satisfy these boundary conditions, for a given length L. If we define the vector $\mathbf{n} \equiv (n_x, n_y, n_z)$, then we see that Eq. (35) is a condition on $n^2 \equiv |\mathbf{n}|^2 = (n_x^2 + n_y^2 + n_z^2)$. In particular, Eq. (35) describes the *surface of a sphere* of radius n within a three-dimensional grid whose axes are n_x, n_y, and n_z, as shown in Fig. 3. Given Eq. (35), the radius n is given by

$$n = \frac{2L}{\lambda} = \frac{2L}{c}\nu\,, \tag{36}$$

where the last expression follows from using $\nu\lambda = c$. All points on the surface of the sphere satisfy Eq. (35) for a given frequency ν (or, equivalently, a given wavelength λ).

Each unit cube with integer (n_x, n_y, n_z) represents a radiation mode that vanishes at the boundaries of the cavity, given the form of $E(t, x, y, z)$ in Eq. (33). The number of such unit cubes that correspond to radiation modes with frequency within the range ν and $\nu + d\nu$ is given by the volume of the thin spherical shell of radius n and thickness dn indicated in Fig. 3. However, we do not want to include *every* unit cell within the entire spherical shell, because our radiation modes are restricted to *positive* values of n_x, n_y, and n_z. We therefore restrict attention to one-eighth of the total spherical shell, as shown in Fig. 3. Moreover, lightwaves have *two* independent polarization states: each combination of (n_x, n_y, n_z) corresponds to *two* independent radiation modes. Combining these factors, we find the number of modes $N(\nu)\,d\nu$ within the spherical shell of thickness dn:

$$N(\nu)\,d\nu = \underbrace{\frac{1}{8}}_{\text{restriction to } n_i > 0} \times \underbrace{2}_{\text{polarization states}} \times \underbrace{4\pi n^2\,dn}_{\text{volume of spherical shell}} = \pi n^2\,dn = \frac{8\pi}{c^3}L^3\nu^2\,d\nu\,, \tag{37}$$

where the last expression follows upon using Eq. (36) to relate n to ν. The quantity of interest for Eq. (2) is the number *density* of modes per unit frequency, that is

$$\begin{pmatrix} \text{number of modes} \\ \text{per frequency per unit volume} \end{pmatrix} = \frac{1}{V}N(\nu) = \frac{8\pi\nu^2}{c^3}\,, \tag{38}$$

where the last expression follows upon using the fact that the volume of the cavity is $V = L^3$.

Note that our derivation of Eq. (38) relied upon Maxwell's treatment of electromagnetic waves; it was completely consistent with 19th century physics. Planck incorporated this part of the derivation when arriving at his expression for $u(\nu, T)$ in Eq. (13), and tinkered instead with the expression for the average energy per mode, $\bar{\epsilon}$.