5

THERMALIZED RADIATION

Introduction. Consider an evacuated enclosure of volume V. Though devoid of material particles (except for the blizzard of “virtual particles” contemplated by quantum field theorists), such an enclosure will inevitably—and demonstrably—contain electromagnetic radiation in thermal equilibrium with the walls, which we will assume to have temperature T (Figure 72). Our objective will be to describe the thermodynamic properties of that radiation and—with Planck, who did not consider his work done until he had done so (and in the doing opened Pandora’s box!)—to trace the thermodynamics to its statistical underpinnings.

It is not immediately obvious that such radiation is *susceptible* to thermodynamic analysis . . . not obvious that the radiation within a cavity is not as laden with information *about* that individual cavity (which is to say: as far from equilibrium) as is the image-modulated radiation that streams in through my office window, or down from the starry sky.

But look into a kiln. You see a rosy glow, but nothing of the differentiated interior: you do not see the pots on the shelves, the designs on the pots. You see radiation that is

- isotropic
- spatially homogeneous
- completely unpolarized
- completely incoherent
- polychromatic
- independent of all wall-properties except temperature

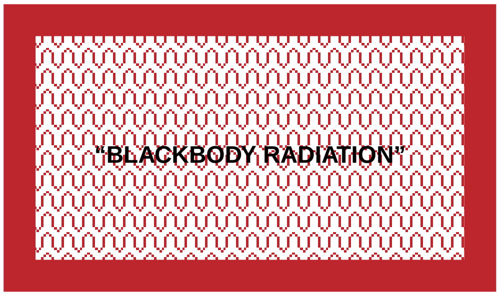

FIGURE 72: *Evacuated enclosure of volume V, with walls maintained at temperature T. We seek to describe the thermodynamic (and underlying statistical) properties of the* **thermalized electromagnetic radiation** *that is inevitably present in any such "hohlraum."*

The electromagnetic radiation within the kiln is, in a certain informal sense, *maximally uninteresting*, at least in leading approximation.[154]

It will emerge that thermalized radiation is in some respects rather like—though in important respects profoundly *un*like—a material gas. I will allow myself to employ the terms

$$\text{thermalized (or "blackbody") radiation} \equiv \text{photon gas}$$

as though they were equivalent/synonymous, but must emphasize that the latter terminology will acquire its justification *from* our arguments (becomes hazardous if used to *shape* arguments) . . . and, at this early point in the discussion, is certainly anachronistic: it was the blackbody radiation problem that led Planck (1900) to write the first physical equation containing an $\hbar$, and only five years later did Planck's accomplishment lead Einstein to the "invention of the photon." The historical sequence was

$$\text{blackbody thermodynamics} \ \mapsto\ \text{blackbody statistical mechanics} \ \mapsto\ \text{photon}$$

and not the reverse. It is remarkable that quantum mechanics came to us from what we might today characterize as the "statistical mechanics of indefinitely many massless (therefore ultrarelativistic) particles" and not—as the textbooks suggest—from the non-relativistic interaction of a single particle with a double slit . . . but on that we have already heard from Planck himself.[155]

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[154] We set aside such qualifications as may become necessary if the temperature is very high (so high that kT exceeds the energy required to produce particle/antiparticle pairs), or the box very small (compared to relevant wavelengths), of the gravitational field gradient too extreme.

[155] See again the quotation on page 93.

1. Point of departure: the Stefan-Boltzmann law. The classical thermodynamics of blackbody radiation proceeds from two simple statements:

$$
\begin{aligned}
U &= Vu(T) && (270.1)\\
p &= \tfrac{1}{3}\,u(T) && (270.2)
\end{aligned}
$$

where the structure of $u(T)$ will be enforced by the *laws* of thermodynamics. Made conspicuous by its absence from (270) is any reference to the *number* N of "atoms of radiation" (photons) present in the radiation field. It is instructive to compare the statements (270) with their counterparts in the theory of ideal gases:

It was the upshot of Joule's free expansion experiment that for ideal gases (no molecular interaction) the internal energy U depends only upon T, while for radiation it is U/V—the energy *density*—that depends only upon T. If a similar result were to pertain to material gases then the isotropic expansion of a gas would have necessarily to be accompanied by a *magical creation of new molecules*:

$$N_{\text{old}} \longmapsto N_{\text{new}} = (V_{\text{new}}/V_{\text{old}})N_{\text{old}}$$

Equation (270.2) is the work of Boltzmann (1884), and records one of the first continental applications of Maxwellian electrodynamics.[156] To derive (270.2) one looks to the time-averaged momentum and energy densities of incoherently superimposed plane waves of any assigned frequency.[157] For an ideal gas one has $U = \frac{3}{2}NkT = \frac{3}{2}pV$ which gives

$$p = \tfrac{2}{3}u$$

This equation resembles (270.2) except[158] for a factor of 2, that can be traced to the following circumstance: for a relativistic particle one has

$$
\begin{aligned}
p &= \sqrt{(E/c)^2 - (mc)^2}\\
&\downarrow\\
&= E/c \quad \text{in the case } m = 0, \text{ as for a photon}
\end{aligned}
$$

while for a non-relativistic particle one has

$$p = 2 \cdot E/v$$

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[156] What makes this remarkable is that Maxwell's theory was slow to gain acceptance in Europe, where several competing theories of electricity and magnetism were alive at the time.

[157] For the details see, for example, W. K. H. Panofsky & M. Phillips, *Classical Electricity & Magnetism* (1955), pages 172–175.

[158] We are here ignoring the fact that for ideal gases is it *not* true that u depends only upon T.

But, while the preceding remarks may serve imperfectly to illuminate the physical basis of (270), we will be content henceforth to look upon those equations as *given*—and to derive their justification from the results to which they lead.

Turning now to the thermodynamics of the situation, we—as Boltzmann was the first to do—insert (270) into

$$dS = \frac{1}{T}dU + \frac{1}{T}p\,dV$$

and obtain

$$\begin{aligned} dS = \frac{1}{T}\Big\{V\frac{du}{dT}\,dT + u\,dV\Big\} + \frac{1}{T}\Big\{\tfrac{1}{3}u\,dV\Big\} &= \frac{V}{T}\frac{du}{dT}\,dT + \frac{4}{3}\frac{u}{T}\,dV \\ &= \Big(\frac{\partial S}{\partial T}\Big)_V dT + \Big(\frac{\partial S}{\partial V}\Big)_T dV \end{aligned}$$

It follows therefore from equality of the cross derivatives that

$$\Big(\frac{\partial}{\partial V}\frac{V}{T}\frac{du}{dT}\Big)_T = \Big(\frac{\partial}{\partial T}\frac{4}{3}\frac{u}{T}\Big)_V$$

which after a little calculation/simplification reads

$$T\frac{du}{dT} = 4u \tag{271}$$

and integrates at once, to supply

$$u(T) = aT^4 \tag{272}$$

The argument just presented is standard to the literature,[159] and was held by Lorentz to be "a veritable pearl of theoretical physics." Curiously, it is formulated in the "S-representation," rather than in the much more common "U-representation."[160] Alternatively, we could bring equations (270) to the "thermodynamic equation of state" (72) and obtain (271) *in a single step*, as was remarked by Chandrasekhar.[161]

The "4th power law" was announced by J. Stefan in 1879 on the basis of "relatively meager experimental evidence" (Max Jammer's phrase). Boltzmann devised his theoretical argument in 1884, but it was not until 1897 that the **Stefan-Boltzmann law** (272) gained the status of a well-established experimental fact. At that point in history the "Stefan-Boltzmann constant" a had to be determined emperically, but in 1900 Planck produced—among many other things, by an argument that will soon concern us—the theoretical evaluation

$$a = \frac{\pi^2 k^4}{15\hbar^3 c^3} = 7.564\times 10^{-15}\text{erg cm}^{-3}\text{K}^{-4} \tag{273}$$

Note particularly the presence of the $\hbar$ in the preceding formula.

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[159] See, for example, A. Sommerfeld, *Thermodynamics & Statistical Mechanics* (1964), page 139; A. H. Wilson, *Thermodynamics & Statistical Mechanics* (1960), page 183; P. M. Morse, *Thermal Physics* (1964), page 82.

[160] See again page 41.

[161] *Introduction to the Study of Stellar Structure* (1939), page 54.

Although the blackbody energy density and pressure are, for most purposes, negligible at room temperature, their 4^{th} power T-dependence means that they can assume major importance at temperatures just a few orders of magnitude higher. For example: at the center of the sun ($T \approx 10^7$K) the radiation pressure is exceeds to the material pressure, and supports more than half of the overload.[162]

2. Thermalized radiation as an instance of a "null-G system." We are in position now to write out the thermodynamics of blackbody radiation. I propose, however, to approach this objective by eccentric indirection. Specifically, I propose to examine the thermodynamics of systems for which the Gibbs potential (or "free enthalpy") vanishes identically: $G \equiv 0$.

Using $p = -\frac{\partial}{\partial V}F(T,V)$ in $G = F + pV$ we have, for null-G systems,

$$F = V\Big(\frac{\partial F}{\partial V}\Big)_T$$

which, by Euler's theorem, is just the condition that F be homogeneous of unit degree in V:

$$F(T,V) = Vf(T) \tag{274}$$

This states, in effect, that the free energy *density* F/V depends only upon T. The same can therefore be said of

$$p = -\Big(\frac{\partial F}{\partial V}\Big)_T \quad = -f \tag{275.1}$$

$$s = -\frac{1}{V}\Big(\frac{\partial F}{\partial T}\Big)_V = -f\,' \tag{275.2}$$

$$u = f + Ts \qquad = f - Tf\,' \tag{275.3}$$

$$h = f + Ts + p \quad = -Tf\,' \tag{275.4}$$

where $f\,' \equiv df/dT$. We impose now the **restrictive assumption** that

$$p = \frac{1}{\lambda}\,u \tag{276}$$

Then (275.1) and (275.3) give $-\lambda f = f - Tf\,'$ or

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[162] For additional physical commentary, see P. M. Morse,[159] page 83. I leave to my reader the instructive pleasure of working out the temperatures that by

$$\text{mass density} = \frac{aT^4}{c^2}$$

correspond to various natural mass densities (density of nuclear matter, average density of the universe, etc.) and—inversely—the mass densities that correspond to various natural temperatures (electron-positron production temperature $2mc^2/k$, the temperatures characteristic of stars and nuclear processes, etc.). R. H. Dicke, in *Gravitation and the Universe* (1970), provides many relevant facts and references.

$$T\frac{df}{dT} = (1+\lambda)f$$

which upon integration becomes

$$f(T) = -\frac{a}{\lambda}\,T^{1+\lambda} \tag{277.0}$$

> REMARK: The constant of integration has been written $-(a/\lambda)$ in order to force certain corollary statements to assume their conventional forms. The minus sign insures the positivity of p and u.

Then

$$p(T) = \frac{1}{\lambda}\,a\,T^{1+\lambda} \tag{277.1}$$

$$s(T) = \frac{1+\lambda}{\lambda}\,a\,T^{\lambda} \tag{277.2}$$

$$u(T) = a\,T^{1+\lambda} \tag{277.3}$$

$$h(T) = \frac{1+\lambda}{\lambda}\,a\,T^{1+\lambda} \tag{277.4}$$

These results make it clear that blackbody radiation can be characterized as a null-G system with $\lambda = 3$. Equation (277.1) is, in effect, the *equation of state* of the null-G system, and is notable for the fact that it contains no reference either to N or to V. This means that for such systems p and T are welded together, and that it has become improper to speak of such expressions as $\left(\frac{\partial}{\partial T}\right)_p$ or $\left(\frac{\partial}{\partial p}\right)_T$. The isotherms of such a system are trivial, while the adiabats (curves of constant entropy) can be described

$$VT^{\lambda} = \text{constant} \quad : \quad \text{equivalently} \quad pV^{\frac{1+\lambda}{\lambda}} = \text{constant} \tag{278}$$

Equation (278) resembles the adiabat of an ideal gas with $\gamma = \frac{1+\lambda}{\lambda}$, but this circumstance is deceptive: for a null-G system

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V = (1+\lambda)aVT^{\lambda} \tag{279}$$

but $$C_p = T\left(\frac{\partial S}{\partial T}\right)_p \text{ is } \underline{\text{undefined}}$$

Inserting $T = \left(\frac{\lambda}{1+\lambda}\frac{S}{aV}\right)^{1/\lambda}$ into $U = aVT^{1+\lambda}$ we obtain

$$U(S,V) = \Big(\frac{1+\lambda}{\lambda}\,S\Big)^{\frac{1+\lambda}{\lambda}}\Big(\frac{1}{aV}\Big)^{\frac{1}{\lambda}} \tag{280.1}$$

Similarly

$$H(S,p\,) = S\Big(\frac{\lambda p}{a}\Big)^{\frac{1}{1+\lambda}} \tag{280.2}$$

$$F(T,V) = -\frac{a}{\lambda}VT^{1+\lambda} \tag{280.3}$$

$$G(T,p\,) \equiv 0 \tag{280.4}$$

Setting $\lambda = 3$ we obtain the following partial listing of the **thermodynamic properties of a specified volume V of blackbody radiation**:

$$\left.\begin{aligned}
p &= \tfrac{1}{3}aT^4 && : \quad \text{EQUATION OF STATE}\\
s &= \tfrac{4}{3}aT^3 &&\\
u &= \ \ aT^4 && : \quad \text{STEFAN-BOLTZMANN LAW}\\
f &= -\tfrac{1}{3}aT^4 &&\\
U(S,V) &= \big(\tfrac{4}{3}S\big)^{\frac{4}{3}}\big(aV\big)^{-\frac{1}{3}} &&\\
H(S,p\,) &= S\big(3p/a\big)^{\frac{1}{4}} &&\\
F(T,V) &= -\tfrac{1}{3}aVT^4 &&\\
G(T,p\,) &= 0 &&\\
C_V &= 4aVT^3 &&\\
C_p &: \ \text{undefined} &&\\
pV^{\frac{4}{3}} &= \text{constant} && : \quad \text{EQUATION OF AN ADIABAT}
\end{aligned}\right\} \tag{281}$$

At (58·G) on page 60 we had

$$G = \mu N$$

for bulk systems (of which blackbody radiation provides an instance). Evidently "null-G systems" are systems for which the **chemical potential μ vanishes**, systems in which the conjugate variable N has become meaningless. It becomes, in this light, senseless to speak of the "number of photons" present within a sample of blackbody radiation.

Bringing the first to the last of equations (281) we find that the equation of a radiative adiabat can be written

$$TR = \text{constant} \quad : \quad R \equiv V^{\frac{1}{3}} \tag{282}$$

This is the source of the familiar—if in several respects highly informal—statement that as the "radius of the universe" increases the wavelength of individual photons is "stretched," and the energy $E = hc/\lambda$ of each (whence the temperature of the entire system) is decreased. Thus do cosmologists account for the observed 3° blackbody radiation that they interpret to be adiabatically cooled radiation left over from events that took place fairly soon after the Big Bang.[163]

3. Spectral decomposition of blackbody radiation. In 1860 Maxwell, in the first of his contributions to the kinetic theory of gases, demonstrated (by an argument that I reserve for the next chapter) that if an ideal gas is constructed from molecules of mass m and has temperature T, then the probability that a molecule chosen at random will be found to have speed in the neighborhood dv of v can be described

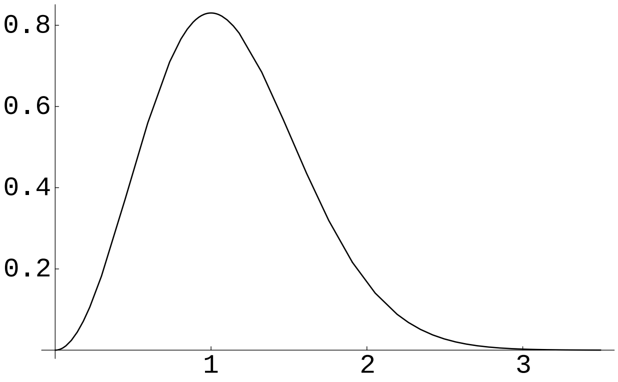

FIGURE 73: *Graph of the Maxwellian distribution function*

$$f(v) = \tfrac{4}{\sqrt{\pi}} v^2 \, e^{-v^2}$$

that plays in the theory of thermalized gases a role roughly analogous to the role played by the spectral density function $u(\nu, T)$ *in the theory of thermalized radiation.*

$$f(v)\,dv = 4\pi v^2 \Big(\frac{m}{2\pi kT}\Big)^{\frac{3}{2}} e^{-mv^2/2kT}\,dv \tag{283}$$

I would emphasize that this information (see the figure), though it relates to a basic physical property of thermalized gases, lies beyond the reach of the *thermodynamics* of gases, as standardly conceived. And that a similar situation pertains to the physics of thermalized light: it makes sense to write

$$u(T) = \int_0^\infty u(\nu, T)\,d\nu \tag{284}$$

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[163] See P. T. Landsberg & D. A. Evans, *Mathematical Cosmology* (1977), §9.4 for an excellent account of the details . . . and, more generally, of the cosmological applications of basic thermodynamic principles.

and to attribute the properties of $u(T)$ to properties of the underlying **spectral density** function $u(\nu,T)$, the importance of which was first emphasized by Kirchhoff.[164]

> **Kirchhoff's Law**: The spectral density function is *universal* in the sense that it depends only upon ν and T, and is independent of all material properties of the walls that confine the radiation.

Maxwell's accomplishment, Kirchoff's discovery and all that has been said thus far concerning the thermodynamics of blackbody radiation was well known by the time Planck (1858–1947)—soon after joining the faculty at the University of Berlin (1889)—decided to participate in the already vigorous experimental/theoretical effort to understand the universal function $u(\nu,T)$. The story of how he proceeded to crack the problem provides a fascinating example of the power of thermodynamic analysis . . . and an inspiring picture of a virtuoso engaged in what he acknowledged to be the most intense work of his life.

We know of $u(\nu,T)$ only that

$$\int_0^\infty u(\nu,T)\,d\nu = aT^4 \tag{285}$$

but it is fairly easy to cook up infinitely many functions $u(\nu,T)$ with that property. How to proceed?

If we contemplate a *classical* theory of spectral density then the only variables/constants we have to work with are ν, T, c and k. By dimensional analysis we come easily to the conclusion that necessarily

$$u(\nu,T) = (\text{dimensionless constant})\cdot kT\nu^2c^{-3}$$

and that detailed physical analysis can serve only to assign a value to the dimensionless constant. A theory along those lines was, in fact, proposed by Lord Rayleigh,[165] who noticed that the number of radiation modes in the neighborhood $d\nu$ of ν is

$$N(\nu)\,d\nu = 8\pi V\nu^2c^{-3}\,d\nu \tag{286}$$

from which, by the **equipartition principle** (at kT per mode because each has two independent polarizational states), it would follow that

$$u(\nu,T) = 8\pi kT\nu^2c^{-3} \quad : \quad \text{RAYLEIGH-JEANS DISTRIBUTION} \tag{287}$$

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[164] Kirchhoff's theoretical proof turns on energy-balance considerations that are reviewed in M. Jammer, *Conceptual Development of Quantum Mechanics* (1966), pages 2–5. See also Sommerfeld,[159] page 136; Wilson,[159] page 182.

[165] "Remarks upon the law of complete radiation," Phil. Mag. **49**, 539 (1900).

Though consistent with the experimental data at sufficiently low (infrared) frequencies (data that was only then becoming available), the Rayleigh-Jeans distribution[166] was **physically unacceptable** because it leads—inconsistently with (285)—to the so-called **ultraviolet catastrophy**

$$\int_0^\infty u(\nu,T)\,d\nu=\infty$$

One can conclude that the correct theory of $u(\nu,T)$ must contain one or more additional constants. Assuming—conservatively—that it contains but *one* such constant (call it α), we are led to contemplate expressions of the form

$$u(\nu,T)=8\pi kT\nu^2c^{-3}\cdot\phi(\alpha\nu T^n)$$

where $x\equiv\alpha\nu T^n$ is (by assumption) dimensionless. We then have

$$\begin{aligned}\int_0^\infty u(\nu,T)\,d\nu&=8\pi kT^{1-3n}(\alpha c)^{-3}\int_0^\infty\phi(x)\,x^2\,dx\\&\sim T^4\text{ if and only if we set }n=-1\end{aligned}\tag{288}$$

which motivates us to set $x=\alpha\nu/T\equiv h\nu/kT$, h being at this point simply a constant of undetermined value with

$$[h]=\text{energy}\cdot\text{time}=\text{action}$$

That the spectral density should be described by a function of the form

$$u(\nu,T)=8\pi kT\nu^2c^{-3}\cdot\phi\big(\frac{h\nu}{kT}\big)\tag{289}$$

was a pivotal discovery of W. Wien (1894):[167] it is called **Wien's displacement law** because it contains the prediction—consistent with physical experience—that the frequency at which $u(\nu,T)$ is maximal will be displaced upward with increasing T. From (288) we see that Wien's displacement law assigns to the Stefan-Boltzmann constant the value

$$a=8\pi\frac{k^4}{h^3c^3}\cdot\int_0^\infty\phi(x)\,x^2\,dx\tag{290}$$

In 1890 Wien went one step further and proposed (on unconvincing theoretical

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[166] Sir James Jeans' contribution was a factor of 8 that Rayleigh had missed in his original calculation.

[167] Wien's original argument concerned Doppler effects in the adiabatic expansion of a thermalized radiation sample. See Jammer[164] for the details and references.

grounds) that $\phi(x) = x\,e^{-x}$, giving

$$u(\nu, T) = 8\pi h\nu^3 c^{-3} \cdot \exp\Big\{-\frac{h\nu}{kT}\Big\} \quad : \quad \text{WIEN DISTRIBUTION} \tag{291}$$

By the summer of 1900 it had become evident that

- the Wien distribution is accurate for $h\nu \gg kT$, but breaks down at low frequencies, while
- the Rayleigh-Jeans distribution is accurate for $h\nu \ll kT$, but breaks down at high frequencies.[168]

Enter Planck, whose self-appointed assignment was (*i*) to devise and (*ii*) *to trace to its statistical underpinnings* a distribution law that interpolated between the Wien and Rayleigh-Jeans distributions.

Planck's mode of approach to the first phase of his problem was deeply and characteristically thermodynamical, and—stripped to its essentials—can be summarized as follows: Let the **modal internal energy function** $U_\nu(T)$ be defined

$$u(\nu, T) = U_\nu(T)\cdot n(\nu) \tag{292}$$

where $n(\nu) = N(\nu)/V = 8\pi\nu^2 c^{-3}$ refers to the **modal density** in frequency space. Evidently

$$U_\nu(T) = \begin{cases} kT & : \quad \text{RAYLEIGH-JEANS} \\ h\nu\cdot\exp\Big\{-\dfrac{h\nu}{kT}\Big\} & : \quad \text{WIEN} \end{cases} \tag{293}$$

Solving the preceding equations for T^{-1} and drawing upon (27.1)—which again lives in the "S-representation"—Planck writes

$$\frac{1}{T} = \frac{\partial S_\nu}{\partial U_\nu} = \begin{cases} +\dfrac{k}{U_\nu} & : \quad \text{RAYLEIGH-JEANS} \\ -\dfrac{k}{h\nu}\log\dfrac{U_\nu}{h\nu} & : \quad \text{WIEN} \end{cases} \tag{294}$$

where S_ν refers to the **modal entropy**, and from which it follows that

$$\frac{\partial^2 S_\nu}{\partial U_\nu^2} = \begin{cases} -\dfrac{k}{U_\nu^2} & : \quad \text{RAYLEIGH-JEANS} \\ -\dfrac{k}{h\nu U_\nu} & : \quad \text{WIEN} \end{cases} \tag{295}$$

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[168] Contrary to the impression I may have conveyed, the Wien distribution was old news in 1900 while the Rayleigh-Jeans distribution was a fresh new idea. Also new (and not published until 1901) was the infrared data obtained by H. Rubins & F. Kurlbaum (colleagues of Planck at Berlin) that tended to support Rayleigh's proposal—data that, when brought to Planck's attention in late October, precipitated his creative burst. It is well to remember that infrared and ultraviolet technologies were both in their infancy in 1900.

It was—ingeniously—between *these* elementary functions that Planck elected to interpolate. Of the infinitely many ways to accomplish such an objective, Planck—for no particular reason (he called it "a lucky guess"!)—settled upon

$$\frac{\partial^2 S_\nu}{\partial U_\nu^2} = -k\,\frac{1}{U_\nu^2 + h\nu U_\nu} \qquad : \quad \text{PLANCK} \tag{296}$$

Written

$$= -\frac{k}{h\nu}\Big\{\frac{1}{U_\nu} - \frac{1}{U_\nu + h\nu}\Big\}$$

this equation integrates at once to yield

$$\frac{\partial S_\nu}{\partial U_\nu} = \frac{1}{T} = -\frac{k}{h\nu}\log\frac{\lambda U_\nu}{U_\nu + h\nu} \quad : \quad \lambda \text{ is a constant of integration}$$

whence

$$U_\nu(T) = \frac{h\nu}{\lambda \cdot e^{h\nu/kT} - 1} \tag{297}$$

To recover (293) in the relevant limits we are forced to set $\lambda = 1$. Returning with this information to (292), Planck obtains

$$u(\nu, T) = 8\pi h\nu^3 c^{-3}\frac{1}{e^{h\nu/kT} - 1} \qquad : \quad \text{PLANCK DISTRIBUTION} \tag{298}$$

This equation is of the form (289) with

$$\phi(x) = \frac{x}{e^x - 1}$$

which, as it happens, differs only slightly from the form conjectured by Wien. From (290) we now (with the assistance of *Mathematica*) obtain

$$a = 8\pi\frac{k^4}{h^3c^3}\cdot\frac{\pi^4}{15} = \frac{\pi^2 k^4}{15\hbar^3 c^3}$$

as was reported at (273). Planck found that (298) came into nice quantitative agreement with the experimental facts when the solitary free parameter h was assigned the value 6.55×10^{-27}erg sec. The modern value is

$$h = 6.62608 \times 10^{-34}\text{Joule second}$$

Equation (298) records the first occurance of h in a physical equation (and also the first time k was used to denote Boltzmann's constant).

Comparison of (291) with (298), and a glance at Figure 74, indicates the sense in which Wien[169] very nearly got it right (and Rayleigh, except at the lowest frequencies, got it grotesquely wrong), and causes one to wonder what motivated Planck to work so intensely hard to resolve such a small low-frequency discrepency: he must have been powerfully impressed by the significance of Rubins' data . . . and perhaps by the germ of Rayleigh's idea.

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[169] Wilhelm Carl Werner Otto Fritz Franz Wien (1864–1928) was six years *younger* than Planck, and died nineteen years before him. He was awarded the Nobel Prize for his blackbody work in 1911, Planck not until 1918.

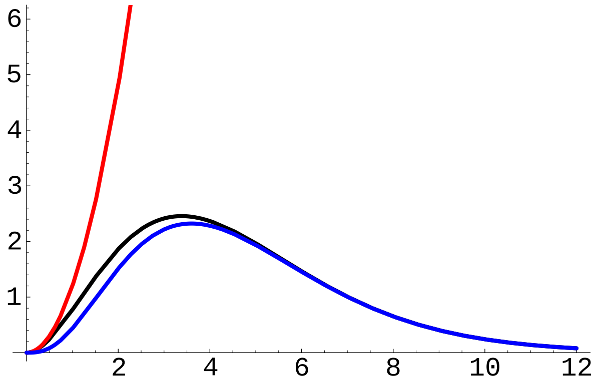

FIGURE 74: *Comparison of* **Planck**'*s spectral distribution function with the* **Rayleigh** *and* **Wien** *distributions at the same temperature. The Planck and Wien distributions bring to mind the Maxwell distribution of Figure 73. The clear failure (except at the lowest frequencies) of the Rayleigh distribution announces a* **gross violation of the equipartition principle**.

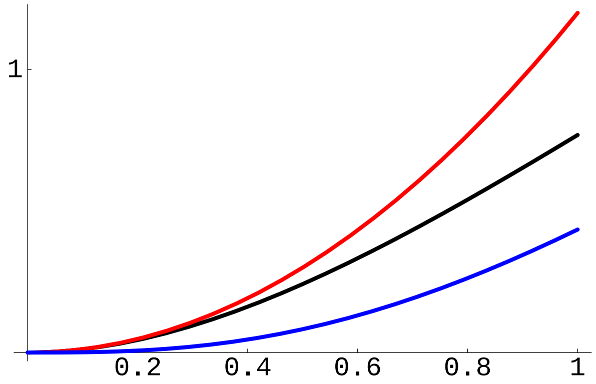

FIGURE 75: *Magnified view of the low-frequency portion of the preceding figure. Notice that the* **Planck** *and* **Rayleigh** *distributions agree perfectly at the lowest frequencies.*

Turning now to the second part of Planck's program, we observe that integration of the equation from which we extracted (297) gives

$$S_\nu = \frac{k}{h\nu}\Big\{\Big[(U_\nu + h\nu)\log(U_\nu + h\nu) - (U_\nu + h\nu)\Big] - \Big[U_\nu \log U_\nu - U_\nu\Big]\Big\} + S_0$$

The **spectral density of the specific entropy** (or entropy per unit volume) is given therefore by (compare (292))

$$s(\nu, T) = S_\nu(T)\cdot n(\nu) \tag{299}$$

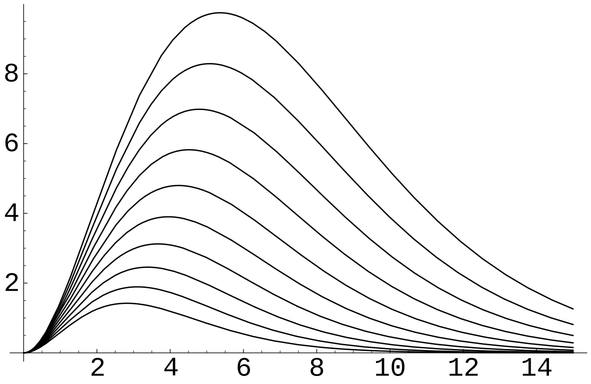

FIGURE 76: *Planck distributions at ascending temperatures* αT *with* $\alpha = 1.0, 1.1, 1.2, \ldots, 1.9$ *in some units. Note that the* T*-dependence of* $\nu_{\max}$ *is not quite linear.*

where (as before) $n(\nu) = V^{-1}N(\nu)$ describes the modal density per unit volume. By straightforward calculation

$$\begin{aligned} s(\nu,T) = k\Big\{&\big(n+\tfrac{u}{h\nu}\big)\log\big(n+\tfrac{u}{h\nu}\big) - \big(n+\tfrac{u}{h\nu}\big)\log\tfrac{n}{h\nu} - \big(n+\tfrac{u}{h\nu}\big) \\ &- \tfrac{u}{h\nu}\log\tfrac{u}{h\nu} + \tfrac{u}{h\nu}\log\tfrac{n}{h\nu} + \tfrac{u}{h\nu}\Big\} + s_0 \\ = k\Big\{&\big[(n+\varepsilon)\log(n+\varepsilon) - (n+\varepsilon)\big] - \big[n\log n - n\big] - \big[\varepsilon\log\varepsilon - \varepsilon\big] \\ &- n(1-\log h\nu)\Big\} + s_0 \end{aligned}$$

where $n = n(\nu)$, $u = u(\nu,T) = n(\nu)U_\nu(T)$, $\varepsilon = \varepsilon(\nu,T) = u/h\nu$ and $s_0 = nS_0$, and where the dangling red terms will henceforth be dismissed on the ground that they are relatively insignificant. In Stirling approximation

$$n\log n - n \sim \log n! = \log \Gamma(n+1)$$

so if n and ε were integers[170] one could write

$$s(\nu,T) = k\log\frac{(n+\varepsilon)!}{n!\,\varepsilon!}$$

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[170] It is plausible that n, which refers to the *number of modes* of frequency ν, is an integer, but less plausible (to our classical minds) that $\varepsilon \equiv u/h\nu$ is. Note that if we abandoned the "integrality assumption" we would not be analytically powerless: we could, in place of (300), write

$$s(\nu,T) = k\log\frac{\Gamma(n+\varepsilon)}{\Gamma(n)\Gamma(\varepsilon+1)}$$

or (in that same degree of approximation)

$$s(\nu,T)=k\log\frac{(n-1+\varepsilon)!}{(n-1)!\,\varepsilon!} \tag{300}$$

Planck takes his inspiration now from the idea[171] inscribed on Boltzmann's tombstone: he proposes to write

$$=k\log\big\{\text{number of distinct ways something can happen}\big\}$$

but confronts at once the question: What is the "something" to which he should be referring? His approach to this problem has been clarified by P. Ehrenfest,[172] whom I now follow:

Let ε and n be integers. From ε symbols Q and n strokes $|$ form expressions of the type

$$\big\{Q\cdots\cdots Q|Q\cdots Q|Q\cdots\quad\cdots Q|QQ|Q\cdots Q\big\}$$

These are clearly $\begin{pmatrix}n-1+\varepsilon\\n-1\end{pmatrix}=\begin{pmatrix}n-1+\varepsilon\\\varepsilon\end{pmatrix}=\dfrac{(n-1+\varepsilon)!}{(n-1)!\,\varepsilon!}$ in number.[173] The $n-1$ strokes serve to partition the bracket $\big\{\cdots\big\}$ into n "pigeonholes." Now

- identify "pigeonholes" with "modes of frequency ν
- identify Q's with "energy packets of size $h\nu$," and ε with the number of such packets that can be constructed from an amount u of energy

and we are brought to Planck's reluctant interpretation of (300):

$$\begin{aligned}&\text{spectral entropy density}\\&\quad=k\log\begin{cases}\text{number of distinct ways indistinguishable}\\\text{energy quanta of size } h\nu\text{—of which there}\\\text{are } \#=u(\nu,T)/h\nu\text{—can be distributed}\\\text{among the modes of frequency } \nu\end{cases}\end{aligned} \tag{301}$$

Planck professed to be unhappy with this result, and for a long time struggled—unsuccessfully—to show that "energy quantization" was an unphysical artifact of his computational method. Nor was it immediately clear whether "energy quantization" referred to the electromagnetic field (thought of as a system of oscillating modes), or to the walls (which, according to Kirchhoff's law, could without loss of generality be taken to be assembled from oscillators), or to a thermometer (modeled as an oscillator immersed in the radiation field) . . . or if

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[171] See again page 132.

[172] See M. J. Klein (ed.), *Collected Scientific Papers of Paul Ehrenfest* (1959), page 353.

[173] Note that the preceding statement presumes the Q's to be unindexed/ indistinguishable.

it made a difference. Planck planted the seed, but when he put down his pen the quantum theory lay still in the dim future, on the far side of contributions by Einstein (1905) and Bohr (1913).[174]

4. Einstein's alternative derivation of Planck's result. Einstein was a student at the ETH in Zürich, not quite twenty-one years old, when Planck's accomplishment was announced to the world, and during his most productive years the "problem of blackbody radiation" was never far from his mind. It led him—in the "photoelectric paper" of 1905—to the "invention of the photon," and it led him in 1916–1917—immediately after completion of his first general relativity papers—to write three "photonic" papers, one of which will concern us here.

In the "photoelectric paper" mentioned above—the full title of which (in English translation) is "Heuristic viewpoint concerning the generation and transformation of light"[175]—one encounters a discussion that proceeds from Boltzmann's $S = k\log W$ *via* Wien's law to the conclusion that "...from the standpoint of statistical interaction, light behaves like *particles of energy* $h\nu$," and the almost incidental observation that when light falls upon a metal the evaporated electrons can be expected to have kinetic energy

$$\tfrac{1}{2}mv^2 = h\nu - (\text{work function of the metal})$$

Einstein's idea was appropriated by Bohr, when he wrote

$$h\nu = E_{\text{initial}} - E_{\text{final}}$$

to describe the light emitted by a hydrogen atom when it relaxes from an excited state to a state of lower energy. Note that both of the processes just mentioned are few-body electromechanical processes that take place far from thermal equilibrium ...and to which all thermodynamic concepts are, in fact, irrelevant.

In 1917 asked us to consider a population of **2-state systems in thermal equilibrium with the blackbody radiation in which they have been immersed**. The "systems" might be atoms, molecules or any (spectrally identical) lumps of stuff, and the "two states" in question can be any two states—call them E_1 and E_2—on which we have arbitrarily chosen to fix our attention. We will assume that $E_2 > E_1$.

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[174] In the preceding brief account of one of the most absorbing and instructive chapters in the history of physics I have done violence to many points of chronology, and foreshortened a number of physical arguments. I therefore urge readers to consult the vast literature to gain a more rounded sense of the thrust of events, and of the finer details: Jammer[164] and Thomas Kuhn's *Blackbody Theory and the Quantum Discontinuity:* 1894–1912 (1978) are good places to start.

[175] For a synopsis of the paper see C. Lanczos, *The Einstein Decade* (1974), page 127.

Let N_m denote the number of systems (per unit volume) in state E_m. At thermal equilibrium we expect to have

$$N_2/N_1 = e^{-(E_2-E_1)/kT}$$

We might expect excited systems to relax at a rate given by

$$R_{1\leftarrow 2} = A\cdot N_2 \tag{302.1}$$

where A is a coefficient determined in some way by the electromechanics of the system, and according to Einstein we should expect such transitions to be accompanied by the emission of radiation of frequency

$$\nu = \frac{E_2-E_1}{h}$$

We expect the reversed transitions to occur only when systems are stimulated by the ambient radiation field, and to proceed at a rate that is proportional to how much radiation of the right frequency is present in the field, so we write

$$R_{1\rightarrow 2} = B\cdot N_1\cdot u(\nu,T)$$

where again B derives from the electromechanical specifics of the system.

At equilibrium we expect those two processes to proceed at identical rates: $R_{1\leftarrow 2} = R_{1\rightarrow 2}$ which when written $AN_2 = BN_1u$ gives

$$u = (A/B)\cdot e^{-h\nu/kT}$$

By dimensional necessity $\big[A/B\big] = \frac{\text{energy}}{\text{volume}\cdot\text{frequency}}$ and $h\nu/(c/\nu)^3\cdot\nu = h\nu^3c^{-3}$ is the only such expression that can be assembled from the system-nonspecific material at hand. So we have

$$u(\nu,T) = (\text{constant})\cdot h\nu^3c^{-3}e^{-h\nu/kT}$$

which becomes precisely the Wien distribution (291) when we assign the value 8π to the dimensionless constant.

To deal with the circumstance that Wien's result is—as Planck had been the first to insist—*close but not close enough* to the physical facts of the matter, Einstein posits the existence of a **stimulated emission** phenomenon that contributes additively to the relaxation process, and causes (302.1) to assume the adjusted form

$$R_{1\leftarrow 2} = A\cdot N_2 + B^*\cdot N_2\cdot u(\nu,T) \tag{302.2}$$

The equilibrium condition $R_{1\leftarrow 2} = R_{1\rightarrow 2}$ becomes $AN_2 + B^*N_2u = BN_1u$ or

$$\begin{aligned} u(\nu,T) = \frac{AN_2}{BN_1 - B^*N_2} &= (A/B)\frac{1}{(N_1/N_2)-(B^*/B)} \\ &= (\text{constant})\cdot h\nu^3c^{-3}\frac{1}{e^{h\nu/kT}-(B^*/B)} \end{aligned}$$

which comes into precise agreement with the Planck distribution (298) if, as before, we set (constant) $= 8\pi$ and the dimensionless constant $(B^*/B) = 1$. This Einstein himself was led to do by stipulating that his result should agree with Rayleigh's at low frequencies, and with Wien's at high frequencies.

This is a lovely accomplishment,[176] in which Einstein himself reportedly took exceptional pride.[177] And Einstein's argument can, to good effect, be run both forwards and backwards. Run forwards, it demonstrates that Planck's final result is latent in some very simple assumptions about about *the mechanism by which the blackbody spectrum is established and maintained*, and does so with none of the intricate thermodynamic reasoning upon which Planck leaned so heavily. Einstein's assumptions were mainly these:

- $E = h\nu$, used in a manner reminiscent of Bohr;
- the existence of three state-transition mechanisms (simple absorption, spontaneous emission & *stimulated* emission);
- that the **principle of detailed balance** becomes operative once the system has achieved thermal equilibrium.

Run backwards, it allows us to read Planck's result as evidence that $E = h\nu$ makes sense, and that "stimulated emission" is fact of Nature.[178] It allows us to infer, moreover, that

$$B = 8\pi h\nu^3 c^{-3} A \qquad \text{and} \qquad B^* = B$$

pertain to all quantum structures, whatever their specific electromechanical design: this we can read as a refinement of Kirchhoff's law.

5. Photon gas. The electromagnetic field quantum, as it figured in Einstein's work of 1905 and in the 1917 work discussed just above was an <u>energy quantum</u>, fully described by the equation $E = h\nu$. It was in a companion paper—by extension of the work just described—that Einstein was first motivated to write the equations

$$p = h\nu/c \quad \text{and} \quad E = cp = h\nu$$

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[176] Lanczos[175] (who began his career as Einstein's assistant, and may have been a little biased) called it "undoubtedly one of the most beautiful feats of scientific thought in the entire history of human thought."

[177] See Chapter 21 in A. Pais, *'Subtle is the Lord... ': The Science and Life of Albert Einstein* (1982). Pais has much to say, throughout his book, about Einstein's distinctive approach to statistical mechanical argument, and the principled exception he took to the approaches of Boltzmann and Gibbs.

[178] Note that stimulated emission came into the world in a thermalized context, but that it is in a non-thermalized context—the physics of lasers—that it has become most familiar. And that the latter application hinges on an aspect of the phenomenon—the *coherence* of the stimulated radiation—that would emerge from close study (within the context provided by any selected physical system) of the detailed *dynamics of the stimulated emission process* (any effort, that is to say, to *compute* the value of B: see §**9.3.1** in Griffiths' *Introduction to Quantum Mechanics* (1995) for discussion of how that might be done), but that is masked in the setting initially contemplated by Einstein.

side by side, and to observe that they are precisely the equations that in relativistic mechanics one would write to describe a *particle of zero mass*. But, though he may have had particles on his mind (as he seems to have had since 1909), he gave his "light particles" no name: the word "photon" first appeared in the title—"The conservation of photons"—of a paper by G. N. Lewis, a distinguished physical chemist at Berkeley.[179] Lewis' "photon" was an instant hit, but his idea was dead in the water . . . for if there is one thing that photons are not, it is conserved.

To allay a possible point of confusion: it

- is possible to speak meaningfully about the number and disposition of the photons present in any given sample of blackbody radiation, but
- is not possible to proceed as though that number were (like the number of molecules in a sample of material gas) a conserved feature of the sample when T or V are adjusted.

Most of the work in this connection has already been done: from

$$u(\nu,T)\,d\nu \equiv \frac{\text{energy in the neighborhood } d\nu \text{ of } \nu}{\text{unit volume}}$$

we are led to write

$$\frac{u(\nu,T)}{h\nu}\,d\nu \equiv \frac{\text{number of photons in the neighborhood } d\nu \text{ of } \nu}{\text{unit volume}}$$

so that the dimensionless construction

$$\begin{aligned} N(T,V) &= V\cdot\int_0^\infty 8\pi\nu^2c^{-3}\frac{1}{e^{h\nu/kT}-1}\,d\nu \\ &= V\cdot(kT/hc)^3 16\pi\zeta(3) \\ &= 60.422\cdot V(kT/hc)^3 \end{aligned}$$

describes the *total* number of photons present in the radiation sample, and

$$\begin{aligned} \frac{N(T,V)}{V} &= 60.422\cdot(kT/hc)^3 \\ &= \frac{2.02872\times10^7}{\text{Kelvin}^3\text{meter}^3}\,T^3 \qquad (303) \\ &= \text{net } \textbf{photon density} \text{ at temperature T} \end{aligned}$$

Working from (303), we find that there are 547 photons/cm^3 at 3K, and 10^6 times that many at 300K. Those numbers inspire the following

DIGRESSION: Looking to the equation $du/d\nu = 0$ with the assistance of *Mathematica*, we find that the Planck distribution is maximal at

$$\nu_{\max}(T) = 2.82144\cdot(k/h)T$$

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[179] Nature **118**, 874 (1926).

where the numeric arises by evaluation of an object that *Mathematica* calls `3 + ProductLog[-3/e^3]`. The associated wavelength is

$$\begin{aligned}\lambda_{\text{max}}(T) &= 0.354429 \cdot (hc/kT)\\ &= 0.005099\,\text{Kelvin-Meter}/T\end{aligned}$$

which at 3K gives $\lambda_{\text{max}} = 1.6998\,\text{mm}$. The point to which I draw attention is that such a wave *would not fit* within a box smaller than about 0.8 mm on a side. At the 39×10^{-12}K mentioned on page 215 we have $\lambda_{\text{max}} = 1.30754 \times 10^8$ meters! Boxes of reasonable size would, at that temperature, be essentially *devoid of blackbody radiation*. At temperatures

$$T \ll T_{\mathsf{c}} \equiv 0.005900\,\text{Kelvin-Meter}/V^{\frac{1}{3}}$$

we can expect Planck's theory of blackbody radiation to break down because the typical wavelength

$$\lambda = h/p = hc/E = hc/kT \gg \text{typical box dimension}$$

The modal structure of the radiation field would become evident, and could be expected to show up in (for example) the anomalous Brownian motion of gas molecules bathed in such radiation. In the kinetic theory of gases one speaks of the "Knudsen limit" when the mean free path exceeds $V^{\frac{1}{3}}$, and we have encountered here a rather similar situation. For a box with $V^{\frac{1}{3}} = 1\,\text{cm}$ the effect would become evident at about $T = 1.5\,\text{K}$, and at the temperature of liquid nitrogen (77K) would become evident within boxes of size $V^{\frac{1}{3}} = 0.19\,\text{mm}$. Someday this subject will engage the interest of experimentalists. But enough: as I was saying . . .

. . . By 1924 the "photon" had been endowed (by Einstein in both instances) with both energy $E = h\nu$ and momentum $p = h\nu/c$, and had acquired the status of an object that, in at least some contexts (including the non-thermal context studied by A. H. Compton in 1923), could be regarded as a "massless particle."[180] In that year, Satyendra Nath Bose (1894–1974) devised and sent to Einstein for his approval a derivation of the Planck distribution that proceeded from the conception of **blackbody radiation as thermalized photon gas**, without reference to the enumeration of Maxwellian field modes. To make his approach work he had, however,

- to resort to a novel state-counting procedure and
- to introduce a factor of 2 for which he could not account.

In spite of those circumstances (or perhaps because of them), Einstein attached

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[180] Its description as a "massless particle *with two spin states*" had, however, to await the discovery of spin (1925) and its non-trivial extension from massy particles (initially: electrons) to "massless particles."

high importance to Bose's accomplishment;[181] within a few months he published the first of his own papers indicating how Bose's novel state-counting procedure ("Bose-Einstein statistics") might be applied to *material* gases, and drawing attention to the odd condensation phenomenon one could expect such gases to exhibit at very low temperatures.

Were I to attempt to retrace Bose's original argument in an effort to expose where novelty was allowed to creep in (Bose, it should not be forgotten, knew exactly where he wanted to come out, and was willing to "cheat" in order to get there) I would have to digress to introduce

- a physical idea (due to Boltzmann)
- a mathematical technique ("method of undetermined multipliers," due to Lagrange) essential to the implementation of that idea

—both of which I prefer to treat later. I must for the moment be content, therefore, to direct readers interested in the instructive history of this subject to the literature[182]. . . and to proceed anachronistically: we will take Bose-Einstein statistics *as a given*, and consider where it leads when applied to "photon gas."

Imagine a dilute bosonic gas that is confined to a volume V. To represent such a system we sprinkle points onto 6-dimensional phase space. Proceeding on the assumption that the particle energy is *independent of position* and *depends isotropically on momentum*, we—on the basis of (237.1), page 196—write

$$\langle n(p)\rangle\frac{V4\pi p^2\,dp}{h^3}=\frac{1}{\frac{1}{x_0}e^{\beta\varepsilon(p)}-1}\frac{V4\pi p^2\,dp}{h^3}$$

to describe the number of state points that, at thermal equilibrium, we expect to lie within a spherical shell in momentum space. The total energy of the system then becomes

$$U=\int_0^\infty\frac{\varepsilon(p)}{\frac{1}{x_0}e^{\beta\varepsilon(p)}-1}\frac{V4\pi p^2\,dp}{h^3}$$

If the particles are assumed to be *massless* then $\varepsilon(p)=cp$ and we have

$$=\int_0^\infty\frac{cp}{\frac{1}{x_0}e^{\beta cp}-1}\frac{V4\pi p^2\,dp}{h^3}$$

and this—by Einstein's $p=h\nu/c$—can be written

$$\begin{aligned}&=V\!\cdot\!\int_0^\infty\frac{h\nu}{\frac{1}{x_0}e^{\beta h\nu}-1}\frac{4\pi h^3\nu^2\,d\nu}{h^3c^3}\\&=V\!\cdot\!\int_0^\infty\Big\{4\pi h\nu^3c^{-3}\frac{1}{\frac{1}{x_0}e^{h\nu/kT}-1}\Big\}d\nu\qquad(304)\end{aligned}$$

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[181] Einstein personally translated Bose's paper into German and arranged for its publication: S. N. Bose, "Planck's Gesetz und Lichtquantenhypotheses," Zeitschrift für Physik **26**, 178 (1924).

[182] See §**23b** Pais.[177] Also R. B. Lindsay, *Introduction to Physical Statistics* (1941), Chapter 8, Section 10.

To come into precise agreement with Planck's (298) we must

i) bring into play an additional factor of 2 and

ii) argue that $x_0 = 1$.

Looking to the first of those enforced adjustments: Planck's own 2-factor sprang from recognition (page 225) of the fact that every electromagnetic plane wave possesses two linearly independent polarizational states. To transport that notion into the present "particle picture" we stipulate that photons with momentum $\boldsymbol{p}$ come in two flavors (that ultimately we come, on other grounds, to think of as two "spin states").

Turning now to the x_0 problem: If x_0 were allowed to stand as an adjustable parameter then—working from

$$N = 2\cdot V\cdot\int_0^\infty \frac{1}{\frac{1}{x_0}e^{\beta h\nu}-1}\frac{4\pi h^3\nu^2\,d\nu}{h^3c^3} \quad : \quad \text{compare (237.2)}$$

—we could, in principle, describe x_0 as a function of T, V and N. Returning with this information to (304) we would be led to an internal energy function of the form $U(T,V,N)$ in which—contrary to the physics stipulated at (270)—"photon number" N has joined the list of independent variables.[183] If, on the other hand, x_0 is some/any *constant* then that problem is circumvented and (as was discussed already on page 235) N loses its status as an independent variable: it becomes (like the internal energy) a function $N(T,V)$ of the only surviving independent variables, T and V.

But how to argue that the constant value of x_0 is *unity*? One could observe that

$$\left\{4\pi h\nu^3c^{-3}\frac{1}{\frac{1}{x_0}e^{h\nu/kT}-1}\right\} \longrightarrow \left\{\begin{array}{l}\text{Rayleigh-Jeans (287) at low frequencies}\\ \text{Wien (291) at high frequencies}\end{array}\right.$$

if and only if $x_0 = 1$, but such an approach would seem to violate the spirit of the "photonic philosophy." If one could adapt to photon gas the statement

$$x_0 = e^{\mu/kT}$$

that on page 199 we extracted from the theory of bosonic/fermionic material gases, and if, moreover, we could justify the frequently-encountered assertion that

"the chemical potential μ of photon gas <u>vanishes</u>"

then we would have it: $x_0 = e^0 = 1$. But I *do not think it is meaningful* to write

$$\mu \equiv \left(\frac{\partial U}{\partial N}\right)_{S,V} = 0$$

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[183] Notice that if that were the case then *light would become susceptible to Bose-Einstein condensation*!

to signify that U does not depend upon what one has established to be an *impossible* independent variable.[184] What light might the Einstein's "transition rate argument" (§4) shed on the x_0 problem? At the bottom of page 233 we encountered an equation that can be written

$$u(\nu,T)=\frac{AN_2}{BN_1-B^*N_2}=(A/B^*)\frac{1}{(B/B^*)(N_1/N_2)-1}$$

Arguing as before that, of dimensional necessity,

$$\begin{aligned}(A/B^*)&=(\text{dimensionless constant})\cdot h\nu^3c^{-3}\\(B/B^*)&=\text{another dimensionless constant, call it }\tfrac{1}{x_0}\end{aligned}$$

we set the first constant equal to 8π and obtain

$$u(\nu,T)=8\pi h\nu^3c^{-3}\frac{1}{\frac{1}{x_0}e^{h\nu/kT}-1}$$

where the logic of *Einstein's argument permits us to assign to* x_0 *any value that we please*. We have $B^*=x_0B$ and the question becomes: Does the absorption rate equal the rate of stimulated emission? That is a question that could be addressed by system-specific quantum mechanical calculation.[178] Close study of Planck's original argument might show that it can be read as a demonstration that *of thermodynamic necessity* $x_0=1$, though my guess is that it would not. But Planck's result does comform to observational data, and that fact can be read as *experimental* evidence that for *all* quantum systems $B^*=B$.

Some other slippery aspects of the preceding argument merit comment:

- By representing the elements of our photon gas as "points sprinkled on phase space" we have seemingly endowed them with a degree of spatial localizability for which we can provide no physical justification. In the end, we needed to know only that they were confined to the interior of the box, and concerning that box we needed to know only its volume V (shape, though critical to the design of the field modes, had become irrelevant).
- When we sprinkled points representative of (massless, and therefore) "ultra-relativistic particles" onto non-relativistic phase space we placed ourselves in an odd formal posture. The question of why we were not led thus into error seems to me to merit thought.
- When, on page 237, we wrote $(dxdp/h)^3$ to describe elements of phase space the h's were required to have the dimensionality of action, but—see again page 151—could have been assigned any numerical value. But when, a few lines later, we wrote $p=h\nu/c$ and $E=h\nu$ the h's

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[184] What one can assert (see again §2) is that the Gibbs potential of photon gas vanishes: my claim is that one cannot write $G=\mu N$ and attribute $G=0$ to a statement of the form $\mu=0$.

> had acquired God's value. And when we casually allowed h's of the two types to cancel one another the h's of the former type suddenly acquired an *enforced* numerical value ... a value that appears, however, to have been enforced by nothing more profound than our determination to get the right answer.

6. Concluding remarks. We have, in preceding paragraphs, been led to the blackbody spectral distribution function $u(\nu, T)$ by three quite distinct lines of argument: Planck's (1900), Einstein's (1917) and Bose-Einstein's (1924). Planck's argument makes the most intense—not to say belabored—use of thermodynamic and statistical mechanical principles. It assumes nothing of quantum mechanics, but *yields* the first foreshadowings of the quantum theory of light and matter. Einstein's argument is by far the most deft: from thermodynamics it takes only a conception of the meaning of thermal equilibrium, from quantum theory only the relation $E = h\nu$, and of the concept of bosonic indistinguishability (wave function symmetry) it makes no use at all. The Bose-Einstein argument, as I have presented it, takes a thermodynamic/statistical implication of bosonic indistinguishability as its point of departure, to which it brings a more fulsome conception of the meaning of "photon" (and it adds to that conception, declaring that photons must be 2-state objects): as originally formulated by Bose himself the argument *led to* the concept of bosonic indistinguishability.

Blackbody radiation—applied statistical thermodynamics—has served as the incubator for a wonderfully rich assortment of ideas of the most profound importance—ideas that, in their mature form, may seem on first glance to have (like quantum mechanics) only incidentally to do with what we tend to think of as the "stuff of thermodynamics." It seems to me amazing that the study of gases, of the efficiency of heat engines—work that I fear I would have dismissed as "dull stuff" at the time—and (later) study of the Newtonian underpinnings of discoveries in those fields ... led ultimately to such a rich and unexpected harvest. It strikes me as sad that Maxwell did not live to see the wonders that, within forty-five years of his death, emerged when two of his creations—electrodynamics and kinetic-theory-become-statistical-mechanics—were "put into the same box and shaken." And remarkable at how many points it fell to Einstein to contribute the essential new idea.