Chapter 4

Quantum Mechanics

Statistical M

Photoelectric Effect

Light Quantum Hypothesis

B

Wave-Particle Duality

Bohr-Einstein Atom

Light

Bose-

lities

Born-Einstein Statistical

Chance

Nonlocality

Irreversibility

Nonseparab

Einstein-Podolsky-Rosen

Enta

Schrödinger's Cat

Did Albert Einstein Invent A

Light

Max Planck was just twelve years younger than Ludwig Boltzmann. He wrote his 1879 doctoral thesis two years after Boltzmann's statistical defense of his H-Theorem and entropy increase. In his thesis, Planck vowed to show that the second law of thermodynamics (with its *irreversible* increase of entropy) is an absolute law, fully as deterministic as the first law, the conservation of energy. An absolute law cannot be statistical, he said.

Planck was called to Berlin in 1889 to take Gustav Kirchhoff's chair in theoretical physics. Over the next five years he edited Kirchhoff's lengthy *Lectures on Heat Theory* and came to appreciate the universal (and perhaps absolute?) function K_λ that Kirchhoff had found for the distribution of so-called "blackbody" radiation energy as a function of wavelength λ in conditions of thermal equilibrium. Blackbody radiation is independent of the specific kind of material, a universal fact that impressed Planck deeply.

Kirchhoff showed that the amount of radiation absorbed by a material body at a given wavelength must exactly equal the amount emitted at that wavelength, or else the body would heat up or cool down, providing an energy difference that could run a perpetual motion machine. If the absorbed energy $\alpha_\lambda K_\lambda$ and the emitted energy $\varepsilon_\lambda K_\lambda$ are equal, then the emissity and absorbtivity coefficients must be equal,

$\varepsilon_\lambda = \alpha_\lambda$, which is Kirchhoff's law.

Planck set out to determine the universal function K_λ. And he further hypothesized that the *irreversibility* of the second law might be the result of an *interaction* between matter and radiation. We shall see in chapter 12 that Planck's intuition about irreversibility was correct.

In his lectures, Kirchhoff noted that in a perfectly reflecting cavity, there is no way for monochromatic rays of one frequency to change to another frequency. But he said that a single speck of material would be enough to produce blackbody radiation. His student Planck said that a single carbon particle would be enough to change perfectly arbitrary radiation into black radiation.[1]

---

1   Planck, 1991, p.44

Planck asked whether radiation absorbed by an electrical oscillator coming in as a plane wave from one direction could be emitted by the oscillator as a spherical wave in all directions, producing an irreversible change, since incoming spherical waves are never seen in nature.
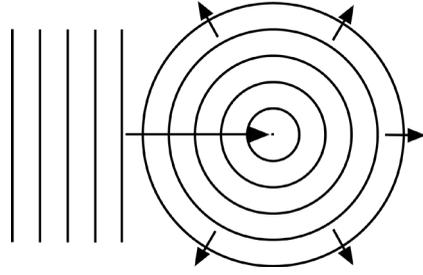
Note that Planck was attempting to locate the source of *macroscopic* irreversibility in the *microscopic* interaction of light with single particles of matter. But his suggestion was not received well. Planck described the strong reaction by Boltzmann.

> [My] original silent hope that the radiation emitted by the oscillator would differ, in some characteristic way, from the absorbed radiation, turned out to have been mere wishful thinking. Moreover, my suggestion that the oscillator was capable of exerting a unilateral, in other words irreversible, effect on the energy of the surrounding field, drew a vigorous protest from Boltzmann, who, with his wider experience in this domain, demonstrated that according to the laws of classical dynamics, each of the processes I considered could also take place in the opposite direction; and indeed in such a manner, that a spherical wave emitted by an oscillator could reverse its direction of motion, contract progressively until it reached the oscillator and be reabsorbed by the latter, so that the oscillator could then again emit the previously absorbed energy in the same direction from which the energy had been received. [2]

This "vigorous protest" from Boltzmann was a pivotal moment in the history of microscopic irreversibility. It led to the eventual understanding of the interaction of matter and light.

It began in 1895 when Planck's brilliant student ERNST ZERMELO (who later developed the basis for axiomatic set theory) challenged Boltzmann's idea of irreversible entropy increase with still another objection, now known as Zermelo's recurrence paradox. Using the

---

2   *Planck, 1949,*, pp.36-37

recurrence theorem of HENRI POINCARÉ, Zermelo said an isolated mechanical system must ultimately return to a configuration arbitrarily close to the one from which it began.

"Hence," Zermelo wrote, "in such a system *irreversible processes are impossible* since no single-valued continuous function of the state variables, such as entropy, can continuously increase; if there is a finite increase, then there must be a corresponding decrease when the initial state recurs." [3]

Beginning in 1897, Planck wrote a series of seven articles all titled "On Irreversible Radiation Processes." In the first three articles, he did not yet think a statistical or probabilistic approach could be the answer. Planck wrote to a friend that reconciling the second law with mechanics is "the most important with which theoretical physics is currently concerned."

> On the main point I side with Zermelo, in that I think it altogether hopeless to derive the speed of irreversible processes…in a really rigorous way from contemporary gas theory. Since Boltzmann himself admits that even the direction in which viscosity and heat conduction act can be derived only from considerations of probability, how can it happen that under all conditions the magnitude of these effects has an entirely determinate value. Probability calculus can serve, if nothing is known in advance, to determine the most probable state. But it cannot serve, if an improbable [initial] state is given, to compute the following state. That is determined not by probability but by mechanics. To maintain that change in nature always proceeds from lower to higher probability would be totally without foundation. [4]

But after Boltzmann's criticism, Planck's fourth article defined irreversible radiation with a maximum of entropy or disorder as "natural radiation," very much analogous to Boltzmann's molecular disorder.

> It will be shown that all radiation processes which possess the characteristic of natural radiation are necessarily irreversible. [5]

---

3   *Annalen der Physik*, 57 (1896). cited in Kuhn, *1978*, p26.
4   Kuhn, op. cit., p.27
5   *On Irreversible Radiation Processes*, IV, 1898, Kuhn, op. cit., p.78

Planck thus apparently began in 1898 to study carefully Boltzmann's approach to entropy and irreversibility, but he did not explicitly employ Boltzmann's identification of entropy with probability and his counting of microstates until late 1900, when Planck stumbled upon his formula for Kirchhoff's universal radiation law and then hastily sought a physical justification for it.

Planck's Discovery of the Blackbody Radiation Law

In 1896, a year before Planck tried to connect Kirchhoff's universal function with the *irreversibility* of his "natural radiation," Willy Wien had formulated an expression for the radiation law that agreed reasonably well with the experimental data at that time. The intensity *I* of energy at each frequency *v*, Wien wrote as

$I_v (v, T) = a'v^3 \, e^{-av/T}$

Wien's radiation "distribution" law agreed with his "displacement" law that the wavelength λ of maximum intensity $λ_{max}$ is inversely proportional to the temperature *T* or that $λ_{max} T$ = constant.

Wien said that his law was inspired by the shape of the Maxwell-Boltzmann velocity (or energy) distribution law, which as we saw in chapter 3 has a negative exponential factor for increasing energy.

Wien also proposed that the distribution over different frequencies might be the result of fast-moving gas particles emitting radiation with Doppler shifts toward higher and lower frequencies.

In May 1899, Planck *derived* the entropy for Wien's energy distribution in his fifth article on irreversible radiation. He used the fact that classical thermodynamic entropy *S* is defined by a change in entropy equaling the change in energy *U* divided by the absolute temperature. ∂S = ∂U/T. He solved Wien's distribution law for *1/T* by first taking its logarithm,

$\log I_v (v, T) = \log (a'v^3) - av/T,$

then solving for *1/T,*

$1/T = ∂S/∂U = -(1/av) \log (U/ea'v).$

He then took the second derivative of entropy with respect to energy to find

$∂^2S/∂U^2 = -(1/av)(1/U).$

When the second derivative of a function is negative, it must have a maximum. Confident that he had thus shown Wien's law to be consistent with the entropy increase to a maximum as required by the second law, Planck called for further experimental tests. But these tests proved to be a shock for him. Measurements for long wavelengths (small v) disagreed with Wien's law and showed a dependence on temperature.

On October 7, 1900, one of the experimenters, Heinrich Rubens, who was a close friend, came to dinner at Planck's home and showed him a comparison of their latest data with five proposed curves, one of which was Lord Rayleigh's proposal of June 1900 that long-wavelength radiation should be proportional to the temperature T. Rubens' graphs showed that the termperature dependence at long wavelength agreed with the recently published theory of Lord Rayleigh.

Planck described his attempt to find an interpolation formula that would include two terms, "so that the first term becomes decisive for small values of the energy and the second term for large values."[6]

His task was to find an equation that approaches Wien's law at high frequencies and Rayleigh's law at low frequencies (long wave-lengths). Initially, he may have simply rewritten Wien's law, putting the exponential in the denominator and added a -1 term to the exponential term,

$$I_v (v, T) = a'v^3 / (e^{\,av/T} - 1) \tag{1}$$

When av/T is large, we can ignore the -1 and this reduces to Wien's law at high frequencies.

For small av/T, we can expand the exponential as a series,

$$e^{\,av/T} = 1 + av/T + 1/2 (av/T)^2 + \ldots$$

Ignoring the squared and higher order terms, the 1 and -1 cancel and we have

$$I_v (v, T) = (a'/a) v^2 T, \text{ which is the Rayleigh expression.}$$

By the evening of October 7, Planck had the new equation with -1 in the denominator, which he called a lucky guess at an interpolation

6   Planck, 1949. p.40.

formula (*eine glückliche Interpolationformel*). He sent a messenger with his new formula to Rubens, who replied the very next morning that Planck's equation was an excellent fit to his experimental data.

Planck submitted his new radiation formula for examination to the Berlin Physical Society at its meeting on October 19, 1900. Rubens and Kurlbaum presented their confirming experimental data and the new Planck radiation law has been accepted ever since.

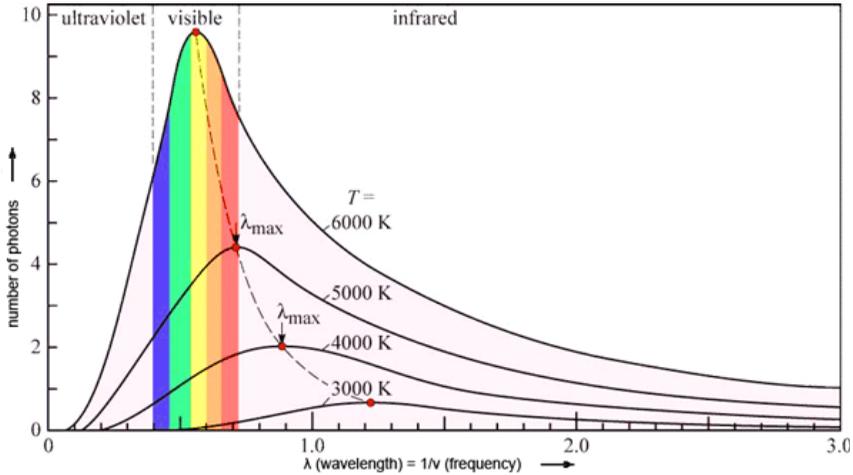Theoretical physicists describe the radiation law as a function of frequency v. Experimenters plot against the wavelength λ.

Figure 4-5. Planck's radiation law plotted against wavelength λ, showing Wien's displacement law, $\lambda_{max} T$ = constant.

Planck immediately started searching for the physical meaning of his new law, which at that point he said had been just a lucky guess.

> This quest automatically led me to study the interrelation of entropy and probability—in other words, to pursue the line of thought inaugurated by Boltzmann. Since the entropy S is an additive magnitude but the probability W is a multiplicative one, I simply postulated that S = k • log W, where k is a universal constant; and I investigated whether the formula for W, which is obtained when S is replaced by its value corresponding to the above radiation law, could be interpreted as a measure of probability.[7]

7   Planck, 1949., p.41

Planck probably pulled his hair out until he found that he could add a second term to $\partial^2 S/\partial U^2$ proportional to $1/U^2$. and then *derive* his new formula by integration. Planck's former student K. A. G. Mendelssohn wrote in 1969 (before the major analyses of Planck's thinking were published) that integrating Planck's radiation law yielded this "semi-empirical formula" for the entropy.

$S = (a'/a)\{(1 + U/a'v)log (1 + U/a'v) - (U/a'v)log (U/a'v)\}$

Mendelssohn says Planck used Boltzmann's method, that the entropy is simply the probability, calculated as the number of ways particles can be distributed or arranged.

> by considering a number N of equal oscillators with average energy U and by assuming the total energy to be made up of a number P of equal energy elements ε so that $NU=P\varepsilon$. Forming the complexion which gives the number of ways in which the P energy elements can be distributed over N, and which is the required probability, he calculated the entropy of the oscillator system as:

$NS = k \ log \ \{(P + N)!/P! \ N!\}$

> which can be written in the form

$S = k \ \{(1 + P/N)log (1 + P/N) - (P/N)log (P/N)\}$

> This theoretical expression is identical with the semi-empirical interpolation formula if a'/a is set equal to k and a' becomes the new universal constant h. [8]

Substituting these values for a and a' in equation 1, and multiplying by the classical density of states with frequency v $(8\pi v^2/c^3)$ we have Planck's radiation law, the hoped for universal function for blackbody radiation first described by Kirchhoff forty years earlier.

$\rho_v \ (v, \ T) = (8\pi hv^3/c^2) \ (1 \ / \ (e^{\ hv/kT} - 1).$ (2)

This was the introduction of Planck's quantum of action h and also "Boltzmann's constant" k. Boltzmann himself never used this constant, but a combination of the number N of particles in a standard volume of matter and the universal gas constnt R.

---

8   "Max Planck," in *A Physics Anthology*, ed. Norman Clarke p.71

The Significance of Planck's Quantum of Action

Planck's quantum of action h restricts the energy in oscillators to integer multiples of hv, where v is the radiation frequency.

Planck could not really justify his statistical assumptions following Boltzmann. They were in conflict with his own deep beliefs that the laws of thermodynamics are absolute laws of nature like the dynamic laws of Newton and the electromagnetic laws of Maxwell.

Planck stopped looking for a *continuous*, deterministic, dynamical, and *absolute* explanation for the second law of thermodynamics and embraced a *discrete*, statistical view that was to lead to the quantization of the physical world, the birth of the quantum theory.

It is important to realize that Planck never *derived* his laws from first principles. In his 1920 Nobel lecture, he said "the whole deduction of the radiation law was in the main illusory and represented nothing more than an empty non-significant play on formulae." [9] In 1925, he called his work "a fortunate guess at an interpolation formula" and "the quantum of action a fictitious quantity... nothing more than mathematical juggling." [10]

 Despite the many modern textbooks and articles claiming that he did, Planck did not suggest that the emission and absorption of radiation itself actually came in quantized (discrete) bundles of energy. We shall see in chapter 6 that that was the work of ALBERT EINSTEIN five years later in his photoelectric effect paper (for which he won the Nobel Prize). For Einstein, the particle equivalent of light, a "light quantum" (now called a "photon") contains hv units of energy.

Einstein hypothesized that light quanta do not radiate as a spherical wave but travel in a single direction as a localized bundle of energy that can be absorbed only in its entirety by an electron. Einstein assumed the light quanta actually have momentum. Since the momentum of a material particle is the energy divided by velocity, the momentum p of a photon is $p = hv/c$, where c is the velocity of light. To make the dual aspect of light as both waves and particles (photons) more plausible, Einstein interpreted the *continuous* light wave intensity as the probable density of *discrete* photons.

---

9   *The Genesis and Present State of Development of the Quantum Theory*, Planck's Nobel Prize Lecture, June 2, 1920

10   Planck, 1993. pp.106, 109.

Despite the "light-quantum hypothesis," Planck refused for many years to believe that light radiation itself existed as quanta. Planck's quantization assumption was for an ensemble of "oscillators" or "resonators" with energy values limited to *hv, 2 hv, 3 hv*, etc.

In 1906 Einstein showed that the Planck radiation law could be derived by assuming light too is quantized. He argued that Planck had essentially made the light quantum hypothesis in his work without realizing it.

Note that in NIELS BOHR's theory of the atom thirteen years later, where Bohr postulated stationary states of the electron and transitions between those states with the emission or absorption of energy equal to *hv,* but in *continuous* waves, because, just like Planck, Bohr denied the existence of light quanta (photons)!

It is unfair to Einstein that today so many books and articles give credit to Planck for the light quantum hypothesis and to Bohr for the idea that quantum jumps between his stationary states are accompanied by the absorption and emission of photons!

Comparison of Matter and Light Distribution Laws

Planck was pleased to find that his blackbody radiation law was the first known connection between the mechanical laws of matter and the laws of electromagnetic energy. He knew this was a great step in physical understanding, "the greatest discovery in physics since Newton," he reportedly told his seven-year-old son in 1900.

It took many years to see the deep connection between matter and light, namely that they both have wave and particle properties. But if we look carefully at the distribution laws for matter and radiative energy, we can begin to see some similarities

T=200K

T=300K

T=500K

T=1000K

Number of Particles

Particle Velocity

The Maxwell-Boltzmann distribution of gas particles (atoms or molecules) has a quadratic power law increase for low velocities and an exponential falloff for high velocities, due to the Boltzmann factor $e^{-mv^2/2kT}$.

The curves overlap because the number of particles (the area under the curve) is constant.

Radiation Energy Density

Frequency (ν)

10,000K

8,000K

6,000K

5,000K

4,000K

This is Planck's radiation law plotted against frequency ν rather than the traditional wavelength λ.

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

It shows the ν-cubed rise in low energy photons and exponential falloff of high energy photons due to the Boltzmann factor $e^{-h\nu/kT}$.

For low energy,
$$\rho_\nu = 8\pi\, \nu^2\, kT/c^3$$

For high energy,
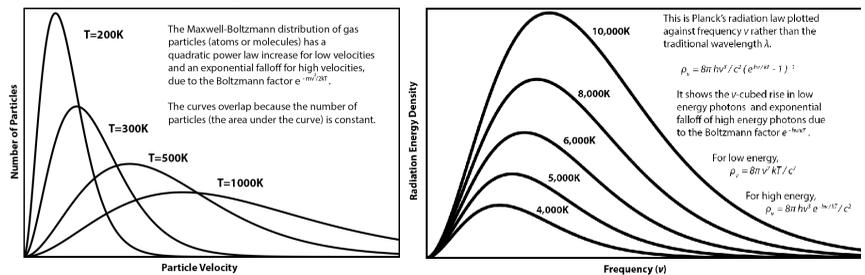$$\rho_\nu = 8\pi\, h\nu^3\, e^{-h\nu/kT}/c^3$$

Figure 4-6. Distribution laws for radiation and matter

Here we plot both matter and light with energy (frequency) increasing to the right to emphasize the similarities and differences.

Both curves increase from zero with a power law (v^2, v^3). Both curves decrease exponentially at higher energies with the Boltzmann factor $e^{-E/kT}$.

Both maxima move to higher energies, matter to higher velocities, just as peak radiation moves to higher frequencies. But matter distribution curves overlap, where light curves do not.

The reason for the different looks is that when temperature increases, the number of gas particles does not change, so the Maxwell-Boltzmann distribution flattens out, preserving the area under the curve.

By contrast, when the temperature of radiation increases, the added energy creates more photons, and the Planck curve gets higher for all frequencies.

We shall argue that the spectroscopic analysis of light has been the most fundamental tool elucidating the atomic structure of matter. The similarity between the velocity distribution of matter and the energy distribution of light led to an expression for the *continuous* spectrum. We will see that the *discrete* spectrum provided even deeper insight into the quantum structure of matter.

With 20-20 hindsight we will show that one can almost "read off" the atomic structure of matter just by taking a careful look at atomic spectra.
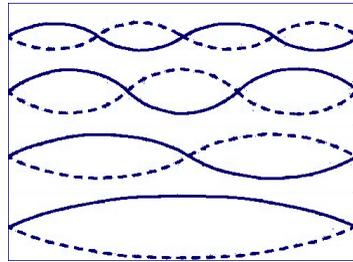
The Ultraviolet Catastrophe

Years after Planck had found a formula that included Wien's exponential decay of energy for higher frequencies of light, it was pointed out by Einstein and others that if Planck had done his calculations according to classical physics, he should have put equal amounts of energy in all the higher frequency intervals, leading to an infinite amount of energy in shorter-wavelength ultraviolet light.

The idea of equipartition of energy assumes that every "degree of freedom" or mode of vibration should get an equal amount of energy. Equipartition was a fundamental tenet of thermodynamic

equilibrium in the nineteenth century. Classical electromagnetic theory claimed each vibration wavelength that could be a standing wave in a container, up to those with infinite frequency and zero wavelength, should be counted. This seems to suggest an infinite amount of energy in the radiation field.

The classical density of states with frequency v is $8\pi v^2/c^3$, and Planck used that to derive his radiation law. Today we know that a Boltzmann factor $e^{-En/kT}$ must be applied to each vibration mode to prevent an infinite amount of energy in the high frequencies.

Einstein criticized Planck for combining classical and quantum ideas, but we shall see that Einstein himself kept this classical density of states in his own derivations of the Planck law until a complete quantum derivation was made by SATYENDRA NATH BOSE and Einstein in 1924, when they discovered the indistinguishability of quantum particles and the origin of the term $8\pi v^2/c^3$ with no reference to classical electromagnetic radiation.

Planck's Accurate Determination of Natural Constants

Planck's blackbody radiation distribution law contains a surprising number of fundamental constants of nature. Some are related to light (the velocity c and the frequency λ), some to matter (Boltzmann's constant $k = R/N$), and his own constant h, important for both. Because the experimental data were quite accurate, Planck realized that he could calculate values for these constants and some others. His calculated values would prove to be more accurate than those available from direct measurements at that time.

It is ironic that a physicist who had denied the existence of discrete particles only a few years earlier would now use the constants in his new law to determine the most accurate values for N, the number of particles in a gram-molecular weight of any gas, and for e, the charge on the electron that was discovered just one year earlier.

Where Planck wrote k, Boltzmann had used R/N, where R is the universal gas constant and N is Avogadro's number. Although it is inscribed on Boltzmann's tomb as part of his famous formula relating entropy to probability, $S = k \log W$, Boltzmann himself had never described the constant k as such. It was Planck who gave "Boltzmann's constant" a symbol and a name.

Planck found $k = 1.346 \times 10^{-16}$ ergs/degree. He had no idea how accurate it was, Today's value is 1.3806×10^{-16}. Planck's value, which was of course dependent on the accuracy of the experimental data, was within an incredible 2.5%. Now together with the well-known gas constant R, Planck could estimate the number of molecules N in one mole (a gram molecular weight) of a gas.

Planck found $N = 6.175 \times 10^{23}$. The modern value is 6.022×10^{23}.

Planck's estimate of the fundamental unit of electrical charge e. was 4.69×10^{-10} esu. The modern value is 4.80×10^{-10} esu. Other estimates in Planck's day were 1.29 and 1.65×10^{-10} esu showing how his numbers were so much more accurate than any others made at that time. These results gave Planck great confidence that his "fictitious," wholly theoretical, radiation formula must be correct.

Planck's discovery of "natural constants" led to the effort to define the constants with no reference to human values for mass, length, time, electric charge, etc.

We describe these new "dimensions" as Planck units. For example, we can set the velocity of light c to 1. Now a particle moving at one-tenth light velocity is moving at 0.1 Planck unit.

Familar and famous equations now look different and may hide some important physical relations. Einstein's $E = mc^2$ becomes $E = m$.

Similar to light velocity $c = 1$, other important constants are defined as 1.

Planck units are defined by

$\hbar = G = k_e = k_B = c = 1,$

$\hbar$ is the reduced Planck constant $h/2\pi$, G is the gravitational constant, k_e the Coulomb constant, and k_B the Boltzmann constant.

In cosmology and particle physics, Planck's natural constants describe the so-called "Planck scale." They can be combined to describe a "Planck time" of 5.4×10^{-44} seconds, a "Planck length" of 1.6×10^{-35} meters, and a "Planck energy" of 1.22×10^{19} GeV.

They are thought to best describe the earliest moment of the Big Bang, the first 10^{-43} seconds of the universe.

No Progress on Microscopic Irreversibility

Although Planck was the first to find equations that involve both matter and light, and though he thought for many years that their interaction could explain microscopic irreversibility, this nineteenth-century problem is thought by many physicists to be still with us today.

Planck's intuition was good that irreversibility depends on both light and matter, but true irreversibility must depart from physical determinism, and that had to wait for ALBERT EINSTEIN's discovery of ontological chance in 1916.

In the intervening years, Planck rightly thought his greatest achievement was not just the discovery of equations involving both discrete material particles and continuous wavelike radiation, both matter and energy. He also found and named the natural constants in these equations, both his h and Boltzmann's k.

Planck knew from his mentor Kirchhoff that monochromatic radiation can not thermally equilibrate to all the frequencies in his new distribution law without at least a tiny bit of matter.

We have seen in chapter 3 that matter by itself can approximate thermal equilibrium with Boltzmann's classical statistics, but deterministic physics leaves it open to the reversibility and recurrence objections of Loschmidt and Zermelo.

So we shall see in chapter 12 that the collision of Einstein's light quanta with particles that have internal quantum structures adds the necessary element of indeterminacy for microscopic irreversibility.

Planck initially hoped for a second law of thermodynamics that was as absolute as the first law. What we now find is only a statistical law, but his insight that it would depend on both matter and energy was confirmed, and their roles are oddly symmetric.

Even a tiny bit of matter will equilibrate radiation. Even a tiny bit of radiation can equilibrate matter. And both are the result of quantum mechanics.