A Reckless Hypothesis
The History of the Light Quantum

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"Why do people always chatter about my theory of relativity? I have worked on other useful things, possibly even better ones. But the public doesn't take any notice of all this. [...] I have thought a hundred times more about quantum theory than about general relativity."

"I promise to send you four papers [...]. The first deals with the energetic properties of light and is very revolutionary, as you will see. [...] The forth paper deals with the electrodynamics of moving bodies. The kinematical part of it will interest you."

Einstein to Conrad Habicht, May 1905

"After fifty years of hard thinking I did not come closer to answer the question of what light quanta are. Today any scoundrel pretends to know it, but he is in error."

Einstein to Michele Besso, 1951

PLAN

- Early radiation theory: Kirchhoff and Wien
- Two vetos by Lummer and Pringsheim
- Planck's 'Act of Despair'
- Young Einstein criticizes Planck
- Einstein's light-quantum hypothesis
- Baffled reactions
- Einstein finally understands what Planck was doing
- Einstein's legacy

Early radiation theory

- Assuming the existence of thermodynamic equilibrium between em-radiation and matter, Gustav Kirchhoff concluded in 1859 the existence of a *universal* function, $\rho(\nu, T)$, for the spectral energy-density of that radiation.

- Clever thermodynamic arguments led Wilhelm Wien in 1893 to

$$\rho(\nu, T) = \nu^3 f(\nu/T) .$$

This reduced the problem to finding the universal function, f, of merely *one* variable. First immediate consequences were the 'displacement law' and the 'Stefan-Boltzmann law':

$$\nu_{\mathrm{max}} \propto T , \qquad \int_0^\infty d\nu\, \rho(\nu, T) \propto T^4 .$$

Einstein on f retrospectively

"It would be elevating if we could estimate the amount of brain-substance that was sacrificed by theoretical physicists on the altar of that universal function f; and there is no end in sight of such cruel doing!
Quite the contrary! Already classical mechanics fell victim to it and it cannot be foreseen whether Maxwell's equations will outlive the crisis brought about by this function f."

Einstein, 1913

Wien's law

- Making an analogy to Maxwell's velocity distribution, W. Wien suggested a radiation law in 1894 which fitted all experimental data until early 1900. It reads :

$$\boxed{\rho(\nu, T) \; = \; a\,\nu^3 \cdot \exp\left(-\,b\nu/T\right)}$$

where a and b are freely adjustable parameters.
(modern notation: $a = 8\pi h/c^3$, $b = h/k = hN/R$)

Planck entering the scene: act 1

- Planck's program is to derive the radiation law by combining Maxwell's theory with the 2nd law of thermodynamics (which at that time he believes to be a rigorous and deterministic statement).
- By Kirchhoff's universality result he may idealize 'matter' by simple monochromatic (frequency ν) harmonic oscillators.
- From equilibrium condition and phase averaging he determines ρ as universal function of the mean oscillator energy at temperature T

$$\boxed{\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \cdot \bar{E}(\nu, T)}$$

Planck's Master Formula

What could/should have happened, but didn’t

- The equipartition theorem(!) of statistical mechanics implies an average energy of kT per oscillator degree of freedom.

- Applied to Planck’s matter model: $\bar{E}(\nu, T) = kT$.

- Get Rayleigh-Jeans formula as unambiguous consequence of classical physics (i.e. electrodynamics and thermodynamics):

$$\boxed{\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \cdot kT}$$

Rayleigh-Jeans law is nonsense

- Linear dependence on T is totally unacceptable. It would e.g. imply that the radiation energy-density at room-temperature ($T \approx 290\,\mathrm{K}$) is $1/6$ of that at the temperature of melting steel ($T \approx 1700\,\mathrm{K}$), which is obviously not the case.

- Integrating the spectral energy distribution over all frequencies yields a divergence for $\nu \to \infty$. This is a first appearance of a catastrophic 'ultraviolet divergence'.

Planck entering the scene: act 2

- Planck, being still an 'anti-atomist', does not (yet!) believe in statistical thermodynamics. His strategy to determine $\bar{E}(\nu, T)$ derives from classical axiomatic thermodynamics:
  - First determine the entropy $S(\bar{E}, \nu)$ of a single oscillator,
  - then solve the general relation $\partial S(\bar{E}, \nu)/\partial\bar{E} = 1/T$ for $\bar{E}(\nu, T)$.

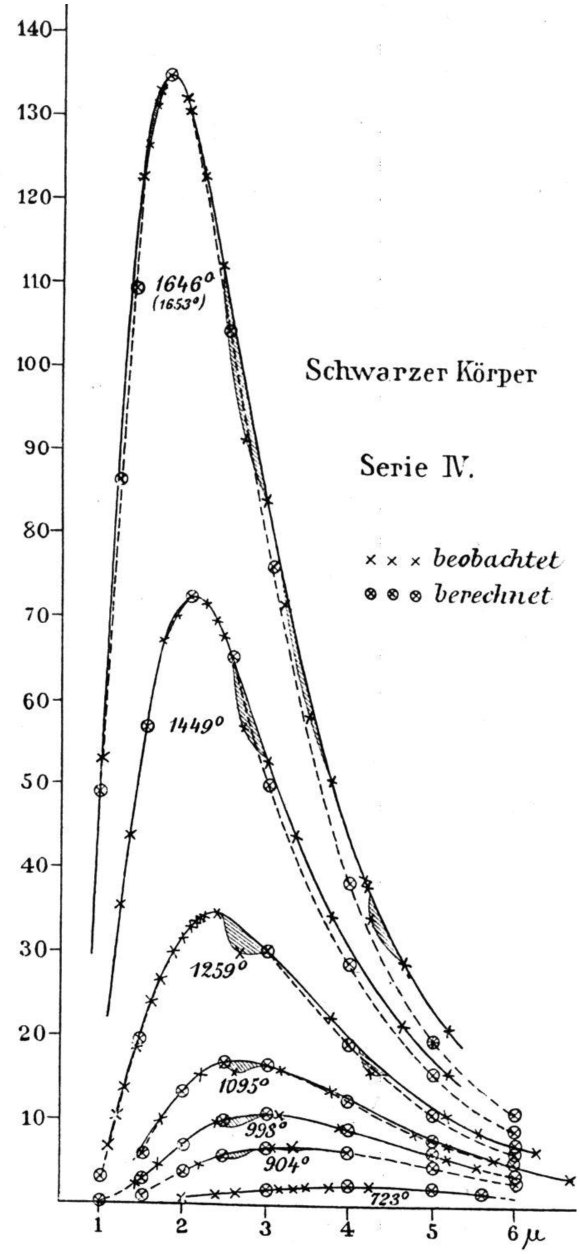
- He thinks he can prove that there is a unique expression for $S(\bar{E}, \nu)$ compatible with 2nd law (entropy increase). But, in fact, he only shows sufficiency, not necessity! This expression leads to Wien's law, which Planck therefore argues to unambiguously follow from first principles of classical physics (though that is, in fact, true for Rayleigh-Jeans' law!).

Planck triumphant

> "I belive to be justified to conclude that the given definition of radiation entropy $[S(\bar{E}, \nu)]$, and hence Wien's law, necessarily results from the application of the principle of entropy increase to electrodynamics. The limitations of Wien's law, should such exist, must therefore coincide with the limitations of the 2nd law of thermodynamics."
>
> *Planck, November 1899*

- So firmly does Planck believe in Wien's law, that he uses its two constants, a and b, together with G and c, to construct 'natural units' (today's 'Planck units'). More than one year before introducing h, the quantum of action!

A first experimental veto by Lummer and Pringsheim



A second veto:
Lummer and Pringsheim pointing out the difference between ‘necessary’ and ‘sufficient’

> “Herr Planck explicitly states that this formula [Wien’s] is a necessary consequence of the entropy law, as applied to electromagnetic radiation, and that its limitations of validity – if at all existent – are those of the 2nd law of thermodynamics. However, it seems to us that Planck’s argument would only be compelling if he had shown that any other radiation formula violates the 2nd law.”
>
> *Lummer and Pringsheim*
> *November 1899*

Planck entering the scene: act 3

- The experimental deviations for large λT are those predicted by the Rayleigh-Jeans formula. By interpolating $T^2\, d\bar{E}/dT$ between R-J and Wien's law, Planck cleverly guessed a new formula that fitted all data.

- After month of seeking a proper derivation, Planck, 'at all costs' and in an 'act of despair', finds a derivation of the new formula by using Boltzmann's statistical definition of entropy

  $$\boxed{S = k \cdot \ln(W)}$$

  where W is the number of microstates that realise the same macrostate (Boltzmann's 'complexions'). Have $k = R/N$ from comparison with entropy of gases.

December 1900: Planck's 'Act of Despair'

- Planck uses his old matter model consisting of n harmonic oscillators of frequency ν at total energy E_n. In order to obtain a finite W, he assumes each oscillator to emit and absorb radiation energy only in integer multiples of some energy unit ε (AoD). With $p := E_n/\varepsilon$ and $\bar{E} = E_n/n$ one gets for the entropy per oscillator:

$$S = \frac{k}{n} \cdot \ln \left[\frac{(n+p-1)!}{p!(n-1)!} \right] \approx k \left[(1+\bar{E}/\varepsilon)\ \ln(1+\bar{E}/\varepsilon) - (\bar{E}/\varepsilon)\ \ln(\bar{E}/\varepsilon) \right]$$

- Wien's general form of the radiation law requires $\varepsilon = h\nu$ for some constant h. Following his old strategy (calculate $\bar{E}(\nu, T)$ from $\partial S/\partial \bar{E} = 1/T$ and insert into the 'master formula', which he still believed in) leads to Planck's famous radiation law:

$$\boxed{\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{\exp(h\nu/kT) - 1}}$$

Einstein's first critique on Planck's derivation

Planck's classical master formula

$$\rho(\nu, T) = \frac{8\pi\nu^2}{c^3} \cdot \bar{E}(\nu, T)$$

is incompatible with his quantisation hypothesis

$$\varepsilon = h\nu$$

The quantum mean $\bar{E}$ may be expected to be approximately the classical one in case $h\nu \ll \bar{E}(\nu, T)$, but this is strongly violated in the – well tested – realm of validity of Wien's law, where $h\nu \gg kT$, so that

$$\bar{E}(\nu, T) = h\nu \cdot \exp\bigl(-h\nu/kT\bigr) \ll h\nu$$

Einstein's second critique on Planck's derivation

Planck was not justified to use Boltzmann's entropy formula $S = k \cdot \ln W$. For this formula to apply, the microstates must be chosen such that, in the given theoretical framework, they appear equally probable. But in the context of Planck's derivation this is true only if $h\nu \ll \bar{E}(\nu, T)$. But, e.g. for $\lambda = 0.5\,\mu m$ and $T = 1700\,K$, we have $h\nu/\bar{E}(\nu, T) = 6.5 \cdot 10^7$.

> "Just as much as every physicist should be delighted that Herr Planck so happily ignored this requirement [to choose W according to theory], one should not forget that Planck's radiation formula is incompatible with the foundations on which its derivation rests."
>
> *Einstein, 1909*

A personal side remark on Quantum Theory: a very ironic history indeed !

The discovery of Quantum Theory was motivated by measurements that showed deviations from Wien's law for large $\lambda \cdot T$. This is the classical regime, where Rayleigh-Jeans' law holds approximately.

MORAL

Quantum Theory was discovered through classical deviations from a cleverly guessed limiting quantum-formula, which was erroneously thought to be a consequence of classical physics.

Einstein's first 'correspondence argument' ever: a new determination of Avogadro's number N

- As a matter of fact, Planck's formula agrees with all measurements to a high level of accuracy. Given that, Einstein makes the following simple but far reaching observation, which is logically independent of Planck's own derivation of his formula:
- Since we know that there is a realm of validity of classical concepts, we must have:

$$\underbrace{\frac{a\nu^3}{\exp(b\nu/T)-1}}_{\text{general Planck-like law}} \Longrightarrow \underbrace{\frac{8\pi\nu^2}{c^3}\cdot\frac{R}{N}T}_{\text{unambiguous classical law}} \qquad \text{for small} \quad \nu/T$$

Hence $$\boxed{N=\frac{b}{a}\cdot\frac{8\pi R}{c^3}}$$

Planck advancing atomism against all intentions

- Radiation measurements allowed to give an improved value of N and, via Faraday's constant, to the by far best value for the elementary charge e at the time. In units of $10^{-10}\,esu$ (electrostatic units):

Richarz (1894):	1.29
J.J. Thomson (1898):	6.50
Planck/Einstein (1901):	4.69
PDG (2000):	4.803 204 20(19)

- The ironic twist of this story is that of all people, it was Planck who led the way to a new determination of a fundamental atomistic quantity.

Einstein understanding Wien's law

- Let $\rho(\nu,T)$ and $\varphi(\nu,T)$ be the spectral densities of energy and entropy, so that $\partial\varphi/\partial\rho = 1/T$. Consider radiation in spectral range $[\nu,\nu+d\nu]$ of energy E in volume V. Calculate entropy change under change of volume in the realm of Wien's law:

$$\frac{\partial\varphi}{\partial\rho} = \frac{1}{T} = -\frac{1}{b\nu}\cdot\ln\left[\frac{\rho}{a\nu^3}\right] \quad \text{(Wien's law used here)}$$

$$\Rightarrow \quad \varphi(\rho,\nu) = -\frac{\rho}{b\nu}\cdot\left\{\ln\left[\frac{\rho}{a\nu^3}\right]-1\right\}$$

$$\Rightarrow \quad S(E,\nu) = -\frac{E}{b\nu}\cdot\left\{\ln\left[\frac{E}{Va\nu^3\,d\nu}\right]-1\right\}$$

$$\Rightarrow \quad S-S_0 = \frac{E}{b\nu}\cdot\ln\left[\frac{V}{V_0}\right] = k\cdot\ln\left[\frac{V}{V_0}\right]^{E/bk\nu}$$

- Compare with gas of n indistinguishable particles:

$$S-S_0 = k\cdot\ln\left[\frac{V}{V_0}\right]^{n}$$

- Conclude (formally) $E/bk\nu = n$, that is,

$$\varepsilon := E/n = bk\nu = h\nu$$

Einstein's Light-Quantum Hypothesis

> "Monochromatic radiation of low density (within the realm of Wien's law) behaves thermodynamically as if it consists of mutually independent energy quanta of magnitude $h\nu$."
>
> ... this suggests to investigate, whether the laws of creation and transformation of light, too, are of a kind as if the light consisted of such quanta of energy."
>
> *Einstein, March 1905*

- One such application was the 'photoelectric effect'. The LQH immediately leads to the following expression for the kinetic energy of escaping electrons, where P is the material's specific escape-energy:

$$\boxed{E = h\nu - P}$$

Reactions: Planck

"Does the absolute vacuum (the free ether) possess any atomistic properties? [...] You seem to answer in the affirmative, whereas I like to negate this question. I do not try to interpret the elementary quantum in [as property of] the vacuum, but rather at the point of absorption and emission. I assume the processes in the vacuum to obey Maxwell's equations *exactly*.

Planck to Einstein, July 1907

"In any case, I think that the whole difficulty concerning quantum theory should be limited to the *interaction* between matter and radiation; then, for the time being, processes in pure vacuum could be explained by Maxwell's equations."

Planck, 1909

Reactions: von Laue & Sommerfeld

“I am happy to hear that you have given up your theory of light quanta. As you know, I never felt positive about it.”

von Laue to Einstein, December 1907

“Einstein translated the quantum aspect from the process of emission and absorption to the structure of pure light-energy in vacuum, though today, I believe, he does not any longer maintain his point of view in its entire boldness.”

Sommerfeld, 1912

Reactions: Millikan

After 10 years of experimental work on Einstein's equation $E = h\nu - P$, in which he succeeded to determine h up to the 0.5% level, Robert Millikan wrote:

> "This hypothesis may well be called reckless, first because an electromagnetic disturbance which remains localized in space seems a violation of the very conception of an electromagnetic disturbance, and second because it flies in the face of the thoroughly established facts of interference." [...]
>
> "Despite then the apparently complete success of the Einstein equation, the physical theory of which it was designed to be the symbolic expression is found so untenable that Einstein himself, I believe, no longer holds to it."
>
> *Millikan, 1916*

Reactions: Planck & Co

In 1913 Einstein was suggested to become a member of the very prestigious Prussian Academy of Science. The decisive letter of recommendation by Planck, Nernst, Rubens, and Warburg ended like this:

> "To sum up one may say that Einstein made remarkable contributions to any of the numerous problems of modern physics. One should not discredit him too much for sometimes overshooting the mark in his speculations, like he did in his light-quantum hypothesis; for without running such a risk there will be no true innovation even in the most exact of all sciences."
>
> *Planck - Nernst - Rubens - Warburg, 1913*

Einstein's energy-fluctuation analysis

(What quantity did Planck interpolate ?)

- Derive probability distribution, $P(\epsilon)$, where $\epsilon := E - \langle E\rangle$, from inversion of Boltzmann's entropy formula $S = k \cdot \ln(W)$. Set $\beta := 1/kT$, then:

$$P(\epsilon) = \sqrt{2\pi/\gamma} \cdot \exp(-\tfrac{1}{2}\gamma\, \epsilon^2)\,, \quad \gamma := -k^{-1}\frac{d^2S}{dE^2}\bigg|_{E=\langle E\rangle} = -\frac{d\beta}{dE}\bigg|_{E=\langle E\rangle}$$

$$\Rightarrow \quad \langle \epsilon^2\rangle = \int_{\infty}^{\infty} P(\epsilon)\epsilon^2\, d\epsilon = 1/\gamma = -\frac{d\langle E\rangle}{d\beta}$$

- Apply to Planckian oscillator:

$$\langle E\rangle = \begin{cases} 1/\beta \\ h\nu\ \exp(-\beta h\nu) \\ \frac{h\nu}{\exp(\beta h\nu)-1} \end{cases} \quad \Longrightarrow \quad \langle \epsilon^2\rangle = \begin{cases} \langle E\rangle^2 & \text{Rayleigh-Jeans} \\ h\nu\, \langle E\rangle & \text{Wien} \\ \langle E\rangle^2 + h\nu\, \langle E\rangle & \text{Planck} \end{cases}$$

Einstein's legacy to the younger generation

- Do not just calculate and predict, but try to understand the overall picture !
- Be faithful to the theoretical basis and listen carefully to what it really says and requires. Take it seriously and don't accept false compromises. A prediction from an inconsistent basis should have no permanent place in physics !
- Be not intimidated by scientific giants !
- Follow your ideas and think hard !
- ... ...

THE END