Role of entropy in Einstein's thoughts on constitution of radiation

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The article describes how Einstein used entropy in arriving at his light quantum hypothesis and how entropy fluctuations led to the discovery of the dual nature of light hidden intrinsically in the radiation formula of Planck.

'THERMODYNAMICS is a theory of principles' it is[1] not a 'constructive' theory and is thus independent of models. Such were the deep impressions created by classical thermodynamics on Einstein. The key note in thermodynamics is the concept of entropy. Einstein used entropy to investigate the nature of thermal radiation and arrived at the hypothesis of light quanta. This was the first step toward unfolding the constitution of radiation. Earlier, Einstein had developed his own theory of statistical mechanics setting a limit to the validity of the laws of thermodynamics by defining the fluctuations of a thermodynamical observable. When Einstein applied his entropy fluctuations to the radiation problem he was led to the dual nature of radiation that was intrinsically hidden in Planck's formula. The present article aims at describing these two developments in the historical sequence as published by Einstein himself.

The light quantum hypothesis

The universal character of the second law of thermodynamics led Einstein to look for an entropy function corresponding to Wien's radiation formula. The mathematical structure of this function suggested that radiation had a corpuscular nature in contrast to the well-accepted wave character of light represented by Maxwell's equations. This was the subject matter of Einstein's paper of 1905 (ref. 3).

The starting point was Wien's suggestion[3] for the entropy function for radiation enclosed in a cavity of volume v,

$$S = v \int_0^\infty \varphi(u, \nu)\, d\nu \quad (1)$$

the integral extends over all the 'colours' (frequencies) of radiation in the cavity. The integration implies the additive property of entropy S. The function $\varphi(u, \nu)$ is unknown and Einstein sought to calculate it. Here u is written in place of u_ν the radiation density in the frequency interval ν, $\nu + d\nu$.

At thermal equilibrium the entropy is a maximum. Therefore,

$$\delta \int_0^\infty \varphi\, d\nu = 0. \quad (2)$$

Energy conservation is expressed by

$$\delta \int_0^\infty u\, d\nu = 0. \quad (3)$$

Introducing λ as a constant of multiplier the above two equations are combined to give

$$\int_0^\infty [\partial\varphi/\partial u - \lambda]\, \delta u\, d\nu = 0. \quad (4)$$

Here λ and therefore $\partial\varphi/\partial u$ are independent of ν. Equation (2) provides the expression for entropy per unit volume,

$$dS = \int_{\nu=0}^{\nu=\infty} (\partial\varphi/\partial u)\, du\, d\nu. \quad (5)$$

If dE is the heat exchanged between radiation and Planck's resonators at temperature T, independence of $\partial\varphi/\partial u$ on ν gives,

$$dS = (\partial\varphi/\partial u)\, dE, \quad (6)$$

$$dS = dE/T. \quad (7)$$

This gives the equivalence

$$\partial\varphi/\partial u \equiv 1/T. \quad (8)$$

To calculate $1/T$ Einstein used Wien's formula

$$u_\nu = \alpha\nu^3 \exp(-\beta\nu/T), \quad (9)$$

where α and β are constants. Equations (8) and (9) give

$$1/T = (1/\beta\nu)\, \ln(u/\alpha\nu^3) \equiv \partial\varphi/\partial u. \quad (10)$$

Integration of the above equation gives

$$\varphi(u, \nu) = (-u/\beta\nu)\,[\ln(u/\alpha\nu^3) - 1]. \quad (11)$$

For a monochromatic radiation in the frequency interval ν, $u+d\nu$ the energy E_ν is expressed as

$$E_\nu = \nu u_\nu \, d\nu. \quad (12)$$

Further, equation (1) defines its entropy as

$$S_\nu = \nu\varphi \, d\nu. \quad (13)$$

From (11) we substitute for φ obtaining

$$S_\nu = \nu\,(-u/\beta\nu)\,[\,\ln(u/\alpha\nu^3) - 1\,]\,d\nu \quad (14)$$

and from (12) we put for u_ν to get

$$S_\nu = (-E_\nu/\beta\nu)\,[\,\ln(E_\nu/\alpha\nu\nu^3) - 1]. \quad (15)$$

If the cavity volume changes from its initial value v_0 to v, the entropy of radiation changes from $(S_\nu)_0$ to S_{ν_1} for the sake of brevity from S_0 to S giving

$$S_0 - S = [\,E_\nu/\beta\nu\,]\,\ln(v/v_0)$$
$$= k\,\ln(v/v_0)^{E_\nu/k\beta\nu} \quad (16)$$

This expression for the entropy change is compared with the corresponding expression for the entropy change of and ideal gas when its volume changes from v_0 to v (Einstein simply hints at the following calculation without giving details).

Using the relation

$$dQ = c_v\, dT + p\, dv,$$

where dQ is the heat given, c_v the sp. ht at constant volume, $p\,dv$ is the work done in expansion. For $dT = 0$,

$$dQ = p\, dv.$$

Using Gay–Lussac and Boyle's law in the form (R is the Gas constant, N the Avogadro number)

$$pv = n\,(R/N)\,T$$

we have

$$dQ = n\,(R/N)T\,(dv/v)$$

or

$$Q = n\,(R/N)T\,\ln\, v + a \text{ const.}$$

giving entropy

$$S = n\,(R/N)\,\ln\, v + a \text{ const.}$$

If the volume changes from v_0 to v at constant temperature we can write

$$S_0 = n\,(R/N)\,\ln v_0 + \text{const.}$$

and

$$S = n\,(R/N)\,\ln v + \text{const.}$$

with the condition that $S > S_0$; entropy increases in the final state giving

$$(S_0 - S)_{gas} = n\,(R/N)\,\ln(v/v_0)$$
$$= (R/N)\,\ln(v/v_0)^n. \quad (17)$$

In Boltzmann's language, if there are n molecules originally moving in a volume v_0 the probability that at any randomly chosen instant of time they are to be found in the partial volume v (sub-volume of v_0) is W given by

$$W = (v/v_0)^n.$$

The above expression for the change in entropy is consistent with Boltzmann's definition. A comparison of equations (16) and (17) gives,

$$n = E_\nu/(R/N)\,\beta\nu. \quad (18)$$

The energy is thus quantized:

$$E_\nu = n\,(R/N)\,\beta\nu. \quad (19)$$

For $n = 1$,

$$E_\nu = (R/N)\,\beta\nu. \quad (20)$$

Einstein observed: 'Monochromatic radiation of low density (within the region of validity of Wien's law) behaves with respect to thermal phenomena as if it consisted of independent energy quanta of magnitude $(R/N)\,\beta\nu$.'

These light quanta were named 'photons' by Lewis[4].

In support of his light quanta, Einstein[2] mentioned three experimental facts:

(a) Stoke's rule in photoluminescence: The incident radiation of frequency ν_1 can excite either a radiation of lower or equal frequency ν_2 in a luminescent material, i.e. higher energy radiation can excite either a radiation of the same or of lower energy.

$$(R/N)\,\beta\nu_1 > (R/N)\,\beta\nu_2$$
$$\nu_1 > \nu_2. \quad (21)$$

(b) The photoelectric effect: Lenard[5] made two main observations in photoelectric emission of electrons from a light metal irradiated by light. The kinetic energy of the ejected electrons is proportional to the frequency of light used (not to the intensity as expected from the wave theory) and there is no time delay in the photo emission.

Einstein wrote, '... The simplest way to imagine this is that a light quantum delivers its entire energy to a single electron; we shall assume that this is what happens ...'

Further details are too well known to be given here.

(c) Ionization of gases by ultraviolet light: A gas molecule is ionized by ultraviolet light only if the energy of the light quantum is greater than the work of ionization J per gram equivalent,

$$R\beta,\ \nu \geq J. \quad (22)$$

The largest effective wavelength is (ref. 5) 1.9×10^{-5} cm for air, thus

$$R\beta,\ \nu = 6.4 \times 10^{12} \text{ erg} \geq J.$$

The upper limit for J was found by Stark[6] to be 9.6×10^{12} erg.

The Salzburg lecture of 1909

On 21 September 1909 Einstein delivered an invited lecture before the Conference of German Natural Scientists and Physicians held in Salzburg. This session was presided over by Max Planck. Einstein summarized his work on relativity and on the radiation problem. The lecture was reproduced verbatum in *Physikalische Zeitscrift*[8]. There are two main features of this lecture with regard to the radiation problem. First a number of facts in support of the light quantum hypothesis were pointed out and then came something astoundingly new—the dual nature of light. When entropy fluctuations were applied to the black body radiation it turned out that Planck's formula itself is a representative of the dual character of light! The derivation was followed by a new thought experiment on the pressure fluctuation of radiation leading again to the dual character of radiation. This made the lecture memorable[7] for Max von Laue and Leise Meitner. However, Planck failed to agree with Einstein! We give below these two features of the lecture that touched upon the constitution of radiation.

Facts supporting the light quantum hypothesis

(i) There are two features of special theory of relativity that support the corpuscular view of light: (a) The speed of light is constant in all the directions. The electromagnetic oscillations are no longer the states of a hypothetical medium, aether but are independent entities sent out from the light source with equal velocity in all the directions. (b) There is a mass energy equivalence. Thus when light is emitted by a source and absorbed by another body, there is a transfer of mass from the former to the latter.

(ii) In luminescence Stoke's rule requires that the frequency of excitation is greater than or equal to that of the emitted light.

(iii) The occurrence or non-occurrence of a photochemical reaction depends on the frequency of the light used. Shorter wavelengths are more effective in producing the reaction.

(iv) The photoelectric emission of electrons suggests that the energy of light is proportional to the frequency rather than intensity.

(v) Higher the temperature of the light-emitting source, higher are the molecular energies and greater is the component of short wavelength in the spectrum of the emitted radiation.

(vi) According to wave theory a point source emits spherical waves in all the directions with equal intensity. Inverse of this process is absorption by a point dipole and a convergent spherical wave front requires a large number of sources even for its approximate realization. The emission is an elementary process but absorption is not. A corpuscule is better in this respect—emission and absorption are symmetrical with respect to each other.

(vii) If moving electrons (primary cathode rays) strike a metal plate P X-rays are emitted. When these are incident on a second metal plate P' again electrons (secondary cathode rays) are ejected out. The speeds of the primary and secondary particles are of the same order of magnitude. If either the intensity of the primary cathode rays or the dimensions of P are reduced such that the collision of an electron with the plate can be looked upon as an isolated process, the second plate P' either shows no emission of secondaries or ejects out electrons with the same velocity as the primaries. It is hard to see how X-rays can be regarded as expanding spherical waves.

(viii) The energies of Planck's oscillators are in multiples of $h\nu$. The emission or absorption of radiation can occur only in such quanta. The light quantum hypothesis can account for such processes.

(ix) The experimentally determined value of the electronic charge is in agreement with the theoretical value of Planck calculated on the basis of quantum theory.

The dual nature of radiation

Einstein[9] had earlier published his ideas on the dual nature of radiation and these were repeated in his 1909 lecture. First he considered the entropy fluctuations of black body radiation. The cavity considered is divided into two volumes, a large one V and another small space v; the two are interconnected. The boundaries of both these spaces are walls that diffusely reflect radiation. The radiation in these spaces has frequencies lying in the interval $d\nu$. The instantaneous energies of V and v are respectively H and η, while the equilibrium values are H_0 and η_0, then $H_0 : \eta_0 = V : v$. At a given instant of time η deviates from η_0 in accordance with the statistical law between entropy S and probability W:

$$dW = \text{const.} \exp[(N/R)S]\, d\eta. \quad (23)$$

Let Σ and σ be the entropies of radiation present in the volumes V and v respectively and S the total entropy. Putting $\eta = \eta_0 + \varepsilon$ gives $d\eta = d\varepsilon$. The suffix 0 will be used for equilibrium values. Thus we have the expansion

$$S = \Sigma + \sigma = (\Sigma_0 + \sigma_0) + \left\{\frac{d(\Sigma+\sigma)}{d\varepsilon}\right\}_0 \varepsilon + \frac{1}{2}\left\{\frac{d^2(\Sigma+\sigma)}{d\varepsilon^2}\right\}_0 \varepsilon^2 + \ldots \quad (24)$$

and since $\{d(\Sigma+\sigma)/d\varepsilon\}_0 = 0$ the above expression reduces to

$$S = \text{const.} + \frac{1}{2}\left\{\frac{d^2\sigma}{d\varepsilon^2}\right\}_0 \varepsilon^2 + \ldots \quad (25)$$

Equation (23) becomes (change in Σ is neglected)

$$dW = \text{const.} \exp\left[-\frac{1}{2}\left(\frac{N}{R}\right)\left(\frac{d^2\sigma}{d\varepsilon^2}\right)_0 \varepsilon^2\right]. \quad (23')$$

Here $(R/N) = k$ the Boltzmann constant. Equation (23′) represents a curve having the shape of an error curve having the width ε at half maximum given by

$$\bar{\varepsilon}^2 = 1/(N/R)\,\{d^2\sigma/d\varepsilon^2\}_0. \quad (26)$$

This is the average energy fluctuation. If the radiation formula is known one can evaluate out $d^2\sigma/d\varepsilon^2$. Einstein mentions that he made such a calculation for Planck's formula but gave no details. Planck's radiation formula

$$u_\nu\, d\nu = \frac{8\pi\nu^2}{c^3}\,\frac{h\nu}{\exp(h\nu/kT) - 1} \quad (27)$$

written in the present context is (with $\eta_0 = u_\nu \cdot v$)

$$\eta_0\, d\nu = \frac{8\pi\nu^2 v}{c^3}\,\frac{h\nu}{\exp(h\nu/kT) - 1} \quad (27')$$

Evaluating the value for $1/T$ one gets

$$\frac{1}{T} = \left(\frac{k}{h\nu}\right)\ln\left[\frac{8\pi\nu^2 v h\nu}{c^3\eta_0\, d\nu} + 1\right] \equiv \frac{\partial\sigma}{\partial\varepsilon}$$

(with $d\varepsilon = d\eta$ as mentioned earlier). Differentiation gives $\partial^2\sigma/\partial\varepsilon^2$ and finally

$$\bar{\varepsilon}^2 = \frac{1}{(1/k)(\partial^2\sigma/\partial\varepsilon^2)} = \left[\eta_0 h\nu + \frac{c^3\eta_0^2}{8\pi\nu^2 v\, d\nu}\right]. \quad (28)$$

This is Einstein's expression for the average energy fluctuation. The first term represents the quantum contribution while the second the wave term. Wien's law leads to the first while the Rayleigh–Jeans law gives the second. Thus the Planck's law contains in itself the dual nature of radiation revealed for the first time by Einstein.

Most of the reviewers (e.g. Klein[10]) do not describe this particular derivation of Einstein but arrive at equation (28) via an earlier derived Einstein formula

$$\bar{\varepsilon}^2 = kT^2\,(d\bar{\varepsilon}/dT), \quad (29)$$

which has an advantage of interpreting k as a measure of thermal stability.

Finally Einstein described his thought experiment evaluating the pressure fluctuation of radiation in a cavity. At thermal equilibrium to each ray with a given frequency, intensity and polarization there is a corresponding ray with the same frequency, intensity and polarization travelling in the opposite direction, so that there is no net flow of energy in any direction. This is called the principle of detailed balancing introduced originally by Max Planck. At any given point in the space of the cavity such an equilibrium exists and the resultant of the radiation pressure from all sides is zero. Einstein considered a cavity containing both radiation as well as some ideal gas, the two were in a state of thermal equilibrium. In such a cavity a mirror plate is suspended that can move freely along the direction of the surface normal. The random motion of the gas molecules set the mirror plate in an irregular motion which is opposed by the radiation incident from all sides. The mirror reflects only from front; this creates a pressure difference at the two faces of the moving plate mirror. The difference in the pressures gives rise to a net force proportional to the mirror velocity and is therefore called radiation friction. Had this been the only force present gradually all the energy of the gas molecules could be converted into the radiation energy. Since the gas and radiation are in thermal equilibrium, the frictional loss in energy of the mirror is compensated by the fluctuations in the radiation pressure.

Let the velocity of the mirror at time t be v and let P be the resistive force per unit velocity due to the radiation pressure. If during time τ the mirror acquires a momentum Δ due to the radiation fluctuations and loses momentum $Pv\tau$ due to radiation friction, the corresponding velocity loss is $Pv\tau/m$ where m is the mass of the mirror. At time $t+\tau$ the mirror velocity is $v-(P\tau v/m)+(\Delta/m)$, which on an average should equal $(\overline{v}^2)^{1/2}$,

$$\overline{\left\langle \left(v - \frac{P\tau v}{m} - \frac{\Delta}{m} \right)^2 \right\rangle} = \overline{v}^2. \qquad (30)$$

In this expression $v\Delta$ and $(P\tau v)^2$ are negligibly small and the expansion of the square gives

$$(\Delta^2/m^{2)} = (2P\tau/m)\,\overline{v}^2. \qquad (31)$$

Using

$$m\overline{v}^2/2 = \frac{1}{2}\,(R/N)\,T,\; R/N = k \qquad (32)$$

leads to

$$\Delta^2/\tau = 2P\,(R/N)T. \qquad (33)$$

To put in the value of P, Einstein assumed that the mirror reflects radiation lying in the frequency interval ν, $\nu+\mathrm{d}\nu$ and is transparent to all other frequencies. Electrodynamics then gives

$$P = \frac{3}{2c}\left[\rho - \frac{1}{3}\,\nu\,\frac{\mathrm{d}\rho}{\mathrm{d}\nu}\right]\mathrm{d}\nu\cdot f, \qquad (34)$$

where f is the surface area of the mirror and ρ the radiation density. Equation (33) then gets transformed into

$$\frac{\overline{\Delta}^2}{y} = \left(\frac{R}{N}\right)T\,\frac{3}{c}\left[\rho - \frac{\nu}{3}\,\frac{\mathrm{d}\rho}{\mathrm{d}\nu}\right]\mathrm{d}\nu\cdot f. \qquad (35)$$

If ρ is substituted from Planck's formula, we obtain

$$\frac{\overline{\Delta}^2}{y} = \frac{1}{c}\left[\rho h\nu + \frac{c^3}{8\pi}\,\frac{\rho^2}{\nu^2}\right]\mathrm{d}\nu\cdot f. \qquad (36)$$

which again represents two kinds of contributions as before—a quantum term and a wave term. The quantum term is not negligible. For $\lambda = 0.5\,\mu$ and $T = 1700$ the quantum term is 6.5×10^7 times larger than the wave term.

Einstein stressed that the wave and quantum nature of radiation resulting from Planck formula are in fact inseparable. Those were the days when physicists talked about *either* wave *or* particle but Einstein introduced a new terminology '*both* wave *as wells as* particle' in the language of physics.

At the end of the lecture the chairman Max Planck expressed his dissatisfaction on Einstein's views. The corpuscular nature of radiation lay completely outside the framework of Maxwell's equations and introducing an ideal gas in the cavity filled with radiation required a through investigation on the process of emission and absorption of radiation based on the quantum theory. Further neither mechanical nor the electrodynamical models of resonator admit discrete energy levels.

The step taken by Einstein was unnescessary according to Planck. However Stark and Rubens supported the quantum view proposed by Einstein. Not only α and β but also γ rays show scintillations, a fact that supports the corpuscular rather than the wave nature of radiation. Also the X-rays emitted by a tube kept at 10 m distance from an object are capable of showing interaction with a single electron in matter. This again shows the existence of particles rather than waves. Another objection raised by Planck was that if two light quanta are to interfere the path difference involved can be of the order of a few thousand wavelengths.

Einstein finally replied that he never looked upon light quanta as independent particles but only as singularities in a wave field. When a large number of light quanta are present they constitute a continuous vector wave field.

At the end of the lecture Stark, the supporter of the quantum hypothesis, went on discussing with different physicists the various aspects of this new idea but always used the terminology either wave or particle (instead of both wave as well as particle). As Hermann[7] puts it, like Hegel, Einstein could have remarked: 'Only one of my auditors understood me, and he misunderstood me.'

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