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Reappraising Einstein’s 1905 application of thermodynamics and statistics to radiation

F E Irons

School of Aerospace, Civil and Mechanical Engineering, University College, The University of New South Wales, Australian Defence Force Academy, Canberra, ACT 2600, Australia

E-mail: f.irons@adfa.edu.au

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Abstract

Einstein’s 1905 application of thermodynamics and statistics to radiation, which led to the hypothesis of the corpuscular light quantum, is rendered uncertain by a lack of information as to how radiation behaves when undergoing a statistical fluctuation of volume. The paper examines this issue and appraises the particular assumption made by Einstein. We find that Einstein assumed for radiation a type of behaviour normally reserved for a gas of particles, in which case a conclusion about radiation behaving thermodynamically as though it consisted of particles (of energy) is not surprising.

1. Introduction

In a paper which was published in 1905 [1] and which has been the subject of at least five English translations [2–6], Einstein advanced the hypothesis of the corpuscular light quantum, presented the argument (‘the line of thought and the facts’ [7]) which led him to that hypothesis (henceforth referred to as Einstein’s argument), and indicated how light quanta could account for a range of phenomena, notably the photoelectric effect.

Einstein’s argument has been well received. For example, the light quantum hypothesis has been described as ‘a necessary consequence of very fundamental assumptions: in no sense did he (Einstein) propose it in an *ad hoc* fashion to “explain” certain experiments’ [8]. Also, physics teachers have been encouraged [9] to take particular interest in the ‘demonstration from thermodynamic and statistical considerations that electromagnetic radiation might be conceived as consisting of finite numbers of discrete corpuscles of energy $h\nu$’. Since the corpuscular light quantum has now given way to the rather more subtle, modern photon [10], it is pertinent to enquire whether Einstein’s argument really does support the notion of a corpuscular light quantum and whether it deserves to be so well received.

Einstein’s argument (described in section 2) proceeds via the application of thermodynamics and statistics to radiation. It is rendered uncertain by a lack of information

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as to how radiation behaves when undergoing a statistical fluctuation of volume. The present paper examines this issue (section 3) and appraises the particular assumption made by Einstein (section 4). We find (in section 5) that Einstein assumed for radiation a type of behaviour normally reserved for a gas of particles, in which case a conclusion about radiation behaving thermodynamically as though it consisted of particles (of energy) is not surprising.

2. Einstein's argument

2.1. Linking the entropy spectrum to the energy spectrum

Readers interested in the background to Einstein's argument may wish to consult [11–21]. Reasonably detailed accounts of the argument may be found in [17–25]. The following summary suffices for our present needs.

Einstein considered radiation occupying a volume V, and assumed that 'the observable properties of this radiation are completely determined when the radiation density $\rho(\nu)$ is given for all frequencies' [26]. He commented that this was an arbitrary assumption and that 'we shall naturally keep this simplest assumption as long as experiment does not force us to abandon it [26]'. On the basis that 'radiations of different frequencies can be regarded as separable from each other without performing any work or transferring any heat [26]', the total entropy of the radiation, S, may then be represented as $S = V \int \phi(\rho, \nu)\, \mathrm{d}\nu$ where ϕ is a function of the radiation energy density ρ and of frequency ν.

Einstein suggested how cavity physics might be enlisted to reduce ϕ to a function of a single variable but did not pursue this approach. Rather, he looked to the equilibrium state, wherein

$$\frac{\partial \phi}{\partial \rho} = \frac{1}{T}. \tag{1}$$

Also, in the equilibrium state, ρ is equal to the blackbody function, indicating that ϕ can be determined by integration of equation (1) once we introduce the blackbody function for ρ. To this end Einstein employed, not Planck's formula, but Wien's formula (being Planck's formula in the regime $h\nu \gg kT$), namely

$$\rho = \alpha \nu^3 \exp(-\beta \nu / T), \tag{2}$$

where α and β are constants. Einstein looked to Wien's law as a source of new physics, having already (in his 1905 paper) derived Planck's law in the regime $h\nu \ll kT$ using classical physics. Upon substituting for T from equation (2) into (1) and integrating, we obtain

$$\phi = -\frac{\rho}{\beta \nu}\left(\ln \frac{\rho}{\alpha \nu^3} - 1\right), \tag{3}$$

where the constant of integration has been chosen (equal to zero) such that $\phi = 0$ when $\rho = 0$. Strictly speaking, the derivation of ϕ in equation (3) should have proceeded by employing *Planck's* formula to obtain an expression for T, by integrating equation (1), and by *then* going to the Wien limit. It is non-trivial (see appendix A) that such a procedure yields the same result as in equation (3).

Equation (3) provided Einstein with a relationship between ϕ and ρ, permitting ϕ to be determined once ρ is known, for radiation which is monochromatic (Einstein's term) and of low density (within the range of validity of Wien's radiation formula). 'Monochromatic radiation' means that any change to radiation of one frequency will occur independently of the presence or absence of radiation of other frequencies [27]. This should not be confused with a more modern usage of the term 'monochromatic radiation' to mean radiation of a single frequency [28].

Equation (3) is of a general nature and should not be seen as restricted to blackbody radiation. There is some confusion in the literature on this point, so it may prove helpful to cite (in appendix B) another example wherein the equilibrium state is called upon to contribute to the derivation of a more general result.

2.2. Entropy difference at constant energy

Following Einstein, we now introduce the energy

$$E(\nu) = V\rho(\nu)\,\mathrm{d}\nu \tag{4}$$

and entropy

$$S(\nu) = V\phi(\nu)\,\mathrm{d}\nu$$

of radiation in the frequency interval ν to $\nu + \mathrm{d}\nu$. Upon substituting equation (4) into (3), we obtain

$$S(\nu) = -\frac{E(\nu)}{\beta\nu}\left(\ln\frac{E(\nu)}{V\alpha\nu^3\,\mathrm{d}\nu} - 1\right).$$

This result has been described as 'the entropy S of that part of the blackbody radiation having frequencies in the interval ν to $\nu + \mathrm{d}\nu$' [29]. However, we would not wish to restrict it to just blackbody radiation.

Consider a state of the system identified by the subscript 0, wherein

$$S(\nu, V_0, E_0) = -\frac{E_0(\nu)}{\beta\nu}\left(\ln\frac{E_0(\nu)}{V_0\alpha\nu^3\,\mathrm{d}\nu} - 1\right), \tag{5}$$

and another state for which

$$S(\nu, V, E) = -\frac{E(\nu)}{\beta\nu}\left(\ln\frac{E(\nu)}{V\alpha\nu^3\,\mathrm{d}\nu} - 1\right). \tag{6}$$

Now assume that

$$E(\nu) = E_0(\nu), \tag{7}$$

i.e. that

$$V\rho(\nu) = V_0\rho_0(\nu), \tag{8}$$

in which case (from equations (5) and (6))

$$S(\nu, V, E) - S(\nu, V_0, E) = \frac{E(\nu)}{\beta\nu}\ln\frac{V}{V_0}. \tag{9}$$

This equation describes the difference in entropy between two states of the system, having the same energy but different volumes, at frequency ν.

There is nothing in the above derivation to associate equation (9) with the change in entropy experienced by monochromatic radiation when undergoing a statistical fluctuation of volume. This will come later, as an assumption.

2.3. Hypothesis of light quanta

Einstein was attracted by the similarity in form between equation (9) and equation (14) for an ideal gas (equation (14) is located in appendix C, which offers a brief account of the relevant physics for an ideal gas). The latter, he argued, describes the change in entropy experienced by an ideal gas when undergoing a statistical fluctuation in volume (see appendix C for details). Prompted by the similarity in form between equations (9) and (14), Einstein proceeded on the basis that equation (9) describes the change in entropy experienced by monochromatic radiation when undergoing a statistical fluctuation in volume (assumption A) and that equation (9) lends itself to a probabilistic interpretation similar to equation (14) (assumption B).

According to Einstein, if one writes equation (9) in the form

$$S(\nu, V, E) - S(\nu, V_0, E) = (R/N)\ln\left(\frac{V}{V_0}\right)^{(N/R)(E/\beta\nu)}$$

and compares this with the general formula for Boltzmann's principle (equation (15)), then one arrives at the following conclusion [30]: 'if monochromatic radiation of frequency ν and energy E is enclosed (by reflecting walls) in the volume V_0, the probability that at a randomly chosen instant the total radiation energy will be found in the portion V of the volume V_0 is $W = (V/V_0)^{(N/R)(E/\beta\nu)}$'.

From this, Einstein further concluded that: 'monochromatic radiation of low density (within the range of validity of Wien's radiation formula) behaves thermodynamically as if it consisted of mutually independent energy quanta of magnitude $R\beta\nu/N$' ($h\nu$ in modern notation) [31].

Issues related to assumption A will occupy our attention during the remainder of the paper. As regards assumption B, we might note the following. On the understanding that assumption A holds, Dorling has argued that Einstein's conclusion about light quanta follows deductively from equation (9) without the need for an analogy with gas behaviour [32]. Dorling's methodology is interesting but (in view of the present controversy surrounding assumption A) might be more profitably applied to equation (14), perhaps allowing a conclusion about an ideal gas as a gas of particles to follow deductively from equation (14).

3. Concerning a statistical fluctuation of volume

Equation (9) is pivotal to Einstein's conclusion about light quanta. It now behoves us to explore the assumption (assumption A) that this equation describes the change in entropy experienced by monochromatic radiation when undergoing a statistical fluctuation of volume. We first elaborate on what is meant by radiation undergoing a statistical fluctuation of volume and then reflect on how the frequency of monochromatic radiation varies during a change of volume.

Einstein embraced the notion that radiation, like a gas, could undergo a statistical fluctuation of volume. He referred to 'the probability that at a randomly chosen instant the entire radiation energy will be contained in the portion v of the volume v_0' [33]. Born refers to Einstein as having obtained 'the probability of finding the total energy E by chance compressed in a fraction αV of the total volume V' [34]. Just what is meant by a 'by chance' or accidental change of volume has been discussed in some detail by Stehle [35] and has been illustrated by McEvoy and Zarate [36]. Suffice to say that it refers to a statistical fluctuation, or to what Pauli describes as 'the rare state in which the entire radiation energy is contained in a certain partial volume' [37]. There is no suggestion that the volume of the enclosure itself is changing, though some accounts of the argument cloud the issue by including such an assumption [38–40].

How does the frequency of monochromatic radiation vary during an accidental change of volume? The answer is, we really do not know. Yet we need to know, if we are to calculate the change of entropy which accompanies such a change of volume. What we do know, however, is that (unlike a molecular gas which can thermalize through inter-particle collisions) radiation lacks an internal mechanism whereby different frequencies can exchange energy[1]. Whatever may be the particulate nature of radiation, it does not impact on the frequency spectrum. And if it does not impact on the frequency spectrum, is it likely to impact on the entropy spectrum, which (see equation (3)) is linked to the frequency spectrum? That is, do we really expect equation (3) to reveal information about a particulate nature for radiation?

Of associated interest is the case of radiation undergoing a reversible adiabatic change of volume. Here, the frequency of monochromatic radiation varies as a consequence of the Doppler shift associated with the moving wall of the enclosure [41] (or, in the case of the cosmic background radiation, as a consequence of the gravitational redshift [42]). If we let V_0 and V denote the initial and final volumes of the enclosure respectively, then the variation in frequency is from ν_0 to ν where [41]

$$\nu^3 V = \nu_0^3 V_0. \tag{10}$$

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[1] This property, of course, underpins the assumption of monochromatic radiation, i.e. the assumption that any change to radiation of one frequency will occur independently of the presence or absence of radiation of other frequencies.

In this case our interest is not in the difference $S(\nu, V, E) - S(\nu, V_0, E)$, but in the difference

$$S(\nu, V, E) - S(\nu_0, V_0, E_0) = -\frac{E(\nu)}{\beta\nu}\left(\ln\frac{E(\nu)}{V\alpha\nu^3\,\mathrm{d}\nu} - 1\right) + \frac{E_0(\nu_0)}{\beta\nu_0}\left(\ln\frac{E_0(\nu_0)}{V_0\alpha\nu_0^3\,\mathrm{d}\nu_0} - 1\right).$$

We do not imagine that the equality indicated by equation (7) could hold for a reversible adiabatic change of volume[2]. Rather, we have $E(\nu)/\nu = E_0/\nu_0$ (the adiabatic invariant), which, in conjunction with $\nu^2 V\,\mathrm{d}\nu = \nu_0^2 V_0\,\mathrm{d}\nu_0$ (from equation (10) [43]), leads to [44]

$$S(\nu, V, E) - S(\nu_0, V_0, E_0) = 0.$$

This is consistent with the well known result that total entropy (entropy integrated over frequency) remains constant during a reversible adiabatic change of volume.

4. Einstein's assumption

What assumption did Einstein make as to how monochromatic radiation behaves when accidentally changing volume? That is, what assumption did Einstein make when deriving equation (9) (which he assumed to describe monochromatic radiation when accidentally changing volume)? The answer is that he assumed *no variation in frequency*. Observe that the frequency ν in equation (5) (which describes the entropy before the change) is the same as the frequency ν in equation (6) (which is assumed to describe the entropy after the accidental change of volume).

During an accidental change of volume, no work is performed and (in an adiabatic enclosure[3]) no heat is transferred. If, additionally, there is no variation in frequency, then the radiation energy contained within some frequency interval ν to $\nu + \mathrm{d}\nu$ after the change will be the same as before the change, in which case equation (7) will hold for all frequencies, and thence (as assumed by Einstein) equation (9) will hold for all frequencies (at least, for all frequencies within the range of validity of Wien's radiation formula).

The assumption of no frequency variation during an accidental change of volume is equivalent to assuming that, in an accidental change of volume from V_0 to V, monochromatic radiation of each frequency simply becomes more dense ($V_0 > V$) by the geometric factor V_0/V. This is apparent from equation (7), or rather from equation (8) when expressed as

$$\rho(\nu) = (V_0/V)\rho_0(\nu).$$

5. Investing monochromatic radiation with particulate behaviour

I can think of no other instance where radiation is assumed to behave as described in the previous section (admittedly, an accidental change of volume is a unique situation). It is quite unlike the type of behaviour described in section 3 for a reversible adiabatic change of volume. One does, however, find a comparison in the world of gaseous particles. An ideal gas will, at the conclusion of an accidental change of volume, rethermalize with no change in temperature (cf a free expansion). The total energy carried by particles within a given (kinetic) energy interval will be the same after the change as before the change. The number density and energy density, within a given energy interval, will vary inversely with volume. It is the particulate nature of a gas which is the key to this type of behaviour. By proceeding on the basis that monochromatic radiation can behave as described in the previous section, we are, in effect, investing monochromatic radiation with a certain gaslike or particle property. We should not then be surprised if an analysis which incorporates such an assumption concludes that monochromatic radiation behaves thermodynamically as if it consists of particles (of energy).

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[2] During a reversible adiabatic change of volume, energy is incremented by the performance of work associated with the moving wall.

[3] Einstein refers to the walls of the enclosure as 'reflecting' [45], presumably meaning completely reflecting.

On what basis might one have supposed (at the turn of the 20th century) that radiation could behave like a gas? Boltzmann (in 1884) had derived Stefan's empirical radiation law by applying the laws of thermodynamics to radiation, 'treating it as a gas whose pressure was the radiation pressure of Maxwell's electromagnetic theory' [46]. Wien (in 1894) had drawn on Boltzmann's work when deriving his displacement law for the blackbody spectrum. Einstein (in 1917) would write 'The formal similarity of the curve of the chromatic distribution of black-body radiation and the Maxwell velocity-distribution is too striking to be hidden for long' [47]. Indeed (as noted by Einstein [47]), Wien was led by this similarity to the formula in equation (2), which he published in 1896 [48]. He (Wien) assumed gaseous molecules to be the source of the radiation and associated radiation of a particular frequency with molecules of a particular velocity. Such an association may be superficial (in hindsight), but it is interesting as a precursor to the similarity noted in the previous paragraph between the behaviour of radiation (as assumed by Einstein) and of a gas of particles.

6. Conclusion

Physics teachers will conceivably take an interest in Einstein's argument, but it may not be for the reason cited in the second paragraph of section 1. Einstein's argument is rendered uncertain by a lack of information as to how monochromatic radiation varies in frequency when undergoing an accidental change of volume. According to the present analysis, what Einstein's argument shows is that, if one chooses to invest monochromatic radiation with a type of behaviour normally reserved for a gas of particles, then it is possible to reach the conclusion that radiation behaves thermodynamically as if it consists of particles (of energy).

Appendix A. Deriving equation (3)

If, instead of Wien's law in equation (2), we introduce Planck's law

$$\rho = \alpha\nu^3[\exp(\beta\nu/T) - 1]^{-1}, \tag{11}$$

we then have

$$\frac{1}{T} = \frac{1}{\beta\nu}\ln\left(\frac{\alpha\nu^3}{\rho} + 1\right).$$

Integration of equation (1) using the above expression for T^{-1} yields

$$\phi = \frac{1}{\beta\nu}[(\alpha\nu^3 + \rho)\ln(\alpha\nu^3 + \rho) - \rho\ln\rho] - \frac{\alpha\nu^3\ln\alpha\nu^3}{\beta\nu}, \tag{12}$$

where the constant of integration has been chosen (equal to $-\alpha\nu^3\ln\alpha\nu^3/\beta\nu$) such that $\phi = 0$ when $\rho = 0$.

In the Wien limit ($\beta\nu/T \gg 1$) we have $\rho/\alpha\nu^3 \ll 1$ (this follows from equation (11)) and thence $\ln(1 + \rho/\alpha\nu^3) = \rho/\alpha\nu^3$, in which case equation (12) reduces to

$$\phi = -\frac{\rho}{\beta\nu}\left(\ln\frac{\rho}{\alpha\nu^3} - 1\right),$$

which is the same as equation (3). In the Rayleigh–Jeans limit ($\beta\nu/T \ll 1$) we have $\rho/\alpha\nu^3 \gg 1$ and thence $\ln(1 + \alpha\nu^3/\rho) = \alpha\nu^3/\rho$, in which case equation (12) reduces to

$$\phi = \frac{\alpha\nu^2}{\beta}\left(\ln\frac{\rho}{\alpha\nu^3} + 1\right).$$

Appendix B. An example

Pursuant to the last paragraph of section 2.1, we offer the following example of how the equilibrium state can be called upon to contribute to the derivation of a more general result.

Consider that, towards the centre of a homogeneous gaseous medium, the energy density within an optically thick spectral line is related to the population density of the lower state (N_m) and of the upper state (N_n) by [49]

$$\rho(\nu) = \left(\frac{4\pi}{c}\right)\frac{A_{nm}N_n}{B_{mn}N_m - B_{nm}N_n}, \tag{13}$$

where A_{nm}, B_{nm} and B_{mn} denote the Einstein coefficients for spontaneous emission, induced emission and induced absorption, respectively, and where (for simplicity) we have assumed non-degeneracy. Quantum mechanics could be enlisted to obtain expressions for the above coefficients and thence a final expression for $\rho(\nu)$. Alternatively, one can call upon the equilibrium state, wherein (Boltzmann's law)

$$N_n/N_m = \exp(-h\nu/kT)$$

and (Planck's law)

$$\rho(\nu) = \left(\frac{8\pi h\nu^3}{c^3}\right)\frac{1}{\exp(h\nu/kT) - 1}.$$

Substitution of the above two equations into (13) leads readily to the relationships $A_{nm}/B_{nm} = 2h\nu^3/c^2$ and $B_{nm} = B_{mn}$. With these relationships, equation (13) may finally be written

$$\rho(\nu) = \left(\frac{8\pi h\nu^3}{c^3}\right)\frac{N_n}{N_m - N_n}.$$

The above equation is of a general nature and is not restricted to only that case where Boltzmann's law and Planck's law prevail.

Appendix C. Entropy change experienced by an ideal gas when changing volume

An ideal gas undergoing an irreversible, adiabatic change of volume (think of a free expansion) will pass through non-thermal states but (as a consequence of inter-particle collisions) will rethermalize at the conclusion of the change, with no loss of energy and no change in temperature. Thermodynamics, when applied to an ideal gas (equation of state $pV = R(n/N)T$), indicates that the associated change of entropy is [50]

$$\Delta S = R(n/N)\ln(V_\mathrm{f}/V_\mathrm{i}). \tag{14}$$

Here V_i and V_f denote the initial and final volumes respectively, n denotes the number of particles or molecules, and N denotes the number of molecules per gram molecule.

Einstein considered a change of volume which was brought about by chance (a statistical fluctuation) and he cited probability theory as a way of deriving the corresponding entropy change. The probability that a particle should accidentally, or by chance, find itself within a subvolume V_f of V_i is $V_\mathrm{f}/V_\mathrm{i}$. The probability that all n particles of a gas moving independently of one another should accidentally find themselves within the subvolume V_f, with no other change to the system, is $W = (V_\mathrm{f}/V_\mathrm{i})^n$; and the corresponding change in entropy is (Boltzmann's principle)

$$\begin{aligned}\Delta S &= (R/N)\ln W \\ &= R(n/N)\ln(V_\mathrm{f}/V_\mathrm{i}),\end{aligned} \tag{15}$$

which is the same as equation (14).

In contrast to the foregoing we have the comment of Pippard [51], that statistical fluctuations in volume are part of the nature of thermal equilibrium and ‘if we ascribe a definite value to the entropy of the gas in equilibrium we must ascribe it not to any particular, most probable set of configurations, but to the totality of configurations of which it is capable. Thus we see that the entropy . . . must be recognised as a property of the system and of its constraints, and that once these are fixed the entropy also is fixed’.

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