Gap in Einstein's Early Argument for the Existence of Photons

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This year is the centennial of Einstein's epochal papers from his miraculous year, which prompted me to read again his paper on the quantum nature of radiation [1]. Surprisingly, I found a gap in his earliest argument for the existence of photons which apparently has remained unnoticed up to the present time. Einstein's argument was based on his proof that for sufficiently large frequencies the entropy of thermal relation varies logarithmically with the volume, in the same manner as an ideal gas. He 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 quanta [photons] of magnitude $h\nu$ " [1], where ν is the frequency of the radiation, and h corresponds to Planck's constant. In a footnote Einstein also gave a derivation, based on his entropy-volume relation, for the familiar formula for the pressure of an ideal gas. But substituting in this formula Einstein's relation for the number of photons, i.e. the energy of the monochromatic thermal radiation divided by $h\nu$, results in an *incorrect* expression for the pressure, This pressure should be one third of the energy density of the radiation, as was originally shown by Maxwell for the case of electromagnetic waves. Moreover, a kinetic theory calculation of the pressure shows that this relation is also valid for photons. Maxwell's relation also played a fundamental role in Boltzmann's derivation of the dependence of thermal radiation on the fourth power of the temperature, and in Wien's derivation of the general dependence of the thermal energy density on both frequency and temperature. I have not found any evidence, however, that Einstein's contemporaries noticed the problem with calculating the pressure

of monochromatic thermal radiation from Einstein's entropy-volume relation, nor has this problem been pointed out in commentaries about this paper [2], [3].

What is the solution to this pressure paradox? Einstein considered the volume dependence of the radiation entropy for fixed frequency ν, but in an actual thermodynamic process, where the volume V is changed by moving a piston, the frequency does not remain fixed, because the wavelength is proportional to the linear dimensions of the cavity. Hence, the frequency ν varies as $V^{-1/3}$, giving an additional volume dependence to the entropy, which was not discussed by Einstein. It can be readily verified that this addition leads to a thermodynamic derivation of Maxwell's relation for the pressure of isotropic radiation, filling in a long standing gap in Einstein's earliest thermodynamic argument for the existence of photons.

References

[1] A. Einstein *On a Heuristic Point of View Concerning the Production and Transformation of Light*
Annalen der Physik **17** (1905) 132. Reproduced in "The Collected Papers of Albert Einstein" vol. 2 edited by John Stachel (Princeton Univ. Press 1989) pp. 150-166.

[2] M. Klein, *Einstein's First Paper on Quanta*
The Natural Philospher 2 (1963) 59-86.

[3] *Einstein's Miraculous Year, Five papers that Changed the Face of Physics* edited and introduced by John Stachel
(Princeton University Press, 1998) pp. 177-198.