Comment on "Hot gases: The transition from the line spectra to thermal radiation," by M. Vollmer [Am. J. Phys. 73 (3), 215–223 (2005)]

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I call attention to several errors in a recent article by Vollmer[1] that invalidate his explanation for how the line spectrum of atoms is transformed into the continuous spectrum of thermal radiation. Following Einstein's 1916 derivation[2] of Planck's black-body formula, the transformation of this line spectrum to thermal radiation at discrete frequencies associated with these transitions has been discussed often, particularly in the astronomy literature.[3] But the question of how discrete atomic transitions can give rise to black-body radiation that is continuous in frequency has been ignored. To fill this gap, I present here a novel derivation of this transformation in a model of a hot gas of atoms with only two energy levels.

Vollmer's arguments are based on Einstein's original model of stationary atoms,[2] but with only two energy levels corresponding to an excited state and a ground state, which are in thermal equilibrium with the emitted and absorbed photons.[5] Such a model cannot give rise to a thermal spectrum which is continuous for a finite range of frequencies because, apart from a line width due to the finite lifetime of the excited state, the photons are essentially monochromatic with a frequency ν_0. This frequency is determined by the well-known Bohr-Einstein relation $h\nu_0=\epsilon$, where ϵ is the energy difference between the two atomic levels and h is Planck's constant. Vollmer ignored this fundamental relation in his derivation of the Planck black-body formula, and misapplied Einstein's detailed balance condition. Instead of setting $N_2/N_1=\exp(-h\nu_0/kT)$ for the ratio of the population of the excited and ground state atomic levels at a temperature T, he incorrectly set $N_2/N_1=\exp(-h\nu/kT)$ for arbitrary values of $\nu\neq\nu_0$ [see Eqs. (11), (15), and (16) in Ref. 1]. Then, he attributed the source of the continuous thermal spectrum to the finite width of the excited level[6] but, as I will show, this attribution is not correct.

Vollmer also argued that the Doppler width in the frequency of photons emitted by the randomly moving atoms in a hot gas can be neglected in the calculation of the thermal spectrum.[7] I will show, however, that in a simplified model of two level atoms, it is precisely the Doppler shift that gives rise, for an optically thick gas of such atoms, to a thermal spectrum which is continuous over a range of frequencies.

The necessary and sufficient conditions for the energy distribution of thermal radiation to be a continuous function of frequency in any given frequency range is the occurrence of radiative processes in thermal equilibrium that emit and absorb photons in this frequency range. It is counter intuitive that the energy density of photons that are emitted and absorbed by various radiative process, which may also differ greatly in intensity and in the rate of transitions, should lead at thermal equilibrium to a universal energy density distribution. But this universality, which was first formulated in 1859 by Kirchhoff on general thermodynamic grounds, is the essence of Einstein's detailed balance derivation of the black-body distribution first obtained in 1900 by Planck.

We illustrate how this universality comes about by considering a hot gas of two level atoms in thermal equilibrium. When an atom in the excited state moving with velocity $\vec{v}_e$ emits a photon with frequency ν, then by conservation of momentum, the velocity in the ground state is changed to

$$\vec{v}_g=\vec{v}_e-\frac{h\nu}{mc}\vec{n}, \tag{1}$$

where m is the mass of the atom, c is the speed of light, and $\vec{n}$ is a unit vector along the direction of the emitted photon. Correspondingly, by conservation of energy

$$h\nu=\epsilon+\frac{1}{2}m(v_e^2-v_g^2). \tag{2}$$

We substitute for v_g^2 in Eq. (2) the result obtained from Eq. (1) and obtain for $v/c\ll 1$

$$\nu=\nu_0\left(1+\frac{v_n}{c}\right), \tag{3}$$

where $\nu_0=\epsilon/h$, and v_n is the component of $\vec{v}_e$ along $\vec{n}$. Equation (3) is the nonrelativistic Doppler change in frequency of a photon emitted by a moving atom,[8] which is obtained by neglecting a small term of order ϵ/mc^2 due to the small loss in photon energy given to the atom as recoil kinetic energy. Hence, the Maxwell–Boltzmann distribution for the excited atoms with velocity component v_n yields a Gaussian probability distribution for the emission of photons with frequency ν centered at $\nu=\nu_0$,

$$P(\nu)=\frac{1}{\sqrt{2\pi}\Delta}e^{-(\nu-\nu_0)^2/2\Delta^2}, \tag{4}$$

where $\Delta=\nu_0\sqrt{kT/mc^2}$ is the Doppler width of the radiation.

If photons of a given frequency ν are in thermal equilibrium with the atoms, the absorption of these photons by atoms in the ground state must be taken into account. Following Einstein's derivation,[2] the radiation energy density ρ is determined by the detailed balance condition between the emission and absorption of photons,

$$(A+B\rho)N_e = B\rho N_g, \tag{5}$$

where A is the Einstein coefficient for spontaneous emission, B is the corresponding coefficient for stimulated emission and absorption of photons, and $A/B=8\pi h\nu^3/c^3$. Here N_g and N_g are the populations of atoms in the ground and excited states respectively, given by the canonical density distribution

$$N_e = C\exp\left(-\left(\epsilon+\tfrac{1}{2}mv_e^2\right)/kT\right) \tag{6}$$

and

$$N_g = C\exp\left(-\tfrac{1}{2}mv_g^2/kT\right), \tag{7}$$

where C is a normalization constant. The range of random atomic velocities is determined by the momentum and energy conservation given in Eqs. (1) and (2) for a given frequency ν of the photon. We solve Eq. (5) for the energy density ρ and obtain

$$\rho = \frac{8\pi h\nu^3}{c^3}\frac{1}{(N_g/N_e-1)}, \tag{8}$$

where by Eqs. (6) and (7) we have

$$\frac{N_g}{N_e} = \exp\left(\left(\epsilon+\tfrac{1}{2}m(v_e^2-v_g^2)\right)/kT\right). \tag{9}$$

If we apply the conservation of energy relation, Eq. (2), and substitute the resulting expression into Eq. (8), we obtain the Planck black-body distribution for the radiation energy density

$$\rho = \frac{8\pi}{c^3}\frac{\nu^3}{(\exp(h\nu/kT)-1)}, \tag{10}$$

for a continuous range of frequencies ν.[4]

This frequency range is restricted by the conservation of momentum and energy in the emission and absorption of photons by the atoms, Eqs. (1) and (2). We have shown that photons of frequency $\nu \neq \nu_0$ are emitted by excited atoms moving with a component of velocity $v_n = c(\nu/\nu_0 - 1)$ along the direction of the propagation of this photon. But according to the Maxwell-Boltzmann distribution, the number of such atoms decreases exponentially as a function of $(\nu-\nu_0)^2/2\Delta^2$, where $\Delta=\nu_0\sqrt{kT/mc^2}$ [see Eq. (4)]. Because the mean free path $\ell(\nu)$ for absorption of photons with frequency ν is inversely proportional to the density of these atoms, the photons for an optically thick gas cloud with linear dimension D are no longer in thermal equilibrium when $\ell(\nu)$ is larger than D. According to Eq. (4), this occurs when

$$|(\nu-\nu_0)| > \Delta\sqrt{\ln(D/\ell(\nu_0))}, \tag{11}$$

which gives the range of frequencies for which continuous thermal radiation occurs in this idealized model of a hot gas cloud.

The model of stationary atoms discussed originally by Einstein[2,5] and treated by Vollmer,[1] corresponds to $m\to\infty$ for which $\Delta\to 0$; in this limit the thermal radiation is essentially monochromatic with frequency $\nu=\nu_0$.

For an optically thin gas, $D < l(\nu_0)$, the probability for the absorption of photons can be neglected, and the Maxwell–Boltzmann distribution for the random velocities of excited atoms gives rise to the Doppler broadening of the line width. If we include the Lorentzian line shape factor for the natural line width of the radiation,

$$\frac{\gamma/\pi}{(\nu-\nu')^2+(\gamma)^2}, \tag{12}$$

where γ is half the line width at half maximum, the final line shape is given by the Voigt form factor[9]

$$F(\nu) = \int d\nu' \frac{\gamma/\pi}{[(\nu-\nu')^2+\gamma^2]}\frac{1}{\sqrt{2\pi}\Delta}e^{-(\nu'-\nu_0)^2/2\Delta^2}. \tag{13}$$

This result differs from the corresponding limit in Eq. (17) of Ref. 1, where the important effect of the Doppler shift has been neglected.

Thermal photons due to additional atomic transitions with different energy level separations, different masses, and different total number of atoms lead to the same universal Planck black-body radiation energy distribution, even if the range of photon frequency for the separate processes overlap. Moreover, due to the finite lifetime of the excited levels of atoms, the energy conservation relation Eq. (2) is not strictly maintained, and photons can also be emitted and absorbed with frequencies confined by the Lorentzian line shape, Eq. (12), in the rest frame of the atoms. These photons also contribute to the thermal spectrum ρ without modifying it.

The universality and continuity in the frequency of thermal radiation is due to the fact that induced emission and absorption of photons in radiative processes is independent of the nature of its sources, provided that these sources emit photons in the frequency range under consideration. However, a derivation of the thermal spectrum by Einstein's detailed balance method requires processes that conserve energy and momentum. Photons in the wings of the Lorentz line width are due to the finite lifetime of the excited state, which implies an uncertainty of the energy of this state. Therefore, although these photons contribute to the thermal spectrum, the transitions associated with these photons cannot be included in the detailed balance equation as has been proposed in Ref. 1. Our treatment answers the question of the nature of the radiation spectrum in an ideal model of a hot gas consisting of atoms with only two levels for which the only source of photons is the transition between the excited and the ground state of the atom.

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[1] M. Vollmer, "Hot gases: The transition from line spectra to thermal radiation," Am. J. Phys. **73**, 215–223 (2005).

[2] A. Einstein, "Zur Quantum Theorie der Strahlung," Phys. Z. **18**, 121–128 (1917). First printed in Mitteilungender Physikalischen Gesellschaft Zurich. No. 18, 1916. Translated into English in Van der Waerden, *Sources of Quantum Mechanics* (North-Holland, Amsterdam, 1967), pp. 63–77.

[3] The first treatment of this transformation in a thermal gas of two level atoms was given by E. A. Milne, "Thermodynamics of the stars," Handbuch der Astrophysik **3**, Part 1, 159–164 (1930). This article is reprinted in *Selected Papers on the Transfer of Radiation*, edited by D. H. Menzel (Dover, New York, 1966), pp. 173–178. Milne's derivation has been reproduced, almost unchanged, in several astrophysics textbooks that discuss radiative transfer. See, for example, S. Chandrasekhar, *An Introduction to the Study of Stellar Structure* (Dover, New York, 1958), pp. 205–207; D. Mihalas, *Stellar Atmospheres* (Freeman, San Francisco, 1978), pp. 336–339; A. Peraiah, *An Introduction to Radiative Transfer* (Cambridge University Press, Cambridge, 2002), pp. 15–16. In all these treatments the effect of the Doppler shift on the radiation frequency due to the random motions of the atoms in a hot gas has been included only for its effect on the line width, although as we show here, it is this shift that can also give rise to thermal radiation continuous in the frequency of the radiation.

[4] In our derivation of Planck's black-body formula we required both conservation of energy and momentum in the emission and absorption of photons. In his original derivation Einstein applied only the conservation of energy, "for we have only formulated our hypothesis on emission and absorption of radiation for the case of stationary molecules." Subsequently, he showed by a very elaborate calculation of the momentum transfer of radiation to the atoms that the mean thermal energy of the atoms satisfies the equipartition theorem, assuming that the elementary process transmits an amount of momentum $h\nu/c$. He concluded that if a radiation bundle has the effect that a molecule struck by it absorbs or emits a quantity of energy $h\nu$ in the radiation, then a momentum $h\nu/c$ is always transferred to the molecule (Ref. 2). Our derivation demonstrates the relevance of this momentum transfer to the formation of a thermal spectrum in hot gases.

[5] M. Nauenberg, "The evolution of radiation towards thermal equilibrium: A soluble model which illustrates the foundations of statistical mechanics," Am. J. Phys. **72**, 313–323 (2004). In this paper I assumed that the atoms are fixed, but the extension to randomly moving atoms in a thermal gas is straightforward along the lines indicated here.

[6] After obtaining Eq. (11), Vollmer writes: "Note we assumed discrete energy levels and transitions between them. But suddenly the result, Eq. (11), is interpreted as a continuous spectrum. Where do all the possible transitions arise? The answer is simple: each atom or molecule possesses at least one resonance frequency for absorption. An absorption line extends over the entire spectrum because it has a finite width, that is, each atom or molecule can absorb radiation at every wavelength, although with different cross sections…," Ref. 1, p. 218.

[7] Vollmer writes: "The justification for the assumption that the Doppler width or collisional width is not important [to explain the formation of the continuous spectrum] comes from a numerical estimate of the Doppler width and the effects of pressure broadening, " Ref. 1, p. 216.

[8] E. Fermi, "Quantum theory of radiation," Rev. Mod. Phys. **4**, 87–132 (1932).

[9] R. Loudon, *The Quantum Theory of Light* (Oxford University Press, New York, 2000), p. 67.

Reply to "Comment on 'Hot gases: The transition from line spectra to thermal radiation,'" by M. Vollmer [Am. J. Phys. 73 (3), 215–223 (2005)]

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Nauenberg[1] has pointed out some problems with my article.[2] Although I agree with parts of his criticism, I cannot follow all of his arguments.

I agree that my approach of using a simple two-level system was oversimplified and that a proper application of Einstein's derivation is not possible if only a two-level system with well-defined energies is assumed. However, I do not agree with Nauenberg[1] that my explanation of how a line spectrum is transformed to the continuous spectrum of thermal radiation is invalidated.

My intent was to provide a simple radiation transfer model to explain how line spectra are transformed into continuous spectra of blackbody radiation. To follow the apparently simplest approach, I used a pure two-level system with the simplest line shape, a Lorentzian, usually related to the natural line width of the transition between two energy levels. I agree that this choice led to an oversimplification of the theory with an incorrect use of Einstein's argument of thermal equilibrium and detailed balance.

Although this oversimplification led to an error in my simple model, all my other arguments would hold if a correct system instead of a simple two-level system is chosen. For example, any extension to more than two energy levels will allow the use of Einstein's argument of detailed balance (detailed balance in a three-level system was discussed, for example, by Lewis[3]). Similarly, any mechanism that can lead to thermal equilibrium such as collisions, leading to the Doppler width as mentioned by Nauenberg[1] will do.

The main thrust of my paper, how continuous blackbody radiation is formed from a line spectrum for a system of atoms in thermal equilibrium is beyond the specific use of a certain energy level system and is hence not invalidated as stated by Nauenberg.[1] The reasoning of my paper just needs a line shape factor for absorption and emission processes in the simple radiation transfer model [Ref. 2, Eq. (14)]. The argument then uses the concept of optical depth to explain how the line shape of the radiation changes as a function of optical thickness of the gas. It also illustrates a simple way of estimating emissivities of gases and explaining the broadening of spectral lines in gases due to self-absorption.

From the spectroscopy of gases, there are three well-known and prominent examples of line shapes, the Lorentz profile of the natural line width, the pure Gaussian profile (approximating the Doppler profile), and the Voigt profile, which could correctly describe the Doppler broadened profile. I chose the Lorentzian (and incorrectly related it to a two-level system) because it is a good approximation to the Voigt profile in the far wings. If we used a more complex system such as a three-level system in thermal equilibrium, a Lorentzian would still be a reasonable choice.

We should keep the following arguments in mind. For a very precise model, the Doppler shift must be included.

However, my intent was not to state that the Doppler shift can be neglected. Instead I argued that the Doppler width is not important (in the context of my simple model) because it is small compared to the width of a thermal spectrum. I agree that a Voigt profile should be used when being very precise. Nauenberg correctly states that his result with the Voigt profile differs from my result with the Lorentzian. However, I stated (Ref. 2, p. 216) that the line shape of a Voigt profile is close to a Gaussian near the center and close to a Lorentzian in the far wings, which are both reasonable approximations.

I want to mention some other ideas that resulted from some discussions with a colleague. When considering far wing phenomena of atoms with two energy levels, the relevant processes could be referred to as Rayleigh scattering (lower frequencies) and Thomson scattering (higher frequencies). Does the argument of detailed balance hold for such scattering processes?

In the simplest description, Rayleigh and Thomson (and also Raman) scattering can be thought of as being due to a three-level system process (see Ref. 3) with the transition from the ground state to an intermediate virtual state and then the transition from the intermediate state to the final state. If the ground state and the final state refer to my assumed two-level system, the whole process, which would be due to a three-level process with a virtual level, would allow one to use detailed balance arguments and correctly extending the simple approach of my paper.[2]

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I thank M. Nauenberg for pointing out the problem and presenting a solution for the ideal case of two-level atoms, which cannot be properly treated by my simple model. In this respect his comment provides a very useful complement to my paper.

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[1]M. Nauenberg, Am. J. Phys. **75**, 947–949 (2007).
[2]M. Vollmer, "Hot gases: The transition from line spectra to thermal radiation," Am. J. Phys. **73**, 215–223 (2005).
[3]H. R. Lewis, "Einstein's derivation of Planck's radiation law," Am. J. Phys. **41**, 38–44 (1973).