The Stefan-Boltzmann Equation

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Conventional derivations of the Stefan-Boltzmann equation are based on the Plank expression for the radiative energy density *in vacuo* with temperature a variable determined by an external agency. The equation predicts a material property, black-body radiation, independent of physical properties specific to the material. The intent of this note is to offer an alternative derivation based on the Einstein *A* and *B* coefficients which are material specific and lead to the Stefan-Boltzmann result only in the limit of material thicknesses much larger than radiation absorption depths.

The Einstein *A* and *B* coefficients describe, respectively, rates for spontaneous and field-induced transitions between an energy level, *n*, and a higher level, *m*:

$$dN_{n\to m}/dt \;=\; N_n B_{n\to m}\,\rho(\nu_{nm}) \qquad (1)$$

$$dN_{m\to n}/dt \;=\; N_m\{A_{m\to n} \;+\; B_{m\to n}\,\rho(\nu_{nm})\}$$

The former process leads only to emission from thermal excitations while the latter corresponds to absorption and stimulated emission by electromagnetic fields.[1]

The Planck energy density over a frequency interval, $\delta\nu$, for a system at thermal equilibrium is

$$\rho(\nu) \;=\; \frac{8\pi h\nu^3}{c^3}\,\frac{1}{e^{h\nu/kT}-1} \qquad (2)$$

Detailed balance of *Eqs. 1* requires,

$$\frac{N_n}{N_m} \;=\; \frac{A_{m\to n} \;+\; B_{m\to n}\,\rho(\nu_{nm})}{B_{n\to m}\,\rho(\nu_{nm})} \;=\; e^{h\nu_{nm}/kT} \qquad (3)$$

or

$$\rho(\nu_{nm}) \;=\; \frac{A_{m\to n}}{B_{n\to m}\,e^{h\nu_{nm}/kT}-B_{m\to n}} \qquad (4)$$

Comparison of *Eqs. 2* and *4* then shows

$$A_{m\to n} \;=\; \frac{8\pi h\nu_{nm}^3}{c^3}\,B_{m\to n} \;=\; 1/\tau_{nm} \qquad (5)$$

$$B_{n\to m} \;=\; B_{m\to n} \;=\; B_{nm}$$

The significance of the Einstein coefficients is a general relationship between spontaneous emission and optical absorption spectra and the proportionality of A and B implies their similarity.

1 To clarify the dimensionality of variables in terms of energy, length and time (ε, l, t): $N(l^{-3})$, $A(t^{-1})$, $B(l^3/\varepsilon\, t^2)$, $\rho(\varepsilon t/l^3)$ and $J(\varepsilon/,l^2)$.

As a radiative beam travels through a material medium, its energy density, $\rho(\nu)d\nu$, decreases due to field-induced transitions with a characteristic distance, ℓ,

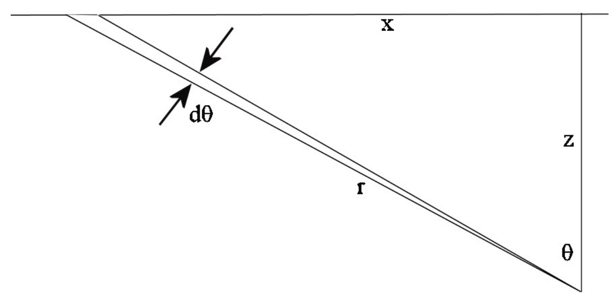
$$\frac{d\epsilon}{dz} = -\frac{\epsilon}{\ell} = -\frac{\rho(\nu)\delta\nu}{\ell} \tag{6}$$

$$c\frac{d\epsilon}{dz} = \frac{d\epsilon}{dt} = -h\nu_{nm}\rho(\nu_{nm})B_{nm}(N_n - N_m) \tag{7}$$

Using *Eq. 5*,

$$\ell_{nm} = \frac{(c\delta\nu/h\nu_{nm})}{B_{nm}(N_n - N_m)} = \frac{8\pi\nu_{nm}^2\tau_{nm}\delta\nu}{c^2(N_n - N_m)} \tag{8}$$

As a model, we shall suppose that black-body radiation arises from the spontaneous decay of thermally excited states within a medium. The probability that this radiation escapes depends upon the ratio of its path length to the distance ℓ_{nm}.



The fraction of isotropic radiation within a cone of thickness $d\theta$ is

$$2\pi x r d\theta/4\pi r^2 = ½\sin\theta\, d\theta \tag{9}$$

The total rate of energy radiation in a bandwidth given by integration over θ and z is thus

$$\begin{aligned} J(\nu_{nm})\delta\nu &= \frac{h\nu_{nm}N_m}{2\tau_{nm}}\int_0^{\pi/2}\sin(\theta)d\theta\int_0^{\infty}dz\, e^{-z/\ell_{nm}\cos(\theta)} \\ &= \frac{h\nu_{nm}\ell_{nm}N_m}{4\tau_{nm}} \end{aligned} \tag{10}$$

where we have assumed infinite limits for x and z. Making use of *Eq. 8,*

$$J(\nu_{nm}) = \frac{2\pi h\nu_{nm}^3}{c^2}\frac{1}{e^{h\nu_{nm}/kT} - 1} \tag{11}$$

and the three material dependent parameters, τ_{nm}, λ_{nm} and N_m are no longer present because of the proportionality of τ_{nm} and $N\,\ell_{nm}$. This expresses the radiance in watts/meter^2/Hz. More conventionally, the radiance is expressed as watts/meter^2/cm^{-1}, in which case

$$J(\nu_{nm}) = \frac{2\pi h\nu_{nm}^3}{c}\frac{1}{e^{h\nu_{nm}/kT} - 1} \tag{12}$$

Integration over all frequencies, using the identity

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \pi^4/15 \tag{13}$$

yields the Stefan-Boltzmann result

$$\int J(\nu) d\nu = \frac{2\pi^5 (kT)^4}{15 c^2 h^3} \tag{14}$$

The upper integration limits in *Eq. 10* for both θ and z are assumptions. For the former, $\pi/2$ presumes no internal reflections. Formally, we might choose a critical angle giving a $sin^2(\theta_c)$ correction factor. Should we set a thickness, d, for the upper limit of *Eq. 10*,

$$\begin{aligned} J(\nu_{nm})\,\delta\nu &= \frac{h\nu_{nm} N_m}{2\tau_{nm}} \int_0^{\pi/2} \sin(\theta) d\theta \int_0^d dz\, e^{-z/\ell_{nm}\cos(\theta)} \\ &= \frac{h\nu_{nm}\ell_{nm} N_m}{4\tau_{nm}} F(d/\ell_{nm}) \end{aligned} \tag{15}$$

where

$$\begin{aligned} F(x) &= 2\int_0^{\pi/2} \sin(\theta) d\theta \int_0^x d\xi\, e^{-\xi/\cos(\theta)} \\ &= \int_0^{\pi/2} d(\sin^2\theta)[1 - e^{-x/\cos(\theta)}] \\ &= 1 - 2\int_1^\infty dy\, y^{-3} e^{-xy} = 1 - 2E_3(x) \end{aligned} \tag{16}$$

with $E_3(x)$ an exponential integral function.[2] $F(d/\ell_{nm})$ is a finite thickness correction for the Stefan-Boltzmann equation. Limiting approximations are:

$$E_n(x) = x^{n-1}\Gamma(1-n) + \left[-\frac{1}{1-n} + \frac{x}{2-n} - \frac{x^2}{2(3-n)} + \frac{x^3}{6(4-n)} - \ldots \right] \tag{17}$$

and

$$E_n(x) = \frac{e^{-x}}{x}\left[1 - \frac{n}{x} + \frac{n(n+1)}{x^2} + \ldots \right] \tag{18}$$

For small x

$$E_3(x) = ½ - x + \frac{x^3}{6} - \ldots \tag{18}$$

as the residue of $\Gamma(-2)$ balances the polynomial pole at $n=3$. The thin layer correction to *Eq. 10* is thus

$$J_{nm}\,\delta\nu = \frac{h\nu_{nm} N_m d}{2\tau_{nm}} [1 - (d/\ell_{nm})^2/6 + \ldots] \tag{19}$$

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2 http://mathworld.wolfram.com/En-Function.html. An online calculator is available at http://keisan.casio.com/exec/system/1180573425.

and 50% of the unattenuated emissions arising within the layer, the remainder exiting through the other interface. As $E_3(0)=0.5$ and the function decreases monotonically with increasing argument, emissions for a finite material thickness will always be less than Stefan-Boltzmann values. For $d= \ell_{nm}$, $E_3(1)=0.10969...$ and emission spectra will show dips at frequencies where absorption is weak and the sample transparent.

A common simplification in radiation calculations is to replace the $cos(\theta)$ factor in Eq. 15 by a mean value, *i.e.*

$$\begin{aligned} F_\alpha(x) &= 2\int_0^{\pi/2} \sin(\theta)\, d\theta \int_0^x d\xi\, e^{-\alpha\xi} \\ &= \frac{2}{\alpha}[1 - e^{-\alpha x}] \end{aligned} \tag{20}$$

When $\alpha = 2$, the solutions coincide at $x=0$ and approach unity for large x.

$$F_2(x) = 1 - \exp(-2x) \tag{21}$$

For values of x near unity, however, $F_2(x)$ can be nearly 14% higher as shown in the plot below.