292(4): The Derivation of the Beer Lambert Law for Polychromatic Radiation.

The energy density of the beam is U/V in joules per cubic metre. The energy flux density is:

$$\underline{\Phi} = c\bar{U} \quad - (1)$$

in joules per second per square metre, or watts per square metre. Define the volume of radiation as:

$$V = A c \Delta t \quad - (2)$$

where the area of the beam is A. The distance in metres covered in a time interval Δt is considered to be $c\Delta t$, so the phase velocity of the beam is c. This is essentially true for a beam incident in a sample from air or the vacuum. The total electromagnetic energy is:

$$U = \left(\frac{U}{V}\right) V = \left(\frac{U}{V}\right) A c \Delta t \quad - (3)$$

The energy density in the range ω to $\omega + d\omega$ is:

$$\frac{1}{V} dU = \rho \, d\omega \quad - (4)$$

where ρ is the density of states. The flux density in the same range is:

$$d\underline{\Phi} = c\rho \, d\omega \quad - (5)$$

$$:= I(\omega) \, d\omega.$$

So the intensity for polychromatic radiation is:

$$\boxed{I(\omega) = c\rho(\omega)} \quad - (6)$$

From eq. (4) the density of states is:

$$\rho(\omega) = \frac{1}{V}\frac{dU}{d\omega} \quad - (7)$$

so the intensity for polychromatic radiation is:

$$\boxed{I(\omega) = \frac{c}{V}\frac{dU}{d\omega}} \quad - (8)$$

in units of joules per square metre, i.e. energy per unit area of the beam.

The intensity (8) is used in the Beer Lambert law.

In the uncorrected Planck distribution:

$$\frac{1}{V}\frac{dU}{d\omega} = \frac{\hbar\omega^3}{\pi^2 c^3}\left(\frac{x}{1-x}\right) \quad - (9)$$

so:

$$I = \frac{\hbar\omega^3}{\pi^2 c^2}\left(\frac{x}{1-x}\right) \quad - (10)$$

or

$$I = \frac{\hbar\omega^3}{\pi^2 c^2}\left(\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right)^{-1} \quad - (11)$$

In the corrected law of UFT291:

$$I = \frac{10}{3}\frac{\hbar\omega^3}{\pi^2 c^2}\left(\exp\left(\frac{\hbar\omega}{kT}\right) - 1\right)^{-1} \quad -(12)$$

The experimental or empirical Beer Lambert law is

$$I = I_0 \exp\left(-\alpha(\omega) r\right) \quad -(13)$$

where $\alpha(\omega)$ is the power absorption coefficient and r the sample length. The initial and final intensities are measured with a Golay detector or bolometer.

If:

$$\hbar\omega \ll kT \quad -(14)$$

then:

$$\boxed{I \sim \frac{10}{3}\frac{kT\omega^2}{\pi^2 c^2}} \quad -(15)$$

It follows that:

$$\left(\frac{\omega}{\omega_0}\right)^2 = \exp\left(-\alpha(\omega) r\right) \quad -(16)$$

i.e.

$$\boxed{\frac{\omega}{\omega_0} = \exp\left(-\frac{\alpha(\omega) r}{2}\right)} \quad -(17)$$

Eq. (17) explains the Evans / Morris and

4) cosmological red shifts in terms of absorption.

The Beer Lambert law can also be derived theoretically as follows.

The number of molecules per unit volume able to absorb light of frequencies in the range ω to $\omega + d\omega$ is $n(\omega)\, d\omega / V$, so the total number density is:

$$\frac{N}{V} = \int \frac{n(\omega)}{V}\, d\omega \quad -(18)$$

Each photon in the beam has an energy $\hbar\omega$ and the rate at which one molecule absorbs a photon is given by Einstein's coefficient of stimulated absorption:

$$W_{i \to f} = B_{if}\, \rho \quad -(19)$$

The rate of change of energy density per unit volume is in the range ω to $\omega + d\omega$ is:

$$\frac{1}{V}\frac{dU}{dt} = -\hbar\omega\, W_{i \to f}\, \frac{n(\omega)}{V}\, d\omega \quad -(20)$$

so

$$\boxed{\frac{d\rho}{dt} = -\frac{n(\omega)}{V}\, \hbar\omega\, B_{if}\, \rho} \quad -(21)$$

The energy entering the volume (2) is:

$$E_i = \Phi(x)\, A\, dt \quad -(22)$$

5) The energy leaving at $x + dl$ is:

$$E_f = \Phi(x+dl) A\, dt \quad -(23)$$

The principle of conservation of energy means that the energy lost by the beam is transferred to the material in the volume, so:

$$\Phi(x+dl) A\, dt - \Phi(x) A\, dt = \frac{dU}{V} A\, dl \quad -(24)$$

i.e.:

$$\boxed{\frac{1}{V}\frac{dU}{dt} = \frac{d\Phi}{dl}} \quad -(25)$$

where

$$d\Phi = \Phi(x+dl) - \Phi(x) \quad -(26)$$

Eq. (25) is true for each frequency component of the beam, so for frequencies in the range ω to $\omega + d\omega$:

$$\frac{dU}{V} = \rho(\omega)\, d\omega \quad -(27)$$

and

$$d\Phi = I(\omega)\, d\omega \quad -(28)$$

from eq. (5). So:

$$\frac{d}{dt}\left(\rho(\omega)\, d\omega\right) = \frac{d}{dl}\left(I(\omega)\, d\omega\right) \quad -(29)$$

and

$$\boxed{\frac{d\rho}{dt} = \frac{dI}{dl}} \quad -(30)$$

6) From eqs. (21) and (30):

$$\frac{dI}{dl} = -\frac{n(\omega)}{V}\hbar\omega B_{if}\rho \quad -(31)$$

$$= -\frac{n(\omega)}{V}\frac{\hbar\omega}{c}B_{if}\, I$$

using eq. (6). Therefore:

$$\frac{dI}{I} = -\alpha(\omega)\, dl \quad -(32)$$

where

$$\alpha(\omega) = \frac{n(\omega)}{V}\frac{\hbar\omega}{c}B_{if} \quad -(33)$$

Eq. (32) is the Beer Lambert law, Q.E.D.:

$$\frac{I}{I_0} = \exp\left(-\alpha(\omega)\, l\right) \quad -(34)$$

It is seen that the photon momentum enters into the definition of the power absorption coefficient:

$$p = \hbar\kappa = \frac{\hbar\omega}{c} \quad -(35)$$

So energy and momentum are conserved.