Emission in Continuous Media

We showed that $\alpha_\lambda = \epsilon_\lambda$ for a material.

→ this requires reconsideration of Beer's Law

Consider case for which only absorption is significant:

Recall Beer's Law

$$dI = -k\rho I\,dx$$

where

k = mass absorption coefficient

To account for emission of radiation along the path, we must add a term of the form

$$J\,\underbrace{k\rho}_{\longrightarrow\ \text{absorptivity} = \text{emissivity}}\,dx$$

Let's derive an expression for J.

First, consider properties of a radiating system:

A molecular system

- emits energy by executing quantum jumps between two states and thus emitting a photon which joins the radiation field
- absorbs energy by absorbing a photon and exciting itself to a higher state
- if it is in an excited state, can also be stimulated to emit a photon by the presence of a radiation field

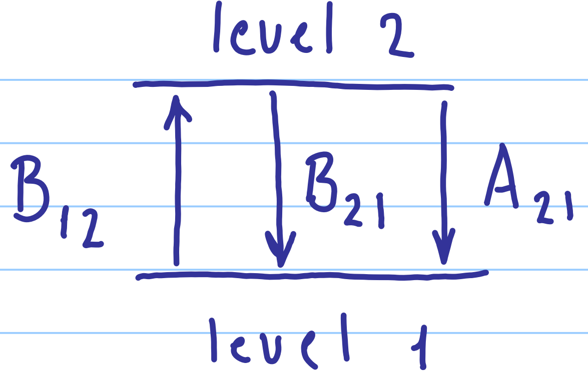
$\rightarrow$ stimulated emission (lasers)

These three processes couple the material to the radiation field.

① absorption of a photon $\Rightarrow$ rate depends on the density of the material and the density of radiation

② spontaneous emission $\Rightarrow$ depends only on the material density

③ stimulated emission $\Rightarrow$ depends on both material density and radiation density



two state system

The rate of excitation (absorption) per unit volume is

$$B_{12} \alpha \rho_1$$

where

B_{12} = coupling term

α = density of the radiation (NOT absorptivity) J/volume

ρ_1 = density of material in state 1

The rate of energy loss (emission) per unit volume is

$$\underbrace{B_{21} \alpha \rho_2}_{\text{stimulated emission}} + \underbrace{A_{21} \rho_2}_{\text{spontaneous emission}}$$

Units: $B\alpha\rho$, $A\rho$ molec/vol/sec

ρ molec/vol

A	1/sec
α	Joules/sec
B	vol/J/sec

For an isolated system (atom, molecule), the two rates balance causing resonant scattering because there is no mechanism coupling to kinetic energy of motion.

Need to extend these equations to deal with coupling to molecular motion through collisions which excite or relax the states by the reaction

$$M + a \longrightarrow M + a^* \longrightarrow M + a$$

↳ second body

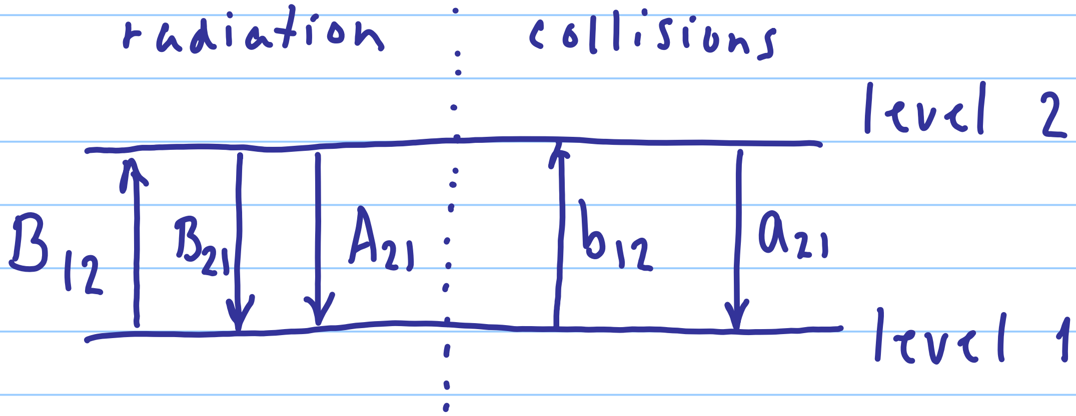
excitation rate $b_{12} f_1$

relaxation rate $a_{21} f_2$

→ a_{21}, b_{12} are called collisional transfer rates

For a system in equilibrium the rates of relaxation and excitation balance:

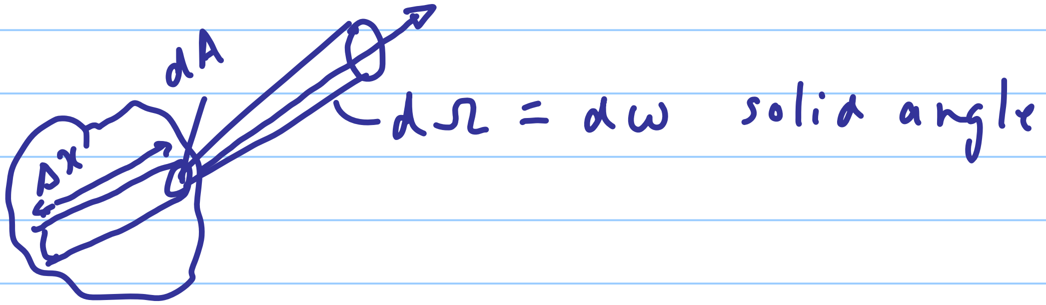
$$f_1 \left(B_{12} \alpha + b_{12} \right) = f_2 \left(A_{21} + B_{21} \alpha + a_{21} \right)$$



In the atmosphere, stimulated emission (B_{21} term) is negligible.

Now let's relate the radiation field parameters I and J to the terms above.

Consider an element of matter in an optically thin radiation field:



Energy absorbed from any given direction is

$$\Delta E \, d\Omega = k\rho \int I \, \Delta x \, dA \, d\Omega$$

where

I is homogeneous over the small volume

$\int$ is over the projected area in the direction of interest (dA)

$$\Delta E \, d\Omega = k\rho \left[\int I \, \Delta V \right] d\Omega = k\rho I V d\Omega$$

The total energy absorbed per unit vol. is

$$\frac{E}{V} = \frac{1}{V} \int \Delta E \, d\Omega = k\rho \int I \, d\Omega$$

$$= 4\pi k \rho \bar{I}$$

where

$$\bar{I} = \frac{1}{4\pi} \int I \, d\Omega$$ = average intensity (for simplicity)

$$\therefore \quad 4\pi k \rho \bar{I} = \underbrace{B_{12} \alpha \rho_1}_{\text{excitation rate (molec/vol/sec)}} \times \underbrace{hc\bar{\nu}}_{\text{photon energy (J/molec)}} \qquad ①$$

combined = energy rate (J/vol/sec)

The energy density of the field, α, is given by the average intensity divided by c, integrated over a sphere to account for all directions:

$$\alpha = \frac{4\pi \bar{I}}{c} \qquad\qquad \frac{W/m^2/sr}{m/s} = \frac{J}{m^3}$$

We can treat emission in a similar way but also assume that it is isotropic.

Thus $4\pi k \rho J = A_{21}\rho_2 \times hc\bar{\nu}$ ②

(ignoring stimulated emission)

Now combine ① and ② with our balance equation and the equation for α:

$$\rho_1 = \frac{4\pi k \rho \bar{I}}{B_{12}\alpha h c \bar{\nu}} \qquad\qquad \rho_2 = \frac{4\pi k \rho J}{A_{21} h c \bar{\nu}}$$

$$\rho_1 (B_{12}\alpha + b_{12}) = \rho_2 (A_{21} + a_{21})$$

$$\Rightarrow J\left(1 + \frac{a_{21}}{A_{21}}\right) = \bar{I}\left(1 + \frac{b_{12}}{B_{12}\alpha}\right)$$

with $\alpha = \frac{4\pi \bar{I}}{c}$

$$J\left(1+\frac{a_{21}}{A_{21}}\right) = \bar{I} + \frac{c\,b_{12}}{4\pi B_{12}}$$

$$J(1+\phi) = \bar{I} + \underbrace{\left[\frac{c\,b_{12}A_{21}}{4\pi a_{21}B_{12}}\right]}_{\text{constant}}\phi$$

where

$$\phi = a_{21}/A_{21}$$

because only the collisional transfer rates b_{12} and a_{21} have any physical state dependence

By elementary reaction kinetics, they are both proportional to the collision rate and so their ratio is independent of this rate.

We can evaluate this constant $\dfrac{c\,b_{12}A_{21}}{4\pi a_{21}B_{12}}$ as follows:

If this system is inside a cavity, then for any collision rate (i.e. for any T, p), both the average intensity and the total emission term must equal blackbody function B, otherwise the field will not be isotropic and homogeneous.

Thus $J(1+\phi) = \bar{I} + B\phi$

$$J = \frac{\bar{I}}{1+\phi} + \frac{B\phi}{1+\phi}$$

specifies the emission term J also known as the <u>source function.</u>

If $\bar{I} = B$ in a cavity, then this simplifies to $J = B$.

Interpretation:

- at high collision rates, a_{21} becomes large, ϕ becomes large, so $J \to B$
- at low collision rates, $a_{21} \to 0$, $\phi \to 0$ so $J \to \bar{I}$ → resonant scattering

The exact conditions for which this happens depend on A_{21} and a_{21} at STP and on the degree to which $\bar{I}$ deviates from B.

In the atmosphere, below ~40 km, the first condition ($J \to B$) for usual processes.

Above ~40 km, this approx ($J \simeq B$) does not necessarily hold.

Summary:

The transfer of radiation in matter is described by

$$\boxed{dI = -Ik\rho\,dx + Jk\rho\,dx}$$

→ Schwarzchild's Equation

This is valid for any process including simple scattering.

For a competing absorption/resonant scattering process:

$$\boxed{J = \frac{\bar{I}}{1+\phi} + \frac{B\phi}{1+\phi}}$$

with $\phi = \dfrac{\text{collisional relaxation rate } a_{21}}{\text{radiative relaxation rate } A_{21}}$

In the lower atmosphere, we can usually replace J by B to get

$$\boxed{dI = -Ik\rho\,dx + Bk\rho\,dx}$$

→ Known as Local Thermodynamic Equilibrium

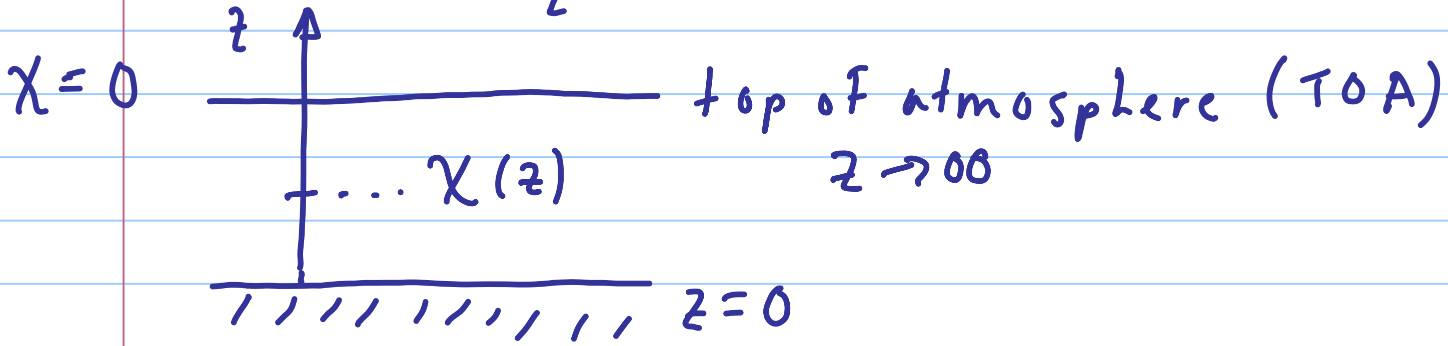
→ LTE

Atmospheric Application of Emission in Continuous Media

For the atmosphere, the most relevant co-ordinate is the vertical → z.

We'll also use optical depth

$$\chi(z) = \int_z^{\infty} k(z)\,\rho(z)\,dz$$



Signs can be confusing!

- χ is measured in the opposite direction to z
- radiation may be travelling upwards or downwards

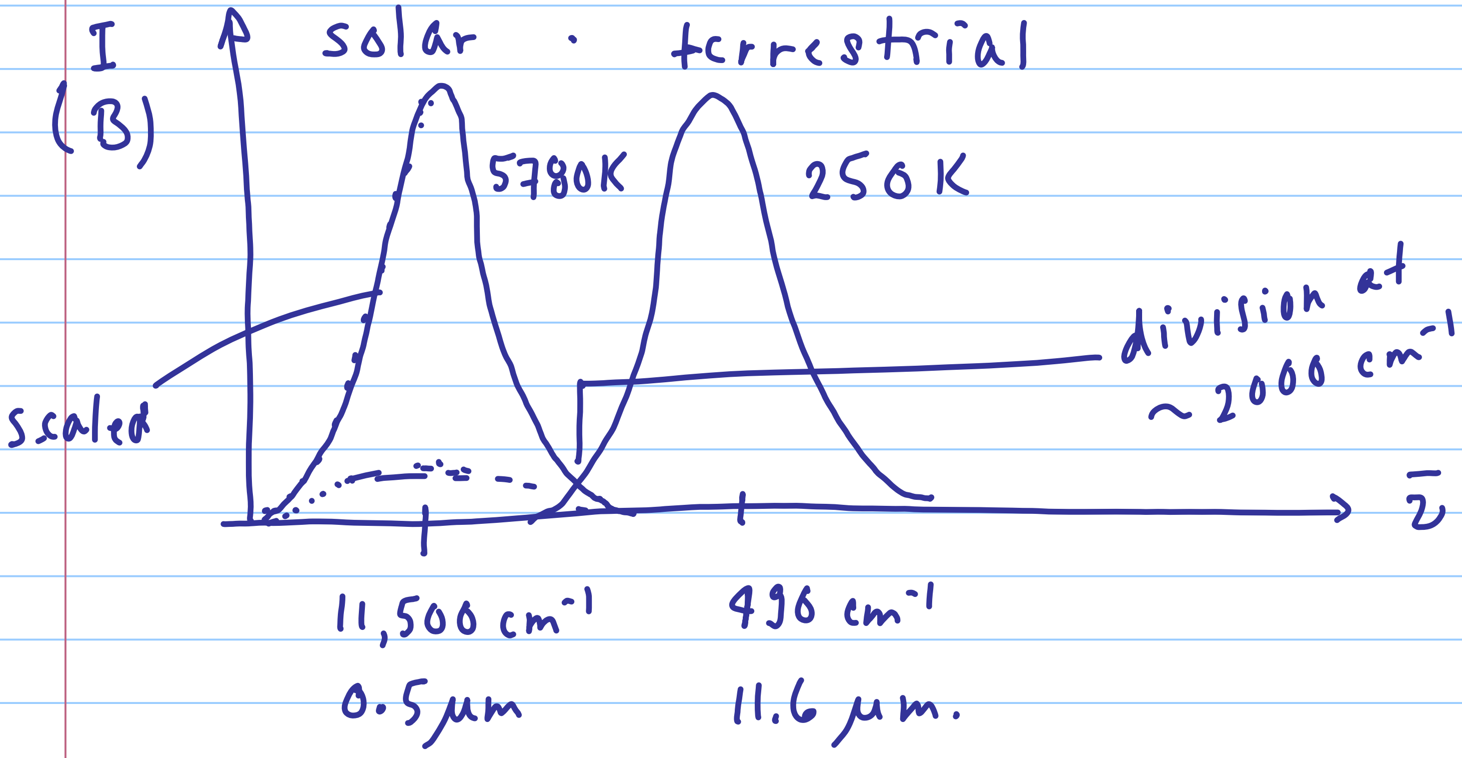
Replace $k\rho\,dz$ by $-d\chi$ to get

$$dI = I\,d\chi - J\,d\chi$$

or $$\frac{dI}{d\chi} = I - J$$ deceptively simple!

We can replace J by B in lower atmosphere.

Two sources of blackbody radiation in the atmosphere:
- sun
- atmosphere



This division between solar shortwave and terrestrial longwave radiation allows them to be treated independently.

Path of energy through Earth system:

shortwave → thermal → longwave

where

thermal = Kinetic energy reservoir

Another simplification:

The solar beam can be treated as a plane-parallel wavefront in the atmosphere before interactions (solar diameter is small from Earth).

→ allows Schwarzchild's Equation to be applied directly because the Sun is a monodirectional source.

If I_s = intensity in the direction of the Sun

then $F_s = I_s \Delta\Omega_s$

true for both monochromatic and total radiation

where

F_s = flux density normal to the solar beam

$\Delta\Omega_s$ = solar solid angle.

solar diameter = 31.99′

$\Delta\Omega_s = 6.8 \times 10^{-5}$ sr.