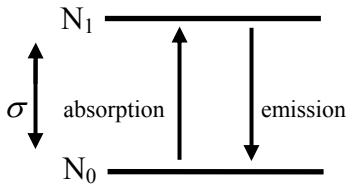
5. Spectroscopic preliminaries: Einstein A and B coefficients

Great detail in **Penner**.

A: Spontaneous emission.
B: Induced absorption and emission; induced by the radiation field $\rho(\sigma)$.

Remember that $R_n(\sigma)\,d\sigma = \dfrac{2\pi c\sigma^3 d\sigma}{e^{c_2\sigma/T}-1}$, in photons s^{-1} cm^{-3}.

The *radiation density* $\rho(\sigma)\,d\sigma = \dfrac{8\pi hc\sigma^3 d\sigma}{e^{c_2\sigma/T}-1}$, in erg cm^{-3}.



Consider a 2-level system at equilibrium:

$N_1 = N_0 e^{-c_2\sigma/T}$

Equilibrium $\Rightarrow dN_1/dT = dN_2/dT = 0$, implying

$N_0\rho(\sigma)B_{01} = N_1\rho(\sigma)B_{10} + N_1A_{10}.$

Apply Boltzmann factor: $\dfrac{N_0}{N_1}\rho(\sigma)B_{01} = \rho(\sigma)e^{c_2\sigma/T}B_{01} = \rho(\sigma)B_{10} + A_{10},$ or

$$\rho(\sigma) = \frac{A_{10}}{B_{01}e^{c_2\sigma/T} - B_{10}} = \frac{8\pi hc\sigma^3}{e^{c_2\sigma/T}-1}.$$

Therefore: $B_{01} = B_{10}$ and $A_{10} = 8\pi hc\sigma^3 B_{10}.$

These are ratios only: absolutes later.
Note σ^3 (or ν^3) dependence of A_{10}; emission at short wavelengths is very fast, and the upper states have very short lifetimes (and broad line shapes – more later).

If the upper and lower **degeneracies** are different,
$N_1 = N_0\left(g_1/g_0\right)e^{-c_2\sigma/T} \Rightarrow A_{10} = 8\pi hc\sigma^3 B_{10}$ as before, but $g_0B_{01} = g_1B_{10}.$

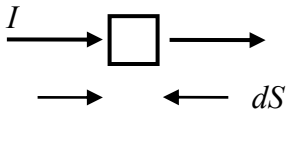
6. Introduction to radiative transfer

See **Goody & Yung**, Section 2.1 and **Chandrasekhar** for even more detail.

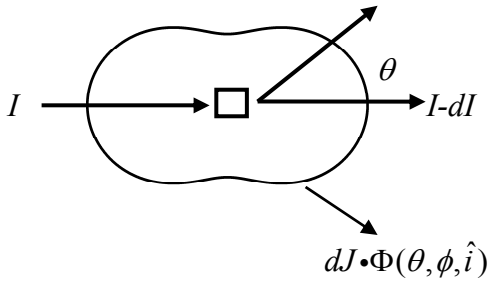
Basic equation of radiative transfer. For intensity I:

$$-dI(\sigma) = d\varepsilon I(\sigma) - dJ(\sigma)$$

extinction **source**



Scattering event:



Extinction completely described microscopically by absorption plus scattering.

- Extinction $\varepsilon = k$ (absorption) + m (scattering)

  - Extinction can be described by an *optical thickness*, τ. τ is equal to the product of the cross section (for absorption and/or scattering) per molecule, Σ (in cm^2), the length of absorption, l (in cm), and the concentration of absorbers/scatterers, c (cm^{-3}): $\tau = \Sigma \times l \times c$. τ is thus dimensionless (*e.g.*, cm^2×cm×cm^{-3}), and extinction is described by $I = I_0 e^{-\tau}$. A differential increment, $d\tau = \Sigma \times c \times dl$.

- *Single scattering albedo* $\equiv m/(k+m)$

- *Phase function* $\Phi(\theta,\phi,\hat{i}),\hat{i}$ = polarization. The phase function describes the angular behavior of source terms. Blackbody emission is isotropic, $\Phi = 1$. *Rayleigh scattering* is not, for reasons that will be presented soon. For *Rayleigh* scattering, $\Phi = \frac{3}{4}(1+\cos^2\theta)$ (Note the normalization: $\int_\Omega \Phi d\Omega = 4\pi$, = the number of steradians in angular integration, in the usual definition. This is important later for geometric scattering and absorption problems: Our solid angle Ω, from the étendue, will accept $\Omega/4\pi \times \Phi$ of the scattered radiation, or other source term. (It would have been easier for some applications to define $\int_\Omega \Phi d\Omega = 1,$ and eliminate the subsequent division by 4π. See *Chandrasekhar*, Chapter I.3 for discussion of the choice of normalization.)

The Rayleigh scattering cross section is:

$$Q_R \times 10^{28} = \frac{1.0455996 - 341.29061\sigma^2 - 0.90230850\sigma^{-2}}{1 + 0.0027059889\sigma^2 - 85.968563\sigma^{-2}}$$ cm^2, where $\sigma = 1/\lambda$ (μm) (σ in μm^{-1}). See **bodhaine.f90** for details.

Aside: Polarization

See **van de Hulst**, Chapter 5, **Chandrasekhar** Chapter 15, and **Goody and Yung** 2.1.3 and following, and my favorite, **Liou**, Chapters 5 and 6.

Consider a monochromatic, coherent light wave with direction of propagation **z**, angular frequency ω, and propagation constant k (assuming an isotropic medium) described by $\mathbf{E} = \mathrm{Re}[E_x\mathbf{x} + E_y\mathbf{y}]$, where $E_x = a_x e^{-i\varepsilon_x} e^{-ikz+i\omega t}$, $E_y = a_y e^{-i\varepsilon_y} e^{-ikz+i\omega t}$. The intensity and polarization state of this wave can be described by the 4-element Stokes vector,

$$\mathbf{S} = \begin{pmatrix} I \\ Q \\ U \\ V \end{pmatrix}, \text{where}$$

$$I = E_x E_x^* + E_y E_y^* = a_x^2 + a_y^2,$$
$$Q = E_x E_x^* - E_y E_y^* = a_x^2 - a_y^2,$$
$$U = E_x E_y^* + E_y E_x^* = 2a_x a_y \cos\delta,$$
$$V = i(E_x E_y^* - E_y E_x^*) = 2a_x a_y \sin\delta, \quad \delta = \varepsilon_x - \varepsilon_y.$$

This general case of a coherent plane wave has elliptical polarization with a polarization ellipse (the ellipse swept out by the electric field vector onto a plane perpendicular to the direction of propagation) determined by the relative amplitudes a_x and a_y and phases ε_x and ε_y. Linear and circular polarizations are simply special cases of the ellipse.

Note that this is not a unique description of the polarization state, although it is the most common one, and also that there is an equivalent geometric version of this description in terms of the polarization ellipse, described by van de Hulst and by Goody and Yung (and others). Also, note that this actually over-determines the polarization state for coherent, elliptically-polarized, light where $I^2 = Q^2 + U^2 + V^2$.

In general, light beams are not coherent, as they are the superposition of many individual waves. If we look at time averages (denoted by $\langle\ \rangle$) over the duration of a scattering event, then

$$I = \langle a_x^2 \rangle + \langle a_y^2 \rangle \equiv I_x + I_y$$
$$Q = \langle a_x^2 \rangle - \langle a_y^2 \rangle = I_x - I_y$$
$$U = \langle 2a_x a_y \cos\delta \rangle$$
$$V = \langle 2a_x a_y \sin\delta \rangle.$$

In this more general case, all four parameters (or their equivalent) are required, and it can be shown that $I^2 \geq Q^2 + U^2 + V^2$. (*Try it!*) The degree of polarization P is given by $P = (Q^2 + U^2 + V^2)^{1/2} / I$.

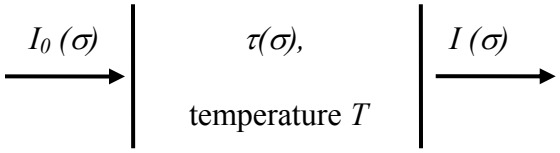
If the light is completely unpolarized, and incoherent over this period (*e.g.*, sunlight), then $\left\langle a_x^2 \right\rangle = \left\langle a_y^2 \right\rangle, \left\langle a_x a_y \right\rangle = 0,$ and $\mathbf{S} = \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}$.

Any interaction, such as a scattering event, transmission, or reflection can be described by a 4 × 4 *Mueller* (or transformation, or scattering) matrix. Google Mueller matrix to see a nice assortment of examples for various optical interactions. Rayleigh scattering is described by the Mueller matrix

$$\frac{3}{2}\begin{pmatrix} \frac{1}{2}(1+\cos^2\theta) & -\frac{1}{2}(\sin^2\theta) & 0 & 0 \\ -\frac{1}{2}(\sin^2\theta) & \frac{1}{2}(1+\cos^2\theta) & 0 & 0 \\ 0 & 0 & \cos\theta & 0 \\ 0 & 0 & 0 & \cos\theta \end{pmatrix} \times Q_R,$$ where Q_R is the scattering cross section. (What would the Mueller matrix for Lambertian reflection be?)

Back to radiative transfer

The basic equation (again), recast, ignoring scattering (for now) but adding emission, for an optical thickness τ:

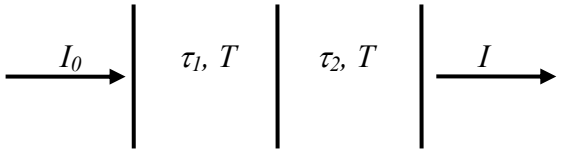


≡ optical thickness vs. optical depth
≡ Beer-Lambert absorption law

$I(\sigma) = I_0(\sigma)e^{-\tau(\sigma)} + B(\sigma,T)(1-e^{-\tau(\sigma)}),$ where $B(\sigma,T)$ is the blackbody emission:

$B(\sigma,T) = R_\sigma = \dfrac{c_1\sigma^3}{e^{c_2\sigma/T}-1}$. *What happened to Ω? See how it cancels?*

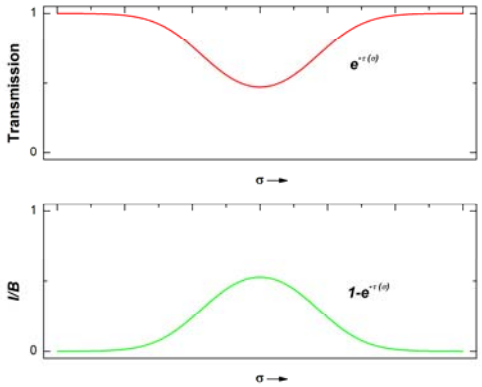
Note that τ increments add:



$I = I_0 e^{-(\tau_1+\tau_2)} + B(\sigma,T)[1-e^{-(\tau_1+\tau_2)}],$ as long as regions are at the same temperature.

For "pure" emission ($I_0 = 0$, ~outer space in background), with a large τ, the emission approaches, but never exceeds, that of a blackbody at the same temperature. For "pure" absorption (approximated in the mid IR and higher for planetary atmospheres), large $\tau \Rightarrow$ $I/I_0 = 0$. Looking at the pure cases:

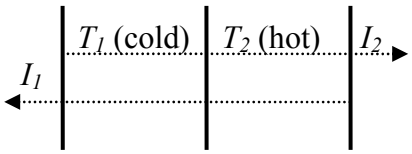
Absorption: $I / I_0 = e^{-\tau}$

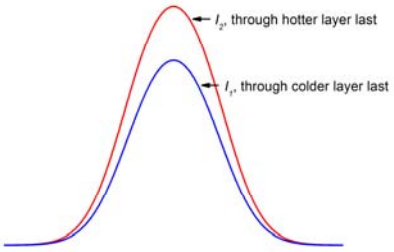


Emission: $\dfrac{I}{B(\sigma,\tau)} = 1 - e^{-\tau}$

Turn the emission spectrum upside-down
and you have, exactly, the absorption spectrum (once the emission spectrum has been normalized to the blackbody emission).

Finally, when there are successive emitting layers at different temperatures, the final intensity is buffered toward the temperature of the final layer:





Discuss problem of nadir measurements in thermal emission (e.g., CO) and thermal contrast.