Set 4:

Thermal Equilibrium Applications

Saha Equation

- What is the equilibrium ionization state of a gas at a given temperature?
- Hydrogen example: $e + p \leftrightarrow H + \gamma$
- Define $n_{\rm tot} = n_p + n_H$ and an ionization fraction $x_e \equiv n_p/n_{\rm tot}$

$$\frac{n_p n_e}{n_H n_{\rm tot}} = \frac{x_e^2}{1 - x_e}$$

- Number densities defined by distribution function in thermal equilibrium. e and p are non-relativistic at the eV energy scales of recombination
- Maxwell-Boltzmann distribution

$$f = e^{-(mc^2-\mu)/kT} e^{-q^2/2mkT}$$

Saha Equation

- Number density:

$$n = g \int \frac{d^3q}{(2\pi\hbar)^3} f = \frac{g e^{-(mc^2-\mu)/kT}}{2\pi^2\hbar^3} \int_0^\infty q^2 dq e^{-q^2/2mkT}$$

$$= g \frac{e^{-(mc^2-\mu)/kT}}{2\pi^2\hbar^3} (2mkT)^{3/2} \left[\int_0^\infty x^2 dx e^{-x^2} = \frac{\sqrt{\pi}}{4} \right]$$

$$= g e^{-(mc^2-\mu)/kT} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} , \quad (x = p/\sqrt{2mkT})$$

- Hydrogen recombination ($n_{\rm tot} = n_p + n_H$)

$$n_p = g_p e^{-(m_p c^2 - \mu_p)/kT} \left(m_p kT/2\pi\hbar^2 \right)^{3/2}$$

$$n_e = g_e e^{-(m_e c^2 - \mu_e)/kT} \left(m_e kT/2\pi\hbar^2 \right)^{3/2}$$

$$n_H = g_H e^{-(m_H c^2 - \mu_H)/kT} \left(m_H kT/2\pi\hbar^2 \right)^{3/2}$$

Saha Equation

- Hydrogen binding energy $B = 13.6\text{eV}$: $m_H = m_p + m_e - B/c^2$

$$\frac{n_p n_e}{n_H n_{\rm tot}} = \frac{x_e^2}{1-x_e} \approx \frac{g_p g_e}{g_H n_{\rm tot}} e^{-B/kT} e^{\mu_p+\mu_e-\mu_H} \left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2}$$

- Spin degeneracy: spin 1/2 $g_p = 2$, $g_e = 2$; $g_H = 4$ product
- Equilibrium $\mu_p + \mu_e = \mu_H$

$$\frac{x_e^2}{1-x_e} \approx \frac{1}{n_{\rm tot}} e^{-B/kT} \left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2}$$

- Quadratic equation involving T and the total density - explicit solution for $x_e(T)$
- Exponential dominant factor: ionization drops quickly as kT drops below B - exactly where the sharp transition occurs depends on the density $n_{\rm tot}$

Saha Equation

- Photon perspective: compare photon number density at T to $n_{\rm tot}$

$$n_\gamma = \frac{2\zeta(3)}{\pi^2\hbar^3}\left(\frac{kT}{c}\right)^3$$

$$\frac{x_e^2}{1-x_e} = \left(\frac{n_\gamma}{n_{\rm tot}}\right) e^{-B/kT}\frac{\pi^2\hbar^3}{2\zeta(3)}\left(\frac{c}{kT}\right)^3\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2}$$
$$= \left(\frac{n_\gamma}{n_{\rm tot}}\right) e^{-B/kT}\frac{\pi^{1/2}}{2^{5/2}\zeta(3)}\left(\frac{m_e c^2}{kT}\right)^{3/2}$$

- Photon-baryon ratio controls when recombination occurs: typically a very large number since baryon number is conserved $(\mu \neq 0)$ -a low baryon density medium is easy to keep ionized with the high energy photons in tail of the black body
- Cosmologically, recombination occurs at an energy scale of $kT \sim 0.3$eV

Saha Equation

- Electron perspective: the relevant length scale is the ("thermal") de Broglie wavelength for a typical particle

$$m_e v^2 \sim kT, \quad q^2 \sim m_e^2 v^2 \sim (m_e kT)$$

$$\lambda_{Te} = \frac{h}{q} = \frac{h}{(2\pi m_e kT)^{1/2}} = \left(\frac{2\pi\hbar^2}{m_e kT}\right)^{1/2}$$

which is the factor in the Saha equation

$$\frac{x_e^2}{1-x_e} = \frac{1}{n_{\rm tot}\lambda_{Te}^3} e^{-B/kT}$$

$N_{Te} = n_e \lambda_{Te}^3 =$ # electrons in a de Broglie volume and is $\ll 1$ for non-degenerate matter

- Equivalently, occupation number $f_e \ll 1$ at average momenta

Saha Equation

- Saha equation

$$\frac{x_e}{1-x_e} = \frac{1}{N_{Te}} e^{-B/kT}$$

- Electron chemical potential

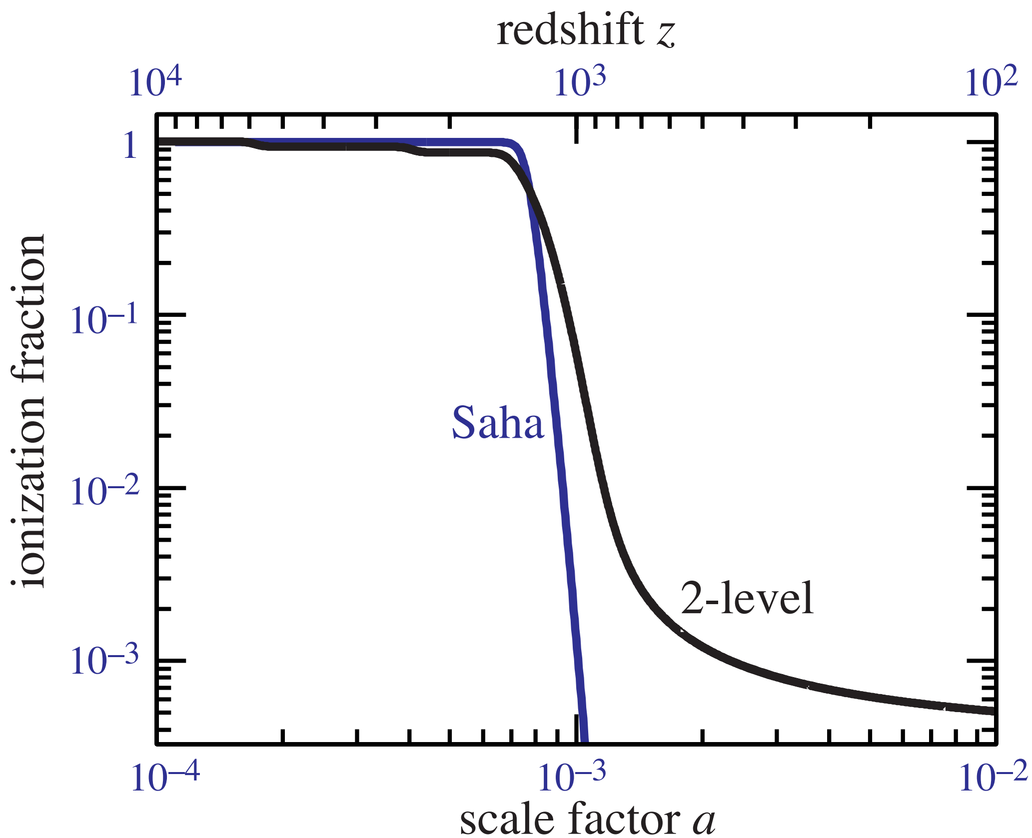
$$N_{Te} = 2e^{-(m_e c^2 - \mu_e)/kT}$$

$$\frac{x_e}{1-x_e} = \frac{1}{2} e^{-[B-(m_e c^2 - \mu_e)]/kT}$$

- Transition occurs when $B_{\rm eff} = B - m_e c^2 + \mu_e = kT$ - chemical potential or number density determines correction to $B \sim kT$ rule
- However equilibrium may not be maintained - 2 body interaction may not be rapid enough in low density environment - e.g. freezeout cosmologically

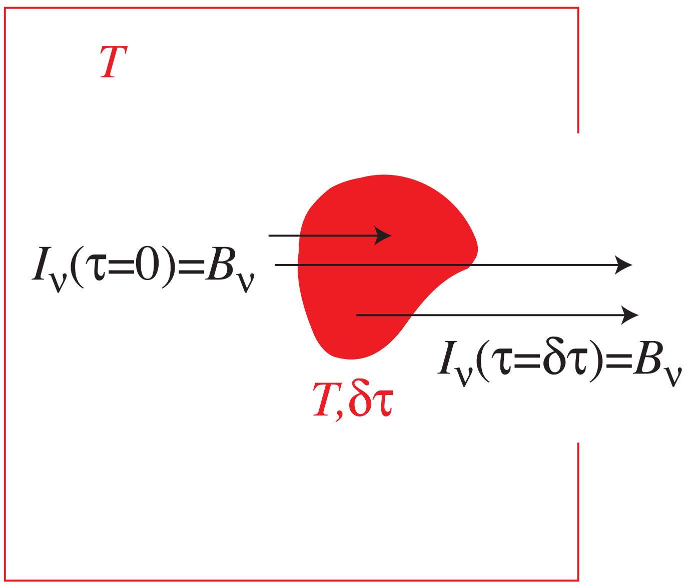
Cosmic Recombination

- Rates insufficient to maintain equilibrium - due to Lyα opacity cosmic recombination relies on forbidden 2 photon decay and redshift



Kirchhoff's Law

- Infer a relationship between absorption and emission based on thermodynamic equilibrium
- Consider a source at temperature T emitting with a source function S_ν
- The general radiative transfer equation says the specific intensity evolves as



$$\frac{dI_\nu}{d\tau} = -I_\nu + S_\nu$$

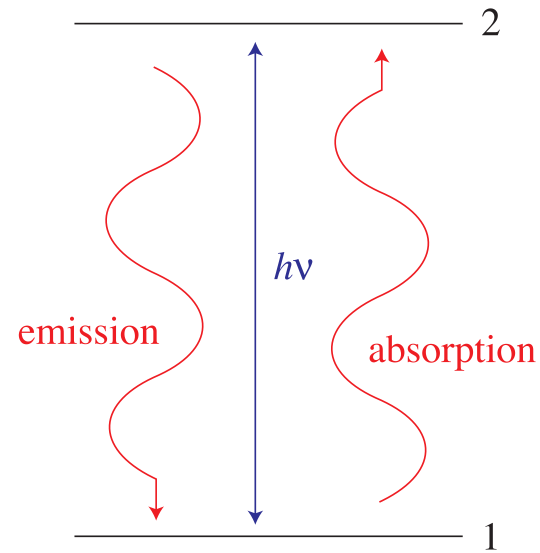
Kirchhoff's Law

- Recall that the source function is the ratio of emission and absorption coefficients

$$S_\nu = \frac{j_\nu}{\alpha_\nu}$$

- Consider the source to be in a black body enclosure of the same temperature. Then $I_\nu(\tau = 0) = B_\nu(T)$
- Radiative transfer must preserve $I_\nu(\tau) = B_\nu(T)$ so $S_\nu = B_\nu$ or or the emission coefficient $j_\nu = \alpha_\nu B_\nu$
- Since α_ν and j_ν are properties of the source and not the initial radiation field, this relationship is general for a black body source

Einstein Relations



- Generalize Kirchhoff's law
- Consider a 2 level atom with energies separated by $h\nu$: in equilibrium the forward transition balances the backwards transition leaving the level distribution with a Boltzmann distribution
- Ignoring stimulated emission for the moment, spontaneous emission balances absorption
- Analog to j_ν for a single atom: A_{21} the emission probability per unit time $[s^{-1}]$

Einstein Relations

- Analog to α_ν is B_{12} where $B_{12}J_\nu$ is the absorption probability per unit time in an isotropic radiation field
- Transition rate per unit volume depends on number densities in states

$$1 \rightarrow 2: \quad n_1 B_{12} J_\nu; \qquad 2 \rightarrow 1: \quad n_2 A_{21}$$

- Detailed balance requires

$$n_1 B_{12} J_\nu = n_2 A_{21} \rightarrow \frac{A_{21}}{B_{12}} = \frac{n_1}{n_2} J_\nu$$

Einstein Relations

- Atoms follow the non relativistic Maxwell-Boltzmann distribution (with $\mu_1 = \mu_2$), radiation a Planck distribution

$$n_1 \propto g_1 \exp[-E_1/kT], \quad n_2 \propto g_2 \exp[-(E_1 + h\nu)/kT]$$

$$J_\nu = \frac{2h}{c^2} \frac{\nu^3}{e^{h\nu/kT} - 1}$$

- So ignoring stimulated emission would imply

$$\frac{A_{21}}{B_{12}} = \frac{g_1}{g_2} e^{h\nu/kT} \frac{2h}{c^2} \frac{\nu^3}{e^{h\nu/kT} - 1}$$

- But the rates should not depend on temperature and so something is missing.

Einstein Relations

- Clue: photons become Maxwell Boltzmann in the Wien tail where there is on average < 1 photon at the line frequency

$$J_\nu \approx \frac{2h}{c^2}\nu^3 e^{-h\nu/kT}$$

- Then

$$\frac{A_{21}}{B_{12}} = \frac{g_1}{g_2}\frac{2h}{c^2}\nu^3$$

- Missing term involves a condition where there is a large number of photons at the transition frequency: stimulated emission
- Suppose there is an additional emission term whose transition rate per unit volume

$$2 \rightarrow 1: \quad n_2 J_\nu B_{21}$$

Einstein Relations

- Then the balance equation becomes

$$n_1 B_{12} J_\nu = n_2 A_{21} + n_2 J_\nu B_{21}$$

$$\begin{aligned} J_\nu &= \frac{2h}{c^2} \frac{\nu^3}{e^{h\nu/kT} - 1} = \frac{A_{21}}{(n_1/n_2) B_{12} - B_{21}} \\ &= \frac{A_{21}}{B_{21}[(g_1 B_{12}/B_{21} g_2) e^{h\nu/kT} - 1]} \end{aligned}$$

- Matching terms

$$g_1 B_{12} = g_2 B_{21}, \quad \frac{2h}{c^2}\nu^3 = \frac{A_{21}}{B_{21}}$$

Einstein Relations

- Import: given spontaneous emission rate, measured or calculated, $A_{21} \rightarrow$ stimulated emission rate $B_{21} \rightarrow$ absorption rate, fully defining the radiative transfer for this process independent of the radiation state I_ν
- Usage: oscillator strength defined against a classical model for absorption, via semiclassical (quantized atomic levels, classical radiation) calculation of absorption and stimulated emission, or line width measurement deterimining the spontaneous emission rate

Einstein Relations

- Relation to j_ν: multiply by energy $h\nu$, divide into 4π and put a normalized line profile $\int d\nu\phi(\nu) = 1$

$$dE_{\rm em} = j_\nu dV d\Omega d\nu dt = h\nu\phi(\nu)d\nu n_2 A_{21} dV \frac{d\Omega}{4\pi}dt$$

$$j_\nu = \frac{h\nu}{4\pi}n_2 A_{21}\phi(\nu)$$

- Relation to absorption $\alpha_{\rm abs}$: similarly

$$\begin{aligned} dE_{\rm abs} &= h\nu\,\phi(\nu)d\nu\,n_1 B_{12} J_\nu\,dV\frac{d\Omega}{4\pi}d\nu dt \\ &= -[dJ_\nu = -\alpha_{\rm abs}J_\nu ds]dtd\nu dAd\Omega \end{aligned}$$

$$\alpha_{\rm abs} = \frac{h\nu}{4\pi}n_1 B_{12}\phi(\nu)$$

Einstein Relations

- Add stimulated term in the emission

$$dE_{\rm em} = h\nu\phi(\nu)d\nu n_2 B_{21} J_\nu dV\,dt\frac{d\Omega}{4\pi}, \quad \alpha_{\rm em} = -\frac{h\nu}{4\pi}n_2 B_{21}\phi(\nu)$$

- Absorption and emission coefficient

$$\begin{aligned}
\alpha_\nu &= \frac{h\nu}{4\pi}\phi(\nu)[n_1 B_{12} - n_2 B_{21}] \\
&= \frac{h\nu}{4\pi}\phi(\nu)\left(\frac{n_1 g_2}{g_1} - n_2\right)\frac{c^2}{2h\nu^3}A_{21} \\
j_\nu &= \frac{h\nu}{4\pi}n_2 A_{21}\phi(\nu)
\end{aligned}$$

Einstein Relations

- Source function

$$S_\nu = j_\nu/\alpha_\nu = \frac{1}{(n_1 g_2/n_2 g_1 - 1)} \frac{2h\nu^3}{c^2}$$

- In thermal equilibrium $n_1 g_2/n_2 g_1 = e^{h\nu/kT}$ and $S_\nu = B_\nu$, Kirchoff's law

Maser/Laser

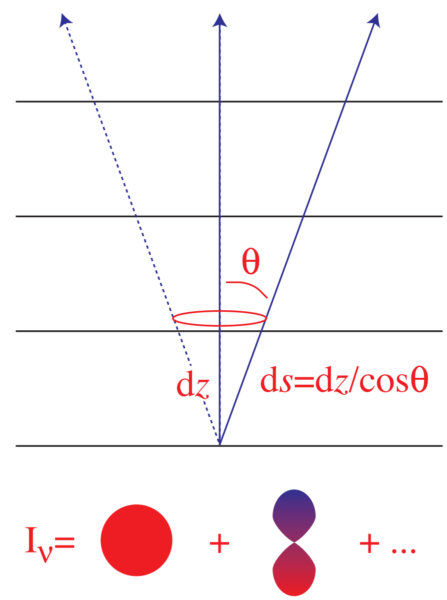
- Net absorption coefficient becomes negative if

$$n_1 g_2/g_1 - n_2 < 0$$

$$n_1/g_1 < n_2/g_2$$

- Requires a population inversion: higher energy state is more populated than lower energy state

Rosseland Approx (Tight Coupling)



- Radiative transfer near equilibrium where the source function $S_\nu = B_\nu$. Recall plane parallel case

$$\mu \frac{dI_\nu}{dz} = -\alpha_\nu (I_\nu - B_\nu)$$

- If interaction is strong then the difference between I_ν and B_ν is small - solve iteratively

$$I_\nu - B_\nu = -\frac{\mu}{\alpha_\nu}\frac{dI_\nu}{dz} \approx -\frac{\mu}{\alpha_\nu}\frac{dB_\nu}{dz}$$

$$I_\nu = B_\nu - \frac{\mu}{\alpha_\nu}\frac{dB_\nu}{dT}\frac{dT}{dz}$$

Rosseland Approx (Tight Coupling)

- Specific flux follows the temperature gradient

$$F_\nu = \int I_\nu(z,\mu)\mu d\Omega = 2\pi \int_{-1}^{1} I_\nu(z,\mu)\mu d\mu$$

$$= -\frac{2\pi}{\alpha_\nu}\frac{dB_\nu}{dT}\frac{dT}{dz}\int_{-1}^{1}\mu^2 d\mu = -\frac{4\pi}{3\alpha_\nu}\frac{dB_\nu}{dT}\frac{dT}{dz}$$

and is inhibited by high absorption

- Net flux

$$F(z) = \int_0^\infty F_\nu d\nu = -\frac{4\pi}{3}\frac{dT}{dz}\int_0^\infty \frac{1}{\alpha_\nu}\frac{dB_\nu}{dT}d\nu$$

and is dominated by the frequencies that have the lowest absorption – generally true: energy transport is dominated by the lowest opacity channel – e.g. lines (dark) vs continuum (bright)

Rosseland Approx (Tight Coupling)

- Flux for a constant α_ν involves

$$\int \frac{dB}{dT} d\nu = \frac{d}{dT} \int_0^\infty B_\nu d\nu = 4\frac{\sigma}{\pi} T^3$$

- Define the Rosseland mean absorption coefficient

$$\alpha_R^{-1} = \frac{\int \alpha_\nu^{-1} \frac{dB_\nu}{dT} d\nu}{\int \frac{dB_\nu}{dT} d\nu}$$

- Net flux becomes

$$F(z) = \frac{4\sigma T^3}{\pi \alpha_R} \left(-\frac{4\pi}{3} \frac{dT}{dz} \right) = -\frac{16\sigma T^3}{3\alpha_R} \frac{dT}{dz}$$