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 \( n_{\text{tot}} = n_p + n_H \) and an ionization fraction \( x_e \equiv n_p / n_{\text{tot}} \)

\[
\frac{n_p n_e}{n_H n_{\text{tot}}} = \frac{x_e^2}{1 - x_e}
\]

- 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

\[
f = e^{-(mc^2-\mu)/kT} e^{-q^2/2mkT}
\]
• Number density:

\[ n = g \int \frac{d^3q}{(2\pi\hbar)^3} f = \frac{ge^{-(mc^2-\mu)/kT}}{2\pi^2\hbar^3} \int_{0}^{\infty} q^2 dq e^{-q^2/2mkT} \]

\[ = g \frac{e^{-(mc^2-\mu)/kT}}{2\pi^2\hbar^3} (2mkT)^{3/2} \left[ \int_{0}^{\infty} x^2 dx e^{-x^2} = \frac{\sqrt{\pi}}{4} \right] \]

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

• Hydrogen recombination \((n_{\text{tot}} = n_p + n_H)\)

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

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

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

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

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

- Spin degeneracy: spin $1/2$ $g_p = 2$, $g_e = 2$; $g_H = 4$ product

- Equilibrium $\mu_p + \mu_e = \mu_H$

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

- 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 $n_{tot}$
**Saha Equation**

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

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

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

\[
  = \left( \frac{n_\gamma}{n_{\text{tot}}} \right) e^{-B/kT} \frac{\pi^{1/2}}{2^{5/2} \zeta(3)} \left( \frac{m_e c^2}{kT} \right)^{3/2}
\]

- 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 $kT \sim 0.3\text{eV}$
Saha Equation

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

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

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

which is the factor in the Saha equation

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

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

- 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

\[
N_{Te} = 2e^{-(me^2 - \mu_e)/kT}
\]

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

- Transition occurs when \( B_{\text{eff}} = B - me^2 + \mu_e = kT \) - 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 Ly$\alpha$ opacity
  cosmic recombination relies on forbidden 2 photon decay and redshift

![Graph showing ionization fraction and scale factor against 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 $S_\nu$.
- 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 the emission coefficient \( j_\nu = \alpha_\nu B_\nu \)

- Since \( \alpha_\nu \) and \( j_\nu \) 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 $j_\nu$ for a single atom: $A_{21}$ the emission probability per unit time $[s^{-1}]$
Einstein Relations

- Analog to $\alpha_\nu$ 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

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

- 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

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

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

- So ignoring stimulated emission would imply

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

- 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

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

- Then

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

- 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

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

\[ J_\nu = \frac{2\hbar}{c^2} \frac{\nu^3}{e^{\hbar\nu/kT} - 1} = \frac{A_{21}}{(n_1/n_2) B_{12} - B_{21}} \]

\[ = \frac{A_{21}}{B_{21}[(g_1 B_{12}/B_{21} g_2) e^{\hbar\nu/kT} - 1]} \]

- Matching terms

\[ g_1 B_{12} = g_2 B_{21}, \quad \frac{2\hbar}{c^2} \nu^3 = \frac{A_{21}}{B_{21}} \]
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 $I_\nu$

- 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 determining the spontaneous emission rate
Einstein Relations

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

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

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

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

$$dE_{abs} = h\nu \phi(\nu) d\nu n_1 B_{12} J_\nu dV \frac{d\Omega}{4\pi} d\nu dt$$

$$= - [dJ_\nu = - \alpha_{abs} J_\nu ds] dt d\nu dA d\Omega$$

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

- Add stimulated term in the emission

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

- Absorption and emission coefficient

\[ \alpha_\nu = \frac{h\nu}{4\pi} \phi(\nu) [n_1 B_{12} - n_2 B_{21}] \]

\[ = \frac{h\nu}{4\pi} \phi(\nu) \left( \frac{n_1 g_2}{g_1} - n_2 \right) \frac{c^2}{2h\nu^3} A_{21} \]

\[ j_\nu = \frac{h\nu}{4\pi} n_2 A_{21} \phi(\nu) \]
Einstein Relations

- Source function

\[ S_\nu = j_\nu / \alpha_\nu = \frac{1}{(n_1g_2/n_2g_1 - 1)} \frac{2h\nu^3}{c^2} \]

- In thermal equilibrium \( n_1g_2/n_2g_1 = e^{h\nu/kT} \) 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 $I_\nu$ and $B_\nu$ 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 $\alpha_\nu$ 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

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

\[
\int \frac{dB_\nu}{dT} d\nu
\]

- Net flux becomes

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