Most of the baryonic matter in the Universe is in a gaseous state, made up of \( \sim 75\% \) Hydrogen (H), \( \sim 25\% \) Helium (He) and only small amounts of other elements (called ‘metals’). Gases can be neutral, ionized, or partially ionized. The degree of ionization of any given element is specified by a Roman numeral after the element name. For example HI and HII refer to neutral and ionized hydrogen, respectively, while CI is neutral carbon, CII is singly-ionized carbon, and CIV is triply-ionized carbon. A gas that is highly (largely) ionized is called a **plasma**.

**Thermodynamic Equilibrium:** a system is said to be in thermodynamic equilibrium (TE) when it is in
- thermal equilibrium
- mechanical equilibrium
- radiative equilibrium
- chemical equilibrium
- statistical equilibrium

Equilibrium means a state of balance. In a state of thermodynamic equilibrium, there are no net flows of matter or of energy, no phase changes, and no unbalanced potentials (or driving forces), within the system. A system that is in thermodynamic equilibrium experiences no changes when it is isolated from its surroundings.

In a system in TE the energy in the radiation field is in equilibrium with the kinetic energy of the particles. If the system is isolated (to both matter and radiation), and in mechanical equilibrium, then over time TE will be established. For a gas in TE, the **radiation temperature**, \( T_R \), is equal to the **kinetic temperature**, \( T \), is equal to the **excitation temperature**, \( T_{ex} \) (see below for definitions). Since no photons are allowed to escape from a system in TE (this would correspond to energy loss, and thus violate TE), the photons that are produced in the gas (represented by \( T_R \)) therefore must be tightly coupled to the random motions of the particles (represented by
This coupling implies that, for bound states, the excitation and de-excitation of the atoms and ions must be dominated by collisions. In other words, the collision timescales must be shorter than the timescales associated with photon interactions or spontaneous de-excitations. If that were not the case, $T$ could not remain equal to $T_R$.

**Local Thermodynamic Equilibrium (LTE):** True TE is rare (in almost all cases energy does escape the system in the form of radiation, i.e., the system cools), and often temperature gradients are present. A good, albeit imperfect, example of TE is the Universe as a whole prior to decoupling. Although true TE is rare, in many systems (stars, gaseous spheres, ISM), we may apply local TE (LTE), which implies that the gas is in TE, but only locally. In a system in LTE, there will typically be gradients in temperature, density, pressure, etc, but they are sufficiently small over the mean-free path of a gas particle. For stellar interiors, the fact that radiation is ‘locally trapped’ explains why it takes so long for photons to diffuse from the center (where they are created in nuclear reactions) to the surface (where they are emitted into space). In the case of the Sun, this timescale is of the order of 200,000 years.

**Thermal Equilibrium:** Thermal equilibrium in a system for itself means that the temperature within the system is spatially and temporally uniform. Thermal equilibrium as a relation between the physical states of two bodies means that there is actual or implied thermal connection between them, through a path that is permeable only to heat, and that no energy is transferred through that path.

For a gas in thermal equilibrium at some uniform temperature, $T$, and uniform number density, $n$, the number density of particles with speeds between $v$ and $v+dv$ is given by the Maxwell-Boltzmann (aka ‘Maxwellian’) velocity distribution:

$$n(v)dv = n \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp \left( -\frac{m v^2}{2 k_B T} \right) \frac{4\pi v^2}{4} dv$$

where $m$ is the mass of a gas particle. The temperature $T$ is called the kinetic temperature, and is related to the mean-square particle speed,
\[ \langle v^2 \rangle \text{, according to} \]
\[
\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T
\]

The most probable speed of the Maxwell-Boltzmann distribution is \( v_{\text{mp}} = \sqrt{2k_B T/m} \), while the mean speed is \( v_{\text{mean}} = \sqrt{8k_B T/m} \).

Setting up a Maxwellian velocity distribution requires many elastic collisions. In the limit where most collisions are elastic, the system will typically very quickly equilibrate to thermal equilibrium. However, depending on the temperature of the gas, collisions can also be inelastic: examples of the latter are collisional excitations, in which part of the kinetic energy of the particle is used to excite its target to an excited state (i.e., the kinetic energy is now temporarily stored as a potential energy). If the de-excitation is collisional, the energy is given back to the kinetic energy of the gas (i.e., no photon is emitted). However, if the de-excitation is spontaneous or via stimulated emission, a photon is emitted. If the gas is optically thin to the emitted photon, the energy will escape the gas. The net outcome of the collisional excitation is then one of dissipation, i.e., cooling (kinetic energy of the gas is being radiated away). In the optically thick limit, the photon will be absorbed by another atom (or ion). If the system is in (L)TE, the radiation temperature of these photons being emitted and absorbed is equal to the kinetic temperature of the gas. Although in LTE a subset of the collisions are inelastic, this subset is typically small, and one may still use the Maxwell-Boltzmann distribution to characterize the velocities of the gas particles.

Mechanical Equilibrium: A system is said to be in mechanical equilibrium if (i) the vector sum of all external forces is zero and (ii) the sum of the moments of all external forces about any line is zero.

Radiative Equilibrium: A system is said to be in radiative equilibrium if any two randomly selected subsystems of it exchange by radiation equal amounts of heat with each other.

Chemical Equilibrium: In a chemical reaction, chemical equilibrium is
the state in which both reactants and products are present at concentrations which have no further tendency to change with time. Usually, this state results when the forward reaction proceeds at the same rate as the reverse reaction. The reaction rates of the forward and reverse reactions are generally not zero but, being equal, there are no net changes in the concentrations of the reactant and product.

**Statistical Equilibrium:** A system is said to be in statistical equilibrium if the level populations of its constituent atoms and ions do not change with time (i.e., if the transition rate into any given level equals the rate out).

For a system in statistical equilibrium, the population of states is described by the **Boltzmann law** for level populations:

\[
\frac{N_j}{N_i} = \frac{g_j}{g_i} \exp \left( -\frac{h \nu_{ij}}{k_B T} \right)
\]

Here \(N_i\) is the number of atoms in which electrons are in energy level \(i\) (here \(i\) reflects the principal quantum number, with \(i = 1\) referring to the ground state), \(\nu_{ij}\) is the frequency corresponding to the energy difference \(\Delta E_{ij} = h \nu_{ij}\) of the energy levels, \(h\) is the Planck constant, and \(g_i\) is the statistical weight of population \(i\).

**Statistical weight:** the statistical weight (aka ‘degeneracy’) indicates the number of states at a given principal quantum number, \(n\). In quantum mechanics, a total of four quantum numbers is needed to describe the state of an electron: the principle quantum number, \(n\), the orbital angular momentum quantum number, \(l\), the magnetic quantum number \(m_l\), and the electron spin quantum number, \(m_s\). For hydrogen \(l\) can take on the values 0, 1, ..., \(n - 1\), the quantum number \(m_l\) can take on the values \(-l, -l + 1, -1, 0, 1, ..., l\), and \(m_s\) can take on the values \(+1/2\) (‘up’) and \(-1/2\) (‘down’). Hence, \(g_n = 2n^2\).

**Excitation Temperature:** The above **Boltzmann law** defines the excitation temperature, \(T_{ex}\), as the temperature which, when put into the Boltzmann law for level populations, results in the observed ratio of \(N_j/N_i\). For a gas in (local) TE, all levels in an atom can be described by the same \(T_{ex}\), which is
also equal to the kinetic temperature, $T$, and the radiation temperature, $T_R$. Under non-LTE conditions, each pair of energy levels can have a different $T_{ex}$.

**Radiation Temperature:** the radiation temperature, or $T_R$, is a temperature that specifies the energy density in the radiation field, $u_\gamma$, according to $u_\gamma = a_r T_R^4$. In TE $T_R = T$, while for a Black Body, $T_R$ is the temperature that appears in the Planck function that describes the specific intensity of the radiation field (see Chapter 21 for more details).

**Partition Function:** Using the above Boltzmann law, it is straightforward to show that

$$ \frac{N_n}{N} = \frac{g_n}{U} \exp \left( -\frac{\Delta E_n}{k_B T} \right) $$

where $N = \sum N_i$ is the total number of atoms (of all energy levels) and $\Delta E_n$ is the energy difference between state $n$ and the ground-state, and

$$ U = \sum g_i \exp \left( -\frac{\Delta E_i}{k_B T} \right) $$

is called the partition function. (Note: the summation is over all principal quantum numbers up to some maximum $n_{max}$, which is required to prevent divergence; see Irwin 2007 or Rybicki & Lightman 1979 for details).

**Saha equation:** the Saha equation expresses the ratios of atoms/ions in different ionization states. In particular, the number of atoms/ions in the $(K+1)^{th}$ ionization state versus those in the $K^{th}$ ionization state is given by

$$ \frac{N_{K+1}}{N_K} = \frac{2}{n_e} \frac{U_{K+1}}{U_k} \left( \frac{2 \pi m_e k_B T}{\hbar^2} \right) \exp \left( -\frac{\chi_K}{k_B T} \right) $$

where $U_n$ is the partition function of the $n^{th}$ ionization state, $n_e$ is the electron number density, and $\chi_K$ is the energy required to remove an electron from the ground state of the $K^{th}$ ionization state. Note that unlike the Boltzmann equation, the Saha equation for the ionization fractions has a dependence on electron density. This reflects that if there is a higher density of free electrons, there is a greater probability that an electron will recombine with the ion, lowering the ionization state of the gas.
Hydrogen Since Hydrogen is the most common element in the Universe, it is important to have some understanding of its structure. Fig. 14 shows the energy levels of the hydrogen atoms and some of its most important transitions. The Balmer transitions have wavelengths that fall in the optical, and are therefore well known to (optical) astronomers. The Lyman lines typically fall in the UV, and can only be observed from space (or for high-redshift objects, for which the rest-frame UV is redshifted into the optical).

Using the Saha equation, we can compute the ionization fraction for hydrogen as function of temperature and electron density:

$$\frac{N_{\text{HII}}}{N_{\text{HI}}} = 2.41 \times 10^{15} \frac{T^{3/2}}{n_e} \exp \left( -\frac{1.58 \times 10^5}{T} \right)$$

where we have used that $\chi_{\text{HI}} = 13.6 \text{eV}$, $U_{\text{HI}} = 2$ and $U_{\text{HII}} = 1$ (i.e., the ionized hydrogen atom is just a free proton and only exists in a single state). We can also compute, using the Boltzmann law, the ratio of hydrogen atoms in the first excited state compared to those in the ground state. The latter shows that the temperature must exceed 30,000K in order for there to be an appreciable (10 percent) number of hydrogen atoms in the first excited state.
state. However, at such high temperatures, one typically has that most of the hydrogen will be ionized (unless the electron density is unrealistically high). This somewhat unintuitive result arises from the fact that there are many more possible states available for a free electron than for a bound electron in the first excited state. In conclusion, neutral hydrogen in LTE will have virtually all its atoms in the ground state.

If densities are sufficiently low, which is typically the case in the ISM, the collisional excitation rate (which scales with $n_e^2$) is lower than the spontaneous de-excitation rate. If that is the case, the hydrogen gas is no longer in LTE, and once again, virtually all neutral hydrogen will find itself in the ground state. Neutral hydrogen in the ISM is in the ground-state and is typically NOT in LTE. One important consequence of the fact that neutral hydrogen is basically always observed in the ground state, is that observations of hydrogen emission lines (Lyman, Balmer, Paschen, etc) indicates that the hydrogen must be ionized; the lines arise from recombinations, and are therefore called recombination lines. Note that Balmer lines are often observed in an absorption (for example, Balmer lines are evident in a spectrum of the Sun). This implies that their must be hydrogen present in the first excited state, which seems at odds with the conclusions reached above. A small fraction of excited hydrogen atoms, though, can still produce strong absorption lines, simply because hydrogen is so abundant.

**21cm line emission:** The ground state of hydrogen is split into two hyperfine states due to the two possible orientations of the proton and electron spins: The state in which the spins of proton and electron are aligned has slightly higher energy than the one in which they are anti-aligned. The energy difference between these two hyperfine states corresponds to a photon with a wavelength of 21cm (which falls in the radio). The excitation temperature of this spin-flip transition is called the spin temperature. Since, for typical interstellar medium conditions, the spin-flip transition is collisionally induced (i.e., the rate for spontaneous de-excitation is extremely low), the spin-temperature is typically equal to the kinetic temperature of the hydrogen gas. The 21cm line is an important emission line to probe the distribution (and temperature) of neutral hydrogen gas in the Universe.