5.5: Boltzmann Statistics

Energy Level Spin Distribution

In the absence of a magnetic field the magnetic dipoles are oriented randomly and there is no net magnetization (vector sum of μ is zero). Application of an external magnetic field, as was shown above, creates distinct energy levels based on the spin angular momentum of the nucleus. Each energy level is populated by the spins which have the same angular momentum. To illustrate this, consider a I=1/2 system. There are two energy levels, +1/2 and -1/2, which are populated by spins that have aligned against or with the external magnetic field, respectively.

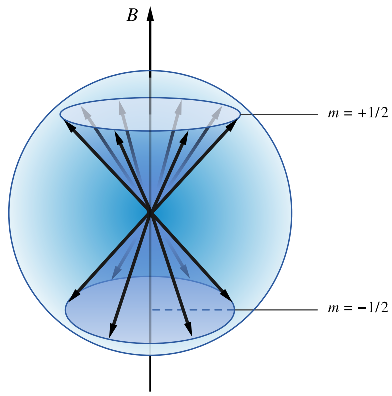

Figure 5.5.1: Spins configurations according to applied magnetic field

The energy separation between these states is relatively small and the energy from thermal collisions is sufficient to place many nuclei into higher energy spin states. The number of nuclei in each spin state can be described by the Boltzmann distribution. The Boltzmann equation expresses the relationship between temperature and the related energy as shown below.

$$\frac{N_{upper}}{N_{lower}} = e^{\frac{-\Delta E}{kT}} = e^{\frac{-h\nu}{kT}}$$

Where N_{upper} and N_{lower} represent the population of nuclei in upper and lower energy states, E is the energy difference between the spin states, k is the Boltzmann constant (1.3805x10-23 J/Kelvin) and T is the temperature in K. At room temperature, the number of spins in the lower energy level, N_{lower}, slightly outnumbers the number in the upper level, N_{upper}.

As the temperature **decreases**, so **does** the ratio N^- / N^+. As the temperature **increases**, the ratio approaches **one**.

The signal in NMR spectroscopy results from the difference between the energy absorbed by the spins which make a transition from the lower energy state to the higher energy state, and the energy emitted by the spins which simultaneously make a transition from the higher energy state to the lower energy state. The signal is thus **proportional** to the population difference between the states. NMR is a rather sensitive spectroscopy since it is capable of detecting these very small population differences. It is the resonance, or exchange of energy at a specific frequency between the spins and the spectrometer, which gives NMR its sensitivity.