PHY2201 Summary Sheet 10

Degeneracy:

More than one "state" can correspond to the same "energy level".

"State": the fullest description of a system allowed by quantum mechanics. A full set of "quantum numbers" must be specified, specifying e.g. the energy, orbital angular momentum and spin of the system.
"Energy level":- a quantized energy value that can be possessed by the system. Specified using a single quantum number (the "principal" quantum number).

e.g. electron of mass m_e in a 1-D infinite potential well of width L

$$\varepsilon_n = n^2 \frac{h^2}{8m_e L}$$

The integer n (=1, 2, 3…) labels the energy levels and is the principle quantum number.

To fully specify the state of an electron in the well we must specify two quantum numbers n and s ($s = -½$ or ½). s is the "spin" quantum number and specifies whether the electron spin is found to be "up" or "down" if measured relative to a given direction in space. In the absence of an external electromagnetic field, the energies of state (n, –½) and (n, ½) are identical. Thus energy level n is said to be two-fold degenerate (or to have a degeneracy factor g equal to 2) in this example.

The Boltzmann distribution gives the probability that a state i of energy ε_i is occupied, given an ensemble in equilibrium at temperature T. To calculate the probability that an energy level of energy ε_i, whose degeneracy factor is g_i, is occupied simply sum the probabilities for all the degenerate states corresponding to the energy level ε_i, i.e. multiply the appropriate Boltzmann factor by g_i. Hence, denoting p_i as the probability that a state i is occupied and $p(\varepsilon_i)$ the probability that an energy level ε_i is occupied, we can write the Boltzmann distribution in two ways

$$p_i = \frac{\exp(-\varepsilon_i / k_\mathrm{B} T)}{\sum_{i=0}^{\text{all states}} \exp(-\varepsilon_i / k_\mathrm{B} T)}$$

$$p(\varepsilon_i) = \frac{g_i \exp(-\varepsilon_i / k_\mathrm{B} T)}{\sum_{i=0}^{\text{all energy levels}} g_i \exp(-\varepsilon_i / k_\mathrm{B} T)}$$

Example: the 1st excited energy level of He lies 19.82 eV above the ground state and is 3-fold degenerate. What is the population ratio between the ground state (which is not degenerate) and the 1st excited level, when a gas of He is maintained at 10,000 K?

$$\frac{p(\varepsilon_1)}{p(\varepsilon_0)} = \frac{g_1}{g_0} \exp\left(-\frac{\Delta\varepsilon}{k_\mathrm{B} T}\right) = 3 \times \exp\left(-\frac{19.82 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23} \times 10^4}\right)$$

$$= 3 \times 10^{-10}$$