Thermal Physics

Hydrogen Atom

Problem 1.- The bound electronic energy states of the hydrogen atom may be described by the set of quantum numbers (n, l, m_l) where the energy is given by $\varepsilon_{nlm_l} = -\frac{A}{n^2}$ with A = 13.6 eV. The allowed values for the quantum numbers are:

$$
\begin{aligned}
n &= 1, 2, 3, 4... \\
l &= 0, 1, 2, 3..., n-1 \qquad \text{for a given } n \\
m_l &= -l, -l+1, ..., l-1, l \qquad \text{for a given } l
\end{aligned}
$$

a) Find the ratio of the number of atoms in the first excited energy level to the number in the lowest energy level at a temperature T.
[Hint: Be careful of the difference between energy levels and states of the system.] Evaluate this for T = 300K and T = 1000K.

b) To find the actual fraction of atoms in any given state one needs the partition function. Show that the partition function diverges even when the unbound states are neglected (unbound states are states with positive energy).

c) Any ideas why statistical mechanics does not seem to work for this simple system?

Solution:

a) Notice that the degeneracy of the first energy level is g(1) = 1 because it happens for the unique combination of quantum numbers $n = 1$, $l = 0$ and $m_l = 0$.
Instead, the first excited level has a degeneracy of g(2)=4 since the quantum numbers can be n = 2, l= 0 and m_l = 0 (1 state) and n = 2, l = 1 and m_l = -1, 0 or +1 (3 states).

Then, the ratio of the number of atoms in the first excited energy level to the number in the lowest energy level will be:

$$\frac{P(n=2)}{P(n=1)} = \frac{4e^{-E_2/\tau}}{e^{-E_1/\tau}} = 4e^{(E_1-E_2)/\tau} = 4e^{(-A+A/4)/\tau} = 4e^{-3A/4\tau} = 4e^{-3A/4k_BT}$$

Where A = 13.6 eV.

For T=300K:

$$\frac{P(n=2)}{P(n=1)} = 4e^{-3(13.6\text{eV})/4(8.62\times10^{-5}\text{eV/K})(300\text{K})} = 2.0\times10^{-171}$$

For T=1000K:

$$\frac{P(n=2)}{P(n=1)} = 4e^{-3(13.6\text{eV})/4(8.62\times10^{-5}\text{eV/K})(1000\text{K})} = 1.6\times10^{-51}$$

These ratios are so small that the probability of finding one atom in the first excited state at these temperatures is practically zero.

b) To find the partition function, recall that the degeneracy of the energy levels is g(*n*) = $2n^2$ so:

$$Z = \sum_{s=1}^{\infty} 2s^2 e^{-\left(-\frac{A}{s^2}\right)/\tau} = \sum_{s=1}^{\infty} 2s^2 e^{\frac{A}{s^2\tau}}$$

Notice that:

$$\sum_{s=1}^{\infty} 2s^2 e^{\frac{A}{s^2\tau}} > \sum_{s=1}^{\infty} 2s^2$$

Because each term in the second summation is less than each term in the first summation. Now, the summation of all the squared integers diverges, so the partition function diverges too.

c) The partition function includes all the levels that are accessible, but levels with large values of the quantum number *n* correspond to large orbits (the orbits grow like n^2) so not all of them are really available. In a real application, we would have to truncate the summation at a reasonable value of *n*.