Ex4213: Chemical equilibrium for $A \rightleftarrows A^+ + e^-$

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The question:

N_0 atoms of type A are placed in an empty box of volume V, such that their initial density is $n_0 = N_0/V$. The ionization energy of the atoms is ε_0. The box is held in temperature T, and eventually a chemical equilibrium $A \rightleftarrows A^+ + e^-$ is reached. The fraction of ionized atoms is $x = N^+/N_0$. The masses of the particles are m_e for the electron, and $m_{A^+} \approx m_A$ for the atoms and the ions.

(a) Define temperature T_0 such that $T \gg T_0$ is a sufficient condition for treating the gas of atoms in the Boltzmann approximation.

(b) Assuming the Boltzmann approximation for both the atoms and the electrons, write an equation for x. Write its *approximate* solution assuming $x \ll 1$. Write the condition for the validity of the latter assumption.

(c) Assuming that $x \ll 1$, write a condition on the density n_0, that above T_0 it was legitimate to treat the electrons in the Boltzmann approximation. Note: the condition is a simple inequality and should be expressed using $(m_e, m_A, \varepsilon_0)$.

Assume that the condition in (3) breaks down. It follows that there is a regimes $T_0 \ll T \ll T_1$ where the atoms can be treated in the Boltzmann approximation, while the electrons can be treated as a low temperature quantum gas.

(d) Write an equation for x assuming that the electrons can be treated approximately as a zero temperature Fermi gas. Exotic functions should not appear. You are not expected to solve this transcendental equation.

(e) What would be the equation for x if the electrons were Bosons instead of Fermions.
Note:
· Express all the final answers using $(m_e, m_A, n_0, \varepsilon_0, T)$, and *elementary* functions.
Exotic functions should not appear. It is allowed to use the notation $\lambda_e(T) = (2\pi/\mathsf{m}_e T)^{1/2}$.
·You can assume that the spin of A, e^- is 1/2 and that A^+ is spinless.

Solution:

(a) The condition for Boltzmann approximation is $|z| \ll 1$. Because of the monotonicity of the Polylogarithm function $Li_\alpha(z)$, in the case of 3D the condition for Boltzmann approximation can by written as $\lambda_A^{-3}(T) \gg n_A$ where the thermal wavelength of the A particles is $\lambda_A(T) = (2\pi/m_A T)^{1/2}$. We don't know the value of n_A but we do know that $n_A \leq n_0$ therefore Boltzmann holds for $T \gg T_0$ where

$$T_0 = \frac{2\pi n_0^{2/3}}{m_A} \tag{1}$$

(b) In chemical equilibrium $\mu_A = \mu_{A^+} + \mu_{e^-}$. The chemical potential in the Boltzmann approximation is $\mu = -T \ln(Z/N)$, where Z is the partition function of a single particle. In our case we have 3 different partition functions for A, A^+ and e^-. It follows that in equilibrium:

$$\ln(Z_A/N) = \ln(Z_{A^+}/N_{A^+}) + \ln(Z_{e^-}/N_{e^-}) \Rightarrow \tag{2}$$

$$\frac{Z_A}{N_A} = \frac{Z_{A^+}}{N_{A^+}} \frac{Z_{e^-}}{N_{e^-}} \tag{3}$$

Using the relations $N_{A^+} = N_{e^-} = xN_0$ and $N_A = (1-x)N_0$ we get:

$$\frac{x^2}{1-x} = \frac{Z_{A^+} Z_{e^-}}{Z_A N_0} \tag{4}$$

Using $m_{A^+} \approx m_A$ the partition function of A^+ ions is $Z_{A^+} = V\lambda_A^{-3}$. For the electrons $Z_{e^-} = 2V\lambda_{e^-}^{-3}$ (the 2 factor comes for the spin) and for the A atoms we used $Z_A = 2V{\lambda_A}^{-3}e^{\beta\varepsilon_0}$, where ϵ_0 is the binding energy required to ionize A. Finally we get the equation

$$\frac{x^2}{1-x} = \frac{1}{n_0\lambda_e^3}e^{-\beta\varepsilon_0} \tag{5}$$

For $x \ll 1$, we use first order approximation for x to get:

$$x^2 = \frac{1}{n_0\lambda_e^3}e^{-\beta\varepsilon_0} \tag{6}$$

(c) When Boltzmann approximation holds for the electrons, the electron density obeys $n_e \ll (\lambda_{e^-}^3)^{-1}$ therefore $x = n_e/n_0 \ll (n_0\lambda_{e^-}^3)^{-1}$ and from (6) we get

$$n_0\lambda_{e^-}^3 \ll e^{\beta\varepsilon_0} \tag{7}$$

(d) Again we are in chemical equilibrium $\mu_A = \mu_{A^+} + \mu_{e^-}$ with the same chemical potential for A, A^+. The difference is in the chemical potential of the electrons that goes to Fermi energy as the temperature goes to zero, $\mu_{e^-} \approx \varepsilon_F$ so now the chemical equilibrium equation get the form

$$T\ln(Z_A/N_A) = T\ln(Z_{A^+}/N_{A^+}) + \varepsilon_F \Rightarrow \tag{8}$$

$$\frac{2x}{1-x} = e^{\beta(\varepsilon_F - \varepsilon_0)} \tag{9}$$

where $\varepsilon_F = (6\pi^2 n_e)/2m_e = (3\pi^2 x n_0)/m_e$

(e) For Bosons $\mu_{e^-} = 0$ so that the chemical equilibrium equation is

$$T\ln(Z_A/N_A) = T\ln(Z_{A^+}/N_{A^+}) + 0 \tag{10}$$

which leads to

$$xe^{\beta\varepsilon_0} = 1 - x \Rightarrow \tag{11}$$

$$\frac{x}{1-x} = e^{-\beta\varepsilon_0} \tag{12}$$