Ex4215: Chemical equilibrium with condensation

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The problem:

N Boson molecules of type B are inserted into a box with volume V, the systems temperature is T. Each molecule is composed from two atoms of type A with mass m. The inner energy of each atom is ε_A and the binding energy of the molecules is ε_B. Assume there are molecules in the condensation state and that the atoms can be treated in the Boltzmann's approximation.

a. What is the condition for the condensation assumption to be valid for the molecules?

b. How many occupied excited states of molecules are in the box?

c. What is the condition for Boltzmann's approximation to be valid for the atoms?

d. How many atoms are in the box?

e. What is the condition on the number of atoms and molecules in order for the system to be in condensation?

f. What is the pressure on the box's walls?

g. Who pressures more (the molecules or the atoms)?

The Solution:

Alert: mass of B molecules is 2m.

a. The ground state for each molecule is ε_B, and

$$N\left(\beta,\mu_B\right) = V\cdot c\int_0^\infty \varepsilon^{\alpha-1}d\varepsilon\left(\frac{1}{e^{\beta(\varepsilon-\mu_B)}-1}\right) \tag{1}$$

When $\mu_B \to \varepsilon_B^-$, we get:

$$N\left(\beta,\mu_B\to\varepsilon_B^-\right) = \infty \tag{2}$$

That's why the condition for the condensation assumption to be valid is $\mu_B \to \varepsilon_B$.

b. The number of occupied excited states of molecules (taking into account that the mass of each molecule is $2m$) is:

$$N = V\xi\left(\frac{3}{2}\right)\left(\frac{mT}{\pi}\right)^{\frac{3}{2}} \tag{3}$$

c. The Hamiltonians describing the atoms and molecules energy are:

$$H^A = \varepsilon^A + \frac{p^2}{2m} \tag{4}$$

$$H^B = \varepsilon^B + \frac{p^2}{2m} \tag{5}$$

Therefore, the graphs of density of states is [see Y04 solution]

The Boltzmann approximation for the atoms is

$$F\left(\varepsilon_A - \mu_A\right) = \frac{1}{e^{\beta(\varepsilon_A - \mu_A)} - 1} \approx e^{-\beta(\varepsilon_A - \mu_A)} \tag{6}$$

It holds whenever the occupation is

$$\beta\left(\varepsilon_A - \mu_A\right) \gg 1 \tag{7}$$

or

$$\varepsilon_A - \mu_A \gg T \tag{8}$$

Since the molecules and the atoms are in chemical equilibrium

$$\mu_B = 2\mu_A \tag{9}$$

While taking into account the condensation condition, one gets

$$\mu_A = \frac{\varepsilon_B}{2} \tag{10}$$

Substituting (10) in (8) one gets:

$$\varepsilon_A - \frac{\varepsilon_B}{2} \gg T \tag{11}$$

So the requirement for Boltzmann's approximation to be valid is:

$$\varepsilon \gg T \tag{12}$$

Where we have defined

$$\varepsilon = 2\varepsilon_A - \varepsilon_B \tag{13}$$

d. We can treat the atoms in the Boltzmann's approximation, therefore the number of atoms in the box is:

$$N_A = V \cdot \left(\frac{mT}{2\pi}\right)^{\frac{3}{2}} \cdot \frac{1}{2} e^{\frac{\mu_A - \varepsilon_A}{T}} \tag{14}$$

(where the prefactor $\frac{1}{2}$ arrose because we are counting molecules and not atoms)
Substituting (10) in (14) one gets:

$$N_A = V \cdot \left(\frac{mT}{2\pi}\right)^{\frac{3}{2}} \cdot \frac{1}{2} e^{-\frac{\varepsilon}{2T}} \tag{15}$$

e. The number of molecules is given by:

$$N = n_0 + V\xi\left(\frac{3}{2}\right)\left(\frac{mT}{\pi}\right)^{\frac{3}{2}} \tag{16}$$

Where n_0 is the number of condensed molecules.
The condition for condensation is:

$$n_0 > 0 \tag{17}$$

The system will be in condensation as long as the number of molecules is bigger than:

$$N > V \cdot \left(\frac{mT}{2\pi}\right)^{\frac{3}{2}} \cdot \left(2^{\frac{3}{2}}\xi\left(\frac{3}{2}\right) + \frac{1}{2}e^{-\frac{\varepsilon}{2T}}\right) \tag{18}$$

f. The pressure from the molecules:

$$p = \xi\left(\frac{5}{2}\right)\left(\frac{m}{\pi}\right)^{\frac{3}{2}} T^{\frac{5}{2}} \tag{19}$$

and the pressure from the atoms :

$$p = \left(\frac{m}{2\pi}\right)^{\frac{3}{2}} T^{\frac{5}{2}} e^{-\frac{\varepsilon}{2T}} \tag{20}$$

Altogether the pressure on the box's walls:

$$p = \left(\frac{m}{2\pi}\right)^{\frac{3}{2}} T^{\frac{5}{2}} \left[2^{\frac{3}{2}}\xi\left(\frac{5}{2}\right) + e^{-\frac{\varepsilon}{2T}}\right] \tag{21}$$

g. Most of the pressure arises from the condensed molecules.