Problem 4 - Almost a phase transition

1 Solution

Let's consider thin wire with linear charge density ρ coaxial with a cylinder of radius R. Negative ions with charge $-q$ are distributed somehow in the cylinder with density n(r), and

$$(-q)\int_0^R n(r)2\pi r dr + \rho' = 0 \tag{1}$$

In general, $\rho \neq \rho'$ because negative charge can be attached to the walls of the cylinder. The electric filed can be found using Gauss theorem:

$$E(r) = \frac{2}{r}(\rho - q\int_0^r n(r_1)r_1 dr_1) \tag{2}$$

Corresponding potential(taking into account radial symmetry):

$$U(r) = U_0 - 2\rho\ln(r) + 2q\int_0^r \frac{dr_1}{r_1}\int_0^{r_1} n(r_2)2\pi r_2 dr_2 \tag{3}$$

Potential energy of one negative ion(-q) in potential U(r):

$$V = -qU(r) = -qU_0 + 2\rho q\ln(r) - 4\pi q^2\int_0^r \frac{dr_1}{r_1}\int_0^{r_1} n(r_2)r_2 dr_2 \tag{4}$$

Using Gibbs measure we can write

$$n(r) = \frac{1}{Z}\exp(\frac{qU_0}{T} - \frac{2\rho q\ln(r)}{T} + \frac{4\pi q^2\int_0^r \frac{dr_1}{r_1}\int_0^{r_1} n(r_2)r_2 dr_2}{T}) \tag{5}$$

Looking at equations (5), (1) one can notice that the system is closed. Taking logarithm and derivative from (5) we obtain:

$$\frac{n'(r)}{n(r)} = -\frac{2\rho q}{rT} + \frac{4\pi q^2}{rT}\int_0^r n(r_2)r_2 dr_2 \tag{6}$$

Taking derivate once again:

$$\frac{n''}{n} - \frac{n'^2}{n^2} = \frac{2\rho q}{r^2 T} - \frac{4\pi q^2}{r^2 T}\int_0^r n(r_2)r_2 dr_2 + \frac{4\pi q^2}{T}n \tag{7}$$

Using expression for integral in (6) and putting it in 7 we obtain:

$$\frac{n''}{n} - \frac{n'^2}{n^2} = -\frac{n'}{rn} + \frac{4\pi q^2}{T} n \tag{8}$$

Finally, we get equation ($A = \frac{4\pi q^2}{T}$)

$$nn'' - n'^2 + \frac{nn'}{r} - An^3 = 0 \tag{9}$$

Using Wolfram Mathematica it's possible to find a solution to this equation(Here $x \equiv r$):

$$n(x) = \frac{1}{Ax^2}(2 + C_1)[-1 + \tanh^2(\sqrt{1 + C_1/2}C_2 - \sqrt{1 + C_1/2}\ln(x)] \tag{10}$$

After renaming constants and simplifying equation:

$$n(x) = -\frac{T}{2\pi q^2 x^2} \frac{C_1}{\cosh^2(\sqrt{C_1}(C_2 - \ln x))} \tag{11}$$

The case of $C_1 > 0$ means that in the solution $n(x) < 0$, which leads to conclusion that in the solvent there are positive charges. This situation is impossible according to the task. It means that in the solvent there are no negative ions - all of them are concentrated on the boundary of the cylinder. And the energy of negative charge per length unit:

$$E_{tot} = -\rho^2 \ln(R) + \frac{1}{2}\rho^2 \ln(R) + C = -\frac{1}{2}\rho^2 \ln(R) + C \tag{12}$$

where C is finite or infinite constant. These observations force us to look for solution with $C_1 < 0$ and its behaviour when $C_1 \longrightarrow 0$.

Making change $C_1 \longrightarrow -C_1$ we obtain:

$$n(x) = \frac{T}{2\pi q^2 x^2} \frac{C_1}{\cos^2(\sqrt{C_1}(C_2 - \ln x))} \tag{13}$$

From equation (2):

$$\frac{\rho'}{2\pi q} = \int_0^R n(x) x dx = \frac{C_1 T}{2\pi q^2} \int_0^R \frac{d\ln x}{\cos^2(\sqrt{C_1}(C_2 - \ln x))} =$$

$$= -\frac{\sqrt{C_1}T}{2\pi q^2}[\tan(\sqrt{C_1}(C_2 - \ln R)) - \tan(\sqrt{C_1}(C_2 - \ln y))], y \longrightarrow 0. \tag{14}$$

Substituting exact form of $n(x)$ into (6):

$$\frac{n'}{n} = -\frac{2}{x} - \frac{2\sqrt{C_1}}{x} \tan \sqrt{C_1}(C_2 - \ln x)$$

$$\frac{n'}{n} = -\frac{2\rho q}{xT} - \frac{2\sqrt{C_1}}{x} [\tan(\sqrt{C_1}(C_2 - \ln R)) - \tan(\sqrt{C_1}(C_2 - \ln y))]$$

$$\Longrightarrow$$

$$\frac{\rho q}{T} - 1 = \sqrt{C_1} \tan(\sqrt{C_1}(C_2 - \ln y)) \tag{15}$$

From (14), (15) we get:

$$\frac{q(\rho - \rho')}{T} - 1 = \sqrt{C_1} \tan(\sqrt{C_1}(C_2 - \ln R))$$

$$\frac{q\rho}{T} - 1 = \sqrt{C_1} \tan(\sqrt{C_1}(C_2 - \ln y)) \tag{16}$$

In the critical case($C_1 = 0$) $T = q\rho$, $\rho' = 0$ which correspond to the situation when there are no negative ions in the solvent - all of them are attached to the walls of the cylinder.

This allows us to write

$$T_c = q\rho \tag{17}$$

Let's find another solution at T_c:

$$C_2 = \ln y + \frac{\pi k}{\sqrt{C_1}}, k \in Z$$

$$\sqrt{C_1}(C_2 - R) \approx \pi/2 + \pi n, n \in Z \tag{18}$$

total amount of charge at an arbitrary x:

$$2\pi \int_y^R n(x) x dx = -\frac{\sqrt{C_1} T}{q^2} [\tan(\sqrt{C_1}(C_2 - \ln R)) - \tan(\sqrt{C_1}(C_2 - \ln y))] \tag{19}$$