Ex 4016: Adsorption of polar molecules to surface

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The problem:
consider a 2D adsorbing surface in equilibrium with a 3D gas of atoms that has temperature T and chemical potential μ.On the surface there are M sites ,each site can absorb at most one atom . At the adsorption site an atom forms an electric dipole d that can be oriented at any direction away from the surface (see figure).
In presence of an electric field $\mathcal{E}$ perpendicular to the surface the dipole has energy $-\mathcal{E}dcos(\theta)$ where $|\theta| < \pi/2$ is the angle between d and $\mathcal{E}$.
(a) Calculate the grand partition function $\mathcal{Z}(\beta, \mu, \mathcal{E})$
(b) Derive the average number N of absorbed atoms.
(c) Use the formal approach to define the average polarization D as the expectation value of a system observable. Derive the state equation for D.
(d) What are the results in the limit $\mathcal{E} \to 0$ and in particular what is the ratio D/N. Explain how this result can be obtained without going through the formal derivation. .

The Solution:

(a) We shell solve this problem in the grand canonical scheme, by doing so we can observe each site individually for they are indifferent to each other, and we got M sites. First of all we calculate the dipole distribution function, one should remember that $|\theta| < \pi/2$ $d\Omega_{total} = 2\pi$ and not $d\Omega_{total} = 4\pi$ whereas $d\Omega_{total}$ is the solid angle.

$$Z_{dipole(\beta\mathcal{E}d)} = \frac{1}{d\Omega_{total}} \int d\Omega e^{\beta\mathcal{E}dcos(\theta)} = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \int_0^{\frac{\pi}{2}} d\theta sin(\theta) e^{\beta\mathcal{E}dcos(\theta)} = \quad (1)$$

$$= [-\frac{e^{\beta d\mathcal{E}cos(\theta)}}{\beta\mathcal{E}d}]_0^{\frac{\pi}{2}} = \frac{e^{\beta\mathcal{E}d} - 1}{\beta\mathcal{E}d} = Z_{dipole(\beta\mathcal{E}d)}.$$

Now we can write the distribution function for a single site (reminder: $N = 0, 1$).

$$\mathcal{Z}(\beta, \mu, \mathcal{E})_1 = 1 + e^{\beta\mu} Z_{dipole(\beta\mathcal{E}d)} = 1 + e^{\beta\mu} \frac{e^{\beta\mathcal{E}d} - 1}{\beta\mathcal{E}d}. \quad (2)$$

no relation between sites

$$\Rightarrow \mathcal{Z}(\beta, \mu, \mathcal{E})_M = \mathcal{Z}(\beta, \mu, \mathcal{E})_1^M \quad (3)$$

(b) $\Omega = -K_b T ln \mathcal{Z}(\beta, \mu, \mathcal{E})_M$.

$$N = -\frac{\partial\Omega}{\partial\mu} = K_b T \frac{\partial ln \mathcal{Z}(\beta, \mu, \mathcal{E})_M}{\partial\mu} = M K_b T \frac{\partial ln(1 + e^{\beta\mu} \frac{e^{\beta\mathcal{E}d}-1}{\beta\mathcal{E}d})}{\partial\mu} = M K_b T \frac{\beta e^{\beta\mu} \frac{e^{\beta\mathcal{E}d}-1}{\beta\mathcal{E}d}}{(1 + e^{\beta\mu} \frac{e^{\beta\mathcal{E}d}-1}{\beta\mathcal{E}d})}. \quad (3)$$

$$\frac{N}{M} = \frac{e^{\beta\mu} Z_{dipole(\beta\mathcal{E}d)}}{1 + e^{\beta\mu} Z_{dipole(\beta\mathcal{E}d)}} = \frac{1}{1 + \frac{e^{-\beta\mu}}{Z_{dipole(\beta\mathcal{E}d)}}}. \quad (4)$$

(c) $D = < cos(\theta) >_M$

$$< dcos(\theta) >_1 = d < cos(\theta) >_1 = -\frac{\partial\Omega}{\partial\mathcal{E}} = K_b T \frac{\partial ln \mathcal{Z}(\beta, \mu, \mathcal{E})_1}{\partial\mathcal{E}} = K_b T \frac{e^{\beta\mu}(\beta^2 d^2 \mathcal{E} e^{\beta\mathcal{E}d} - \beta d(e^{\beta\mathcal{E}d} - 1))}{\mathcal{Z}(\beta, \mu, \mathcal{E})_1 (\beta\mathcal{E}d)^2} \quad (5)$$

$$d < cos(\theta) >_1 = \frac{e^{\beta\mu}(\beta d^2 \mathcal{E} e^{\beta\mathcal{E}d} - d(e^{\beta\mathcal{E}d} - 1))\beta\mathcal{E}d}{(\beta\mathcal{E}d)^2 (\beta\mathcal{E}d + e^{\beta\mu}(e^{\beta\mathcal{E}d} - 1))} \quad (6)$$

Notice that :

$$\frac{\partial\mathcal{Z}(\beta, \mu, \mathcal{E})_1}{\partial\mathcal{E}} = e^{\beta\mu} \frac{\partial Z_{dipole(\beta\mathcal{E}d)}}{\partial\mathcal{E}} = e^{\beta\mu} \frac{\beta}{2\pi} \int_0^{2\pi} d\varphi \int_0^{\frac{\pi}{2}} d\theta dcos(\theta) sin(\theta) e^{\beta\mathcal{E}dcos(\theta)} \quad (7)$$

There for

$$K_b T \frac{\partial ln \mathcal{Z}(\beta, \mu, \mathcal{E})_1}{\partial\mathcal{E}} = e^{\beta\mu} \frac{\int_0^{\frac{\pi}{2}} d\theta sin(\theta) dcos(\theta) e^{\beta\mathcal{E}dcos(\theta)}}{\mathcal{Z}_1} = < dcos(\theta) >_1 \quad (8)$$

And for M sites

$$< dcos(\theta) >_M = Md < cos(\theta) >_1 = dD \quad (9)$$

(d) Now we consider the case $\mathcal{E} \to 0$, which will affect $Z_{dipole(\beta\mathcal{E}d)}$

$$Z_{dipole(\beta\mathcal{E}d)} =_{\mathcal{E}\to 0} \frac{e^{\beta\mathcal{E}d} - 1}{\beta\mathcal{E}d} =_{\mathcal{E}\to 0} \frac{1 + \beta\mathcal{E}d - 1}{\beta\mathcal{E}d} = 1 \tag{10}$$

By putting our limit result in $< N >$ will get

$$\frac{N}{M} =_{\mathcal{E}\to 0} \frac{1}{1 + e^{-\beta\mu}} \tag{11}$$

which is fermi dirac distribution.
This is no surprise, after all if we neglect the electric forces and energy all that is left is the same constrains (conditions) as for fermions.
We now calculate the average polarization D at $\mathcal{E} \to 0$

$$< dcos(\theta) >_1 =_{\mathcal{E}\to 0} \frac{e^{\beta\mu}\beta\mathcal{E}d(\beta\mathcal{E}d^2(1 + \beta\mathcal{E}d) - \beta\mathcal{E}d^2)}{(\beta\mathcal{E}d)^2(\beta\mathcal{E}d + e^{\beta\mu}\beta\mathcal{E}d)} = \tag{12}$$

$$= \frac{e^{\beta\mu}(\beta\mathcal{E}d)^3 d}{(\beta\mathcal{E}d)^3(1 + e^{\beta\mu})} = \frac{d}{1 + e^{-\beta\mu}}.$$

$$dD = Md < cos(\theta) >_1 =_{\mathcal{E}\to 0} \frac{Md}{1 + e^{-\beta\mu}} = d < N >$$

We can see that the ratio $\frac{D}{N} = 1$ and we could explain this by stating that when the external field goes to zero $\mathcal{E} \to 0$ then θ can be referred to as 0 always. so for each absorbed particle will get a donation of 1 to the polarization and will get that $D = N$