EXERCISES - GRAND CANONICAL ENSEMBLE

1. Find the equation of state of the ideal gas using the grand canonical ensemble and find the dependency of the chemical potential on the pressure.

sol: $PV = \langle N \rangle k_B T$; $\mu = k_B T \log\left(\frac{P}{\lambda^3 k_B T}\right)$, with $\lambda = \frac{\sqrt{2\pi m k_B T}}{h}$

2. Consider an adsorbent surface having N_0 sites each of which can adsorb one gas molecule. Suppose that it is in contact with an ideal gas with the chemical potential μ. An adsorbed molecule has energy $-\epsilon_0$ compared to one in a free state. Determine the coverage ratio of adsorbed gas particles at equilibrium Θ.

sol:

3. At a given temperature T a surface with N_0 adsorption centers has $N_a \ll N_0$ adsorbed molecules. Suppose that there are no interactions between molecules. Show that the chemical potential of the adsorbed gas is given by $\mu = K_B T \log \frac{N_{\text{ads}}}{(N_0 - N_{\text{ads}})\, a(T)}$. What is the meaning of the function $a(T)$?

   NOTE: Suppose akin Ex. 3 that an adsorbed particle has energy $-\epsilon_0$.

4. Find the dependency of the expected number adsorbed gas molecules on pressure at equilibrium (use results form Ex 1, 2 and 3 and equate the chemical potentials).

Sol: $\langle N_{\text{ads}} \rangle = N_0 \frac{P\lambda_T^3}{k_B T} e^{\epsilon/k_B T}$ for ($N_{\text{ads}} \ll N_0$)

5. A classical ideal gas is contained in a box of fixed volume V whose walls have N_0 absorbing sites. Each of these sites can adsorb at most two particles, the energy of each adsorbed particle being $-\epsilon_0$. The total number of particles N is fixed and greater than $2N_0$. Use the grand canonical ensemble to obtain the equation of state of the gas in the presence of the absorbing walls and to find the average number of absorbed particles in the limits $T \to 0$ and $T \to \infty$

Sol: $$\frac{PV}{Nk_BT} = 1 - \frac{\langle N_{\text{ads}}\rangle}{N} = 1 - \frac{N_0}{N}\frac{Pf + 2(Pf)^2}{1 + Pf + (Pf)^2}$$

$$\langle N_{\text{ads}}\rangle = N_0 \frac{Pf + 2(Pf)^2}{1 + Pf + (Pf)^2}$$

with $f = \left(\frac{h^2}{2\pi m}\right)^{3/2} \left(k_BT\right)^{-5/2} e^{\beta\epsilon_0} = e^{\beta\epsilon_0}\frac{1}{k_BT\lambda_T^3}$