

Statistical Mechanics - Class Exercise 4

December 5, 2022

Exercise 4016 - Polar adsorption of particles to a surface

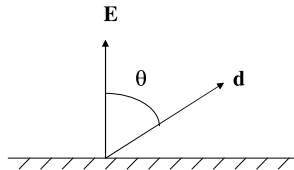
Consider an M site system in an equilibrium with gas of particles that have mass m . The chemical potential of the gas is μ and its temperature is T . A particle can bind to a site. Each site can absorb at most one atom. The binding energy is ε , and the length of the bonds is a . In such state it behaves as a rotor that has moment of inertia $I = ma^2$, and a dipole moment qa . The polarization can be in any direction away from the surface (2π steradians).

Tip: The kinetic part in a rotor Hamiltonian is

$$\frac{1}{2I} \left[p_\theta^2 + \frac{p_\varphi^2}{\sin^2(\theta)} \right]$$

1. Calculate the partition function $Z_\perp(\beta, f)$ for an occupied site, assuming electric field f perpendicular to the surface.
2. Calculate the partition function $Z_\parallel(\beta, f)$ for an occupied site, assuming electric field f parallel to the surface.
3. Express the M site grand partition function $\mathcal{Z}(\beta, \mu, f)$ in terms of Z . Additionally, write an explicit expression for zero field.
4. Express the average number N of adsorbed particles in terms of Z . Additionally, write an explicit expression for zero field.
5. Find a leading order expression for the average polarization D/N for weak perpendicular f .
6. Find a leading order expression for the average polarization D/N for weak parallel f .

(*) Tip: one can use a shortcut in the calculation of Z , bypassing the integration over the momentum variables.



Answer

1. The Hamiltonian for one adsorb atom in perpendicular electric field:

$$H = \frac{1}{2I} \left[p_\theta^2 + \frac{p_\varphi^2}{\sin^2(\theta)} \right] - f \cdot qa \cos(\theta)$$

Where the \hat{z} direction is perpendicular to the surface.

The partition function $Z_\perp(\beta, f)$

$$\begin{aligned} Z_\perp(\beta, f) &= \int \frac{d\theta d\varphi dp_\theta dp_\varphi}{(2\pi)^2} e^{-\beta H} = \int_0^{\frac{\pi}{2}} d\theta \int_0^{2\pi} d\varphi \sqrt{\frac{I}{2\pi\beta}} \sqrt{\frac{I \sin^2(\theta)}{2\pi\beta}} e^{\beta f qa \cos(\theta)} \\ &= \frac{I}{\beta} \int_0^{\frac{\pi}{2}} d\theta \sin(\theta) e^{\beta f qa \cos(\theta)} = \frac{I}{\beta} \int_0^1 du e^{\beta f qa u} = \frac{I}{\beta} \frac{(e^{\beta f qa} - 1)}{\beta f qa} \end{aligned}$$

2. The Hamiltonian for one adsorb atom in parallel electric field is the same Hamiltonian, but now we take the \hat{z} direction to be parallel to the surface.

The partition function $Z_\parallel(\beta, f)$

$$\begin{aligned} Z_\parallel(\beta, f) &= \int \frac{d\theta d\varphi dp_\theta dp_\varphi}{(2\pi)^2} e^{-\beta H} = \frac{I}{2\pi\beta} \int_0^\pi d\theta \int_0^\pi d\varphi \sin(\theta) e^{\beta f qa \cos(\theta)} \\ &= \frac{I}{2\beta} \int_{-1}^1 du e^{\beta f qa u} = \frac{I}{2\beta} \frac{(e^{\beta f qa} - e^{-\beta f qa})}{\beta f qa} = \frac{I}{\beta} \frac{\sinh(\beta f qa)}{\beta f qa} \end{aligned}$$

We can see that for $f \rightarrow 0$

$$Z_\perp(\beta, 0) = Z_\parallel(\beta, 0) = \frac{I}{\beta} = \frac{Tm2\pi a^2}{2\pi} = \frac{2\pi a^2}{\lambda_T^2}$$

3. In the grand canonical formalism

$$\mathcal{Z}(\beta, \mu) = \sum_R e^{-\beta(E_R - \mu N_R)}$$

in our case the “particles” is the sites and this are “Fermionic sites”, so for site that adsorb atom $E = H + \epsilon$, $N = 1$ and for empty site $E = 0$, $N = 0$.

For M sites we get

$$\mathcal{Z}(\beta, \mu, f) = \left(1 + Z(\beta, f) e^{-\beta(\epsilon - \mu)} \right)^M$$

For zero field

$$\mathcal{Z}(\beta, \mu, 0) = \left(1 + \frac{I}{\beta} e^{-\beta(\epsilon - \mu)} \right)^M$$

4. We can obtain the number N of adsorbed particles by derivative of the grand partition function

$$N(f) = \frac{1}{\beta} \frac{\partial \ln \mathcal{Z}}{\partial \mu} = M \frac{Z(\beta, f) e^{-\beta(\epsilon - \mu)}}{1 + Z(\beta, f) e^{-\beta(\epsilon - \mu)}} = \frac{M}{1 + Z^{-1}(\beta, f) e^{\beta(\epsilon - \mu)}}$$

For zero field

$$N(0) = \frac{M}{1 + \frac{\beta}{I} e^{\beta(\epsilon - \mu)}}$$

5. The average polarization D/N is the polarization of one absorb site, we can calculate this from the partition function. for weak perpendicular f

$$Z_{\perp}(\beta, f) = \frac{I}{\beta} \frac{(e^{\beta f q a} - 1)}{\beta f q a} \approx \frac{I}{\beta} \frac{\left(1 + \beta f q a + \frac{1}{2} (\beta f q a)^2 - 1\right)}{\beta f q a} = \frac{I}{\beta} \left(1 + \frac{1}{2} \beta f q a\right)$$

$$\frac{D}{N} = \frac{1}{\beta} \frac{\partial \ln Z_{\perp}(\beta, f)}{\partial f} = \frac{\frac{1}{2} q a}{\left(1 + \frac{1}{2} \beta f q a\right)} \approx \frac{1}{2} q a$$

6. In the same way

$$Z_{\parallel}(\beta, f) = \frac{I \sinh(\beta f q a)}{\beta f q a} \approx \frac{I}{\beta} \frac{\beta f q a + \frac{1}{3!} (\beta f q a)^3}{\beta f q a} = \frac{I}{\beta} \left(1 + \frac{1}{6} (\beta f q a)^2\right)$$

$$\frac{D}{N} = \frac{1}{\beta} \frac{\partial \ln Z_{\parallel}(\beta, f)}{\partial f} = \frac{1}{\beta} \frac{\frac{1}{3} (\beta q a)^2 f}{\left(1 + \frac{1}{6} (\beta f q a)^2\right)} \approx \frac{1}{3} \beta (q a)^2 f$$

Exercise 4211 - The law of mass action for diatomic molecules

Consider a diatomic AB molecule, where A and B are different spin 0 atoms, each having a 1-unit atomic mass m_0 . The length of the molecule is a , the binding energy is $-\epsilon_0$, and the vibration frequency of the bond is ω_0 . The vibration amplitude is much smaller compared with a . The temperatures are not low, namely $T \gg 1/(m_0 a^2)$, such that the rotation-spectrum can be treated as a continuum. For higher temperatures ($T \gg \omega_0$) also the vibration-spectrum can be treated using a classical approximation.

In item (3) below we consider Hydrogen H_2 , Deuterium D_2 , and HD molecules. The respective masses of the atoms are m_H, m_D . Note that the Deuterium nucleus has spin 1. Assume that neither the energy nor the “spring constant” of the binding are affected by the $H \leftrightarrow D$ replacement.

1. Find the one molecule partition function Z^{AB} for an AB molecule that is held in a container that has volume L^3 . Assume that the temperature is not low, but not necessarily high.
2. Write the law of mass action for the reaction $A + B \leftrightarrow AB$. Find an explicit expression for the equilibrium constant $K(T)$ in the high temperature regime.
3. Write the law of mass action for the reaction $H_2 + D_2 \leftrightarrow 2HD$. Express the equilibrium constant $K(T)$ in terms of one-particle partition functions Z^C , were C stands for H_2 , and D_2 , and HD .
4. Find expressions for the ratio Z^C/Z^{AB} in the high temperature regime, where A and B are distinct spinless atoms that have the same masses as that of the C constituents. Explain why the high temperature assumption is essential in order to get a simple result.
5. What is the explicit result for $K(T)$ of item (3) in the high temperature regime?

Tip: The Hamiltonian of a diatomic molecule consist of center of mass degrees of freedom, and of a relative motion degrees of freedom. The latter involves the reduced mass $m_A m_B / (m_A + m_B)$. For intermediate calculations you can use the notation α for spring constant.

Answer

1. To find the one molecule partition function Z^{AB} we need to separate the motion to the center of mass motion, and of a relative motion

$$H = -\epsilon_0 + \frac{P^2}{2M} + \frac{1}{2}m\omega_0^2x^2 + \frac{\ell^2}{2I}$$

When

$$M = m_A + m_B = 2m_0, m = \frac{m_A m_B}{(m_A + m_B)} = \frac{m_0}{2}$$

$$I = 2m_0 \left(\frac{a}{2}\right)^2, \omega_0 = \sqrt{\frac{\alpha}{m}} = \sqrt{\frac{2\alpha}{m_0}}$$

$$E = -\epsilon_0 + \frac{P^2}{2M} + \omega_0 \left(n + \frac{1}{2}\right) + \frac{l(l+1)}{2I}$$

In the continuum limit for the rotation

$$Z_l = \sum_l (2l+1) e^{-\beta \frac{l(l+1)}{2I}} \approx \int_0^\infty 2l e^{-\beta \frac{l^2}{2I}} dl = \frac{2I}{\beta}$$

so we get

$$Z^{AB} = \left(\frac{L}{\lambda_M}\right)^3 e^{\beta\epsilon_0} \frac{1}{2 \sinh\left(\frac{1}{2}\beta\omega_0\right)} \frac{m_0 a^2}{\beta}$$

$$\lambda_M = \sqrt{\frac{2\pi}{MT}} = \frac{1}{\sqrt{2}} \sqrt{\frac{2\pi}{m_0 T}} = \frac{1}{\sqrt{2}} \lambda_T$$

$$Z^{AB} = \left(\frac{\sqrt{2}L}{\lambda_T}\right)^3 e^{\beta\epsilon_0} \frac{1}{2 \sinh\left(\frac{1}{2}\beta\omega_0\right)} \frac{m_0 a^2}{\beta}$$

2. The partition functions for the atoms A and B are

$$Z^A = \left(\frac{L}{\lambda_T}\right)^3 = Z^B$$

for the reaction $A + B \leftrightarrow AB$

$$Z = \sum_n Z_{N_{AB}-n}^{AB} Z_{N_A+n}^A Z_{N_B+n}^B = \sum_n e^{-\beta F(n)}$$

where

$$F(n) = F_{AB}(N_{AB} - n) + F_A(N_A + n) + F_B(N_B + n)$$

to find the Chemical equilibrium we need to find most probable value for n

$$\frac{\partial F}{\partial n} = -\mu_{AB}(N_{AB} - n) + \mu_A(N_A + n) + \mu_B(N_B + n) = 0$$

we remember that

$$\mu = \frac{\partial F}{\partial N} = \frac{\partial}{\partial N} \left(-T \ln \left(\frac{Z_1^N}{N!} \right) \right) = T \ln \left(\frac{N}{Z_1} \right)$$

$$\frac{(N_{AB} - n)}{(N_A + n)(N_B + n)} = \frac{Z^{AB}}{Z^A Z^B}$$

$$\frac{\frac{(N_{AB} - n)}{V}}{\frac{(N_A + n)}{V} \frac{(N_B + n)}{V}} = K(T) = \left(\sqrt{2}\lambda_T\right)^3 e^{\beta\epsilon_0} \frac{1}{2 \sinh\left(\frac{1}{2}\beta\omega_0\right)} m_0 a^2 T$$

in the high temperature regime for vibration $T \gg \omega_0$

$$K(T) \approx \left(\sqrt{2}\lambda_T\right)^3 e^{\beta\epsilon_0} \frac{m_0}{\omega_0} a^2 T^2$$

3. We have three molecule partition functions that differ from one another by the mass and the spin

$$Z^{H_2} = \left(\frac{1}{2}\right)_{\text{Gibs}} (2 \cdot 2)_{\text{spin}} \left(\frac{L}{\lambda_{M_{H_2}}}\right)^3 e^{\beta\epsilon_0} \frac{1}{2 \sinh\left(\frac{1}{2}\beta\sqrt{\frac{\alpha}{m_{H_2}}}\right)} \frac{2m_{H_2}a^2}{\beta}$$

$$Z^{D_2} = \left(\frac{1}{2}\right)_{\text{Gibs}} (3 \cdot 3)_{\text{spin}} \left(\frac{L}{\lambda_{M_{D_2}}}\right)^3 e^{\beta\epsilon_0} \frac{1}{2 \sinh\left(\frac{1}{2}\beta\sqrt{\frac{\alpha}{m_{D_2}}}\right)} \frac{2m_{D_2}a^2}{\beta}$$

$$Z^{HD} = (2 \cdot 3)_{\text{spin}} \left(\frac{L}{\lambda_{M_{HD}}}\right)^3 e^{\beta\epsilon_0} \frac{1}{2 \sinh\left(\frac{1}{2}\beta\sqrt{\frac{\alpha}{m_{HD}}}\right)} \frac{2m_{HD}a^2}{\beta}$$

the law of mass action for the reaction $H_2 + D_2 \leftrightarrow 2HD$

$$\frac{(N_{HD} - 2n)^2}{(N_{H_2} + n)(N_{D_2} + n)} = \frac{(Z^{HD})^2}{Z^{H_2} Z^{D_2}} = K(T)$$

4. in the high temperature regime

$$Z^{H_2} = \left(\frac{1}{2}\right)_{\text{Gibs}} (2 \cdot 2)_{\text{spin}} \left(\frac{L}{\lambda_{M_{H_2}}}\right)^3 e^{\beta\epsilon_0} \frac{1}{2 \sinh\left(\frac{1}{2}\beta\sqrt{\frac{\alpha}{m_{H_2}}}\right)} \frac{2m_{H_2}a^2}{\beta}$$

$$\approx \left(\frac{1}{2}\right)_{\text{Gibs}} (2 \cdot 2)_{\text{spin}} \left(\frac{L}{\sqrt{\frac{2\pi}{T}}}\right)^3 M_{H_2}^{\frac{3}{2}} e^{\beta\epsilon_0} \frac{1}{\sqrt{\alpha}} \frac{2m_{H_2}^{\frac{3}{2}}a^2}{\beta^2} = \left(\frac{1}{2}\right)_{\text{Gibs}} (2 \cdot 2)_{\text{spin}} \left(\frac{L}{\sqrt{\frac{2\pi}{T}}}\right)^3 e^{\beta\epsilon_0} \frac{1}{\sqrt{\alpha}} \frac{2a^2}{\beta^2} (m_H m_H)^{\frac{3}{2}}$$

The ratio

$$\frac{Z^{H_2}}{Z^{AB}} \approx \left(\frac{1}{2}\right)_{\text{Gibs}} (2 \cdot 2)_{\text{spin}} \left(\frac{m_H m_H}{m_A m_B}\right)^{\frac{3}{2}} = 2$$

in the same way

$$\frac{Z^{D_2}}{Z^{AB}} \approx \frac{9}{2}$$

$$\frac{Z^{HD}}{Z^{AB}} \approx 6$$

5. In the high temperature regime

$$K(T) = \frac{(Z^{HD})^2}{Z^{H_2} Z^{D_2}} \approx \frac{6^2 (m_H m_D)^3}{2 (m_H m_H)^{\frac{3}{2}} \frac{9}{2} (m_D m_D)^{\frac{3}{2}}} = 4$$