* Exercise 1 The Gibbs adsorption isotherm

The Gibbs adsorption isotherm relates the changes in surface tension of a mixture to the change in the chemical potential (or concentration) of a solute:

$$\mathrm{d}\gamma = -RT\frac{\Gamma}{c}\mathrm{d}c.$$

Consider the concentration dependence of the surface tension of a water/ethanol mixture at 20 °C:

x_{ethanol}	0.020	0.042	0.065
γ [mN/m]	56.41	48.14	42.72

(a) Find out the relation between the surface excess Γ and the surface tension of the solution at two different concentrations.

(b) Compute the surface excess of ethanol Γ considering the interval between 2% and 4% molar concentration.

(c) Compare it with the excess computed using the interval between 4% and 6.5% molar concentration. How does the surface excess change as a function of concentration?

(d) Is the concentration of ethanol in the vicinity of the surface larger or smaller than in the bulk of the solution?

Solution to Exercise 1

Question (a). Integrate the first equation over a finite concentration change and get

$$\int_{\gamma_1}^{\gamma_2} d\gamma' = -RT\Gamma\int_{c_1}^{c_2}\frac{dc'}{c'} \quad \Rightarrow \quad \gamma_2 - \gamma_1 = -RT\Gamma\ln\frac{c_2}{c_1}.$$

The surface excess is then

$$\Gamma = \frac{\gamma_2 - \gamma_1}{RT\ln c_1/c_2}.$$

Question (b). We can obtain Γ from

$$\Gamma = \frac{\gamma_2 - \gamma_1}{RT\ln c_1/c_2} = \frac{(48.14 - 56.41)\,\mathrm{mN\,m^{-1}}}{8.31\,\mathrm{J\,mol^{-1}\,K^{-1}} \times 293\,\mathrm{K} \times \ln(0.02/0.042)} = \frac{8.27\times10^{-3}\,\mathrm{J\,m^{-2}}}{8.31\times293\times0.74\ \mathrm{J/mol}} = 4.59\times10^{-6}\,\mathrm{mol\,m^{-2}}$$

Question (c). Repeating for the second interval,

$$\Gamma = 5.09\times10^{-6}\,\mathrm{mol\,m^{-2}}.$$

Considering the experimental uncertainty, the Gibbs isotherm holds very well.

Question (d). The surface excess Γ describes the excess of solute relative to the solvent. Since it is positive, there is a larger concentration of ethanol at the surface than in the bulk. Note that we could have seen this just by looking at the fact that γ was decreasing with increasing concentration of ethanol.

*** Exercise 2 Chemisorption: charge transfer in metals

Consider an atom, X, approaching the surface of a metal. The Fermi level and the work function of the metal are E_F and W, respectively. The free atom, X, can be electronically characterized by two energies called the ionization (I) and the affinity (A) energies, respectively.

We denote with:

- X^+ an atom X which **has lost** an electron in its valence shell, with the lost electron being put at the vacuum level;
- X^- an atom X which **has gained** an additional electron taken from the vacuum level.

The ionization energy, I, is the difference between the energies of X^+ and X and is always positive. The affinity energy, A, is the difference between the energies of X and X^-; thus it can be either positive or negative, depending on whether X^- is stable or unstable. These energies are not equal due to the Coulomb repulsion between electrons.

We can define an effective Coulomb integral, U_{at}, which is the energy involved in the reaction

$$2X \rightarrow X^+ + X^-$$

and

$$U_{at} = I - A,$$

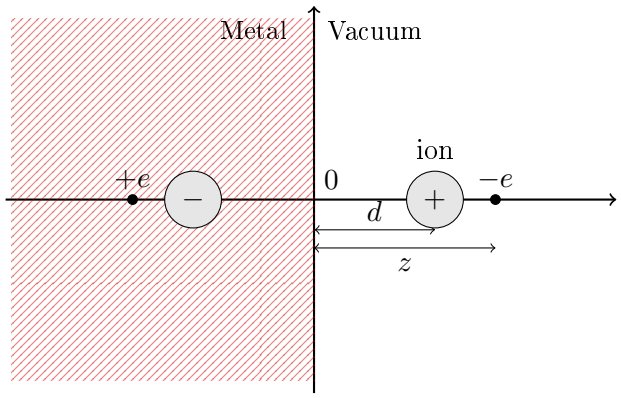
which is positive since $A < I$. As the atom comes nearer to the surface, the electronic interactions with the metal modify the ionization and affinity energies. These modifications can be evaluated with the help of classical electrostatic (the "method of image charges"), at least for distances sufficiently large to neglect overlap between the atom's and metal's orbitals.

(a) Variation of the ionization energy

(i) To determine the variation of the ionization energy, consider the image below which depicts a scheme of a positively ionized adatom at a distance d from a metal surface. Calculate the z-component of the electrostatic force acting on outgoing electron. *Hints: the figure already helps you by drawing the corresponding "image charges" of both the electron and the positive ion. Recall the definition of the electric field generated by a point charge Q placed at $\vec{r}'$:*

$$\vec{E}(\vec{r}) = Q\frac{\vec{r} - \vec{r}'}{\|\vec{r} - \vec{r}'\|^3}$$

Cont.



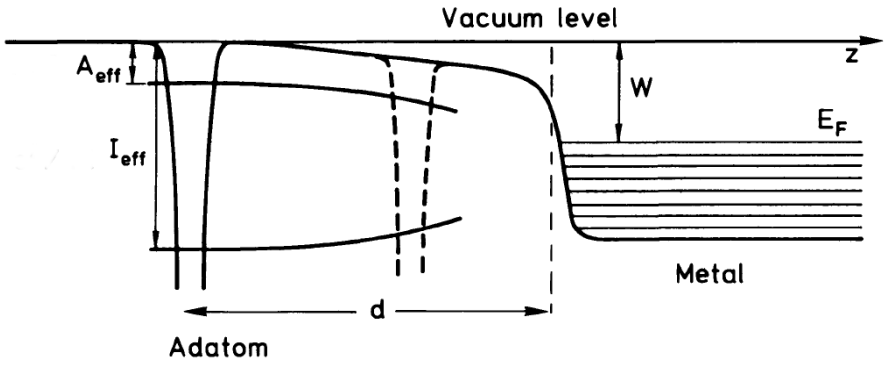
(ii) Is the force repulsive or attractive? What's the effective ionization energy when taking into account this contribution?

(b) Variation of the affinity energy

(i) When an additional electron approaches the adsorbate, there will be a contribution to the affinity energy of the adatom. What's effective affinity energy?

(ii) What's the Coulomb integral? (i.e. $U = I_{\text{eff}} - A_{\text{eff}}$)

(c) In a very qualitative way, and taking into account that physically we must have $I_{\text{eff}} > A_{\text{eff}}$, try to discuss, with the help of the following figure, the three cases that can be distinguished depending on the value of the metal work function W.



Solution to Exercise 2

(a-i) From the figure, there are two contribution to the force acting on the outgoing electron. The first is due to its own image:

$$F_1 = -eE_1 = -\frac{e^2}{4z^2}.$$

The second contribution, F_2, is due to the ion image charge, placed within the metal at $-d$.

Cont.

$$F_2 = -eE_2 = \frac{e^2}{(d+z)^2}.$$

Summing up the two contributions

$$F_z = F_1 + F_2 = -\frac{e^2}{4z^2} + \frac{e^2}{(d+z)^2}.$$

(a-ii) The force is repulsive if $z > d$. The ionization energy is decreased by an amount given by the work done against the electrostatic force to take an electron from the adatom and put it at infinite distance. We must evaluate the integral

$$\int_d^\infty F_z \, dz = \frac{e^2}{4d} = |W_{\text{image}}|,$$

and therefore the effective ionization energy is

$$I_{\text{eff}} = I - |W_{\text{image}}|,$$

so $I_{\text{eff}} < I$ (which make sense, since the force is repulsive).

(b-i) In this case the only contribution comes from the additional electron's image force. This force is attractive and the modification of the affinity energy is

$$\int_{-\infty}^d \frac{e^2}{4z^2} \, dz = \frac{e^2}{4d} = |W_{\text{image}}|,$$

and thus

$$A_{\text{eff}} = A + |W_{\text{image}}|.$$

(b-ii) Finally, the effective Coulomb integral becomes

$$U = I_{\text{eff}} - A_{\text{eff}} = U_{\text{at}} - 2|W_{\text{image}}|$$

(c) The three possible cases are:

1. $A_{\text{eff}} < W < I_{\text{eff}}$: the Fermi level lies between the effective affinity ($-A_{\text{eff}}$) and ionization levels ($-I_{\text{eff}}$). Under these conditions the adatom tends to remain neutral since the transfer of an electron to or from the metal would cost some energy.

2. $(I + A)/2 < I_{\text{eff}} < W$: the effective ionization level is above the Fermi level of the metal. The adatom tends to become a positively charged ion since one gains the energy $W - I_{\text{eff}}$ when transferring an electron from the adatom to the metal.

3. $W < A_{\text{eff}} < (I + A)/2$: the effective affinity level is below the Fermi energy of the metal. The adatom tends to become a negatively charged ion since one gains the energy $A_{\text{eff}} - W$ when transferring an electron from the metal to the adatom.

The End.