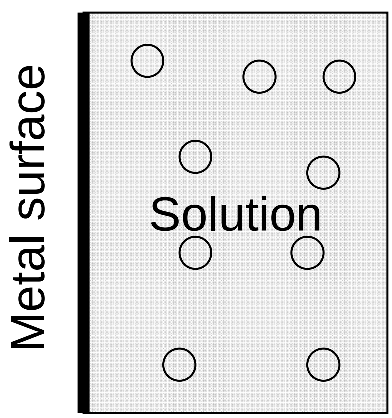
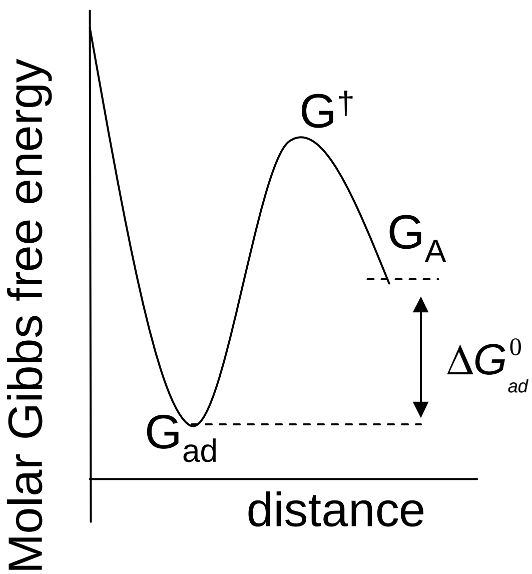
Adsorption / Desorption

Consider a metal electrode and adsorbate in the solution





Adsorption rate ν_{ad}

$$\nu_{ad} \propto (1-\theta)\, exp\left(-\frac{G^{\dagger}-G_A}{RT}\right)$$

Desorption rate ν_{des}

$$\nu_{des} \propto \theta\, exp\left(-\frac{G^{\dagger}-G_{ad}}{RT}\right)$$

At equilibrium: $\nu_{ad} = \nu_{des}$

$$\frac{\theta}{(1-\theta)} = \frac{K_{ad}}{K_{des}} c_A\, exp\left(-\frac{\Delta G_{ad}}{RT}\right)$$

$$\Delta G_{ad} = G_{ad} - G_A$$

We define:

$$\kappa = \frac{K_{ad}}{K_{des}} \quad \text{and} \quad K = \frac{K_{ad}}{K_{des}}\, exp\left(-\frac{\Delta G_{ad}}{RT}\right)$$

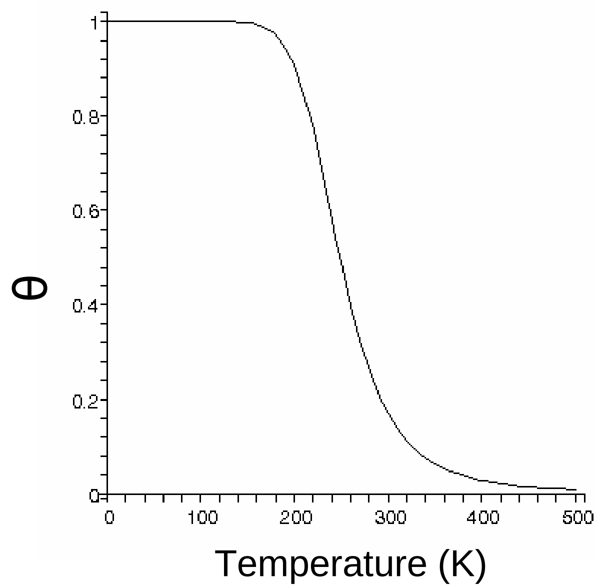
$$\Rightarrow \theta = \frac{Kc_A}{1+Kc_A}$$

Example: H / Pd and H / Cu

• Lets calculate the coverage θ as a function of temperature
For hydrogen adsorption on Pd metal in the solution with c_A=0.1M.

$$\kappa = \frac{K_{ad}}{K_{des}} \approx 0.001$$

$$\Delta G_{ad} \approx -2x10^4 \ J/mol$$



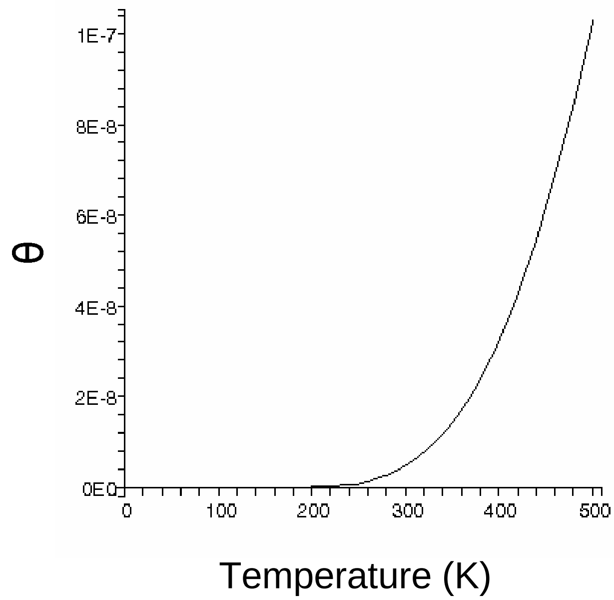
At low temperature the adsorbents can not leave the surface due to their low kinetic energy

What assumptions did we used here?

Now, lets calculate the coverage θ as a function of temperature
For hydrogen adsorption on Cu metal in the solution with c_A=0.1M.

$$\kappa = \frac{K_{ad}}{K_{des}} \approx 0.0001$$

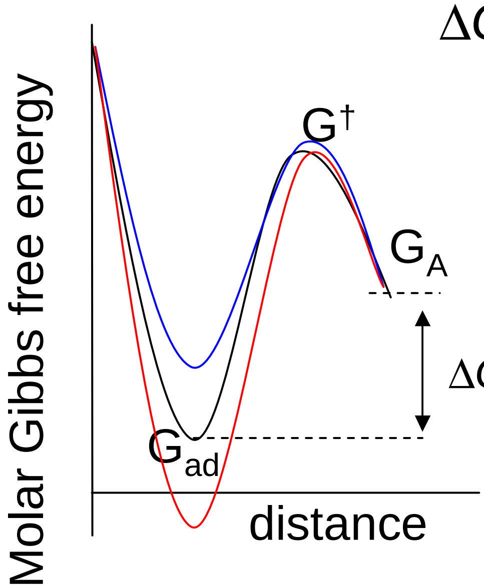
$$\Delta G_{ad} \approx 1.9x10^4 \ J/mol$$



So far we neglect the effect of adsorbate adsorbate interaction and heterogeneity **(Langmuir isotherm)**

Now we consider these interactions **(Frumkin isotherm)**.
We assume a mean field interaction as:

$$\Delta G_{ad} = \Delta G^{0}_{ad} + \gamma\theta$$



How γ affects the shape of the plot?

Blue line: $\gamma > 0$

Red line: $\gamma < 0$

$\gamma < 0$ → larger ΔG → larger θ → attractive

$\gamma > 0$ → smaller ΔG → lowerθ → repulsive

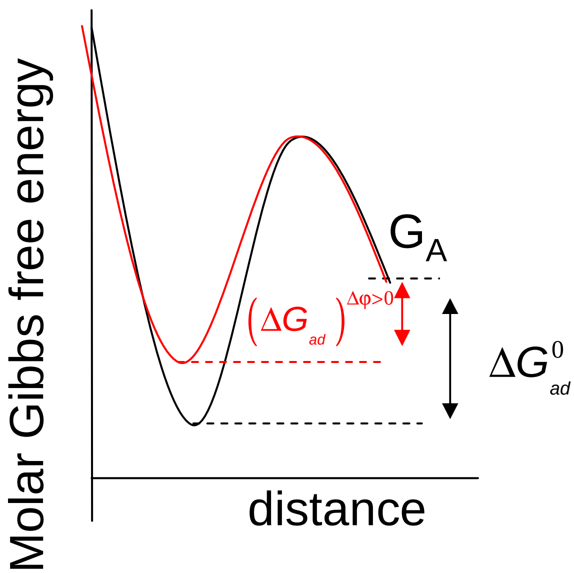
By substituting this into ads./des. equation

$$\frac{\theta}{(1-\theta)} = \frac{K_{ad}}{K_{des}} c_A \, exp\left(-\frac{\Delta G_{ad}}{RT}\right)$$

$$\frac{\theta}{(1-\theta)} = \frac{K_{ad}}{K_{des}} c_A \, exp\left(-\frac{\Delta G^0_{ad}}{RT} - \frac{\gamma\theta}{RT} \right) = \frac{K_{ad}}{K_{des}} c_A \, exp\left(-\frac{\Delta G^0_{ad}}{RT} \right) exp(-\frac{\gamma\theta}{RT})$$

$$\frac{\theta}{(1-\theta)} = \frac{K_{ad}}{K_{des}} c_A \, exp\left(-\frac{\Delta G^0_{ad}}{RT} \right) exp(-g\theta), \quad g = \frac{\gamma}{RT}$$

In the next step we consider the case when apply the potential:



$$\Delta G_{ad} = \Delta G^0_{ad} + zF\Delta\varphi$$

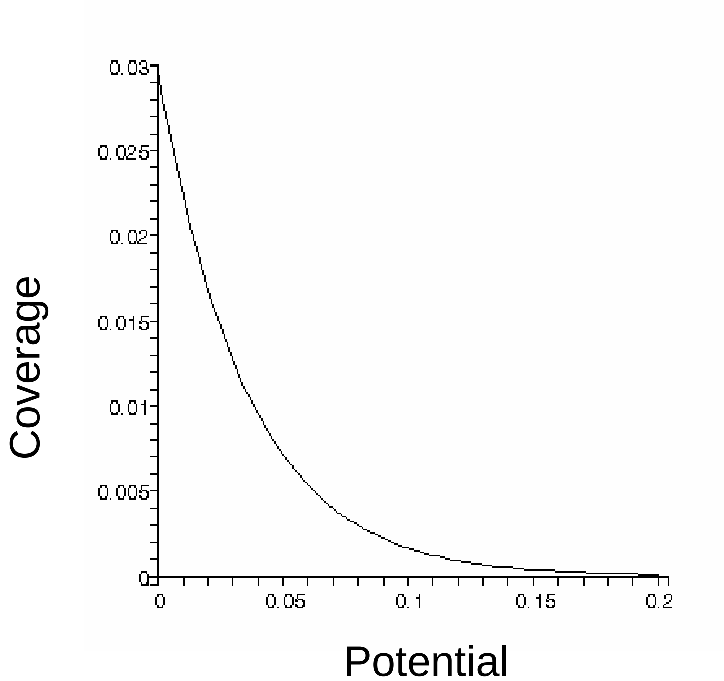
For $\Delta\Phi>0$, ΔG_{ad} becomes smaller → coverage reduced.

Applying this equation we will have:

$$\frac{\theta}{(1-\theta)} = \frac{K_{ad}}{K_{des}} c_A \, exp\left(-\frac{\Delta G^0_{ad}}{RT} - \frac{zF\Delta\varphi}{RT} \right) = Kc_A \, exp(-\frac{zF\Delta\varphi}{RT})$$

$$K = \frac{K_{ad}}{K_{des}} exp\left(-\frac{\Delta G^0_{ad}}{RT} \right)$$

Coverage as a function of applied potential for H/Pd.



Example: Derive the following equation for current I

$$I = Q_0 \frac{d\theta}{dt} = Q_0 \nu_s \left(-\frac{ZF}{RT} \right) \theta(1-\theta), \quad \nu_s = \frac{d\varphi}{dt}$$

By the definition

$$I = Q_0 \frac{d\theta}{dt} = Q_0 \frac{d\theta}{d\varphi} \frac{d\varphi}{dt} = Q_0 \nu_s \frac{d\theta}{d\varphi}$$

Recall the equation for coverage as function of potential

$$\frac{\theta}{(1-\theta)} = c_A K \, exp(-\frac{zF(\varphi-\varphi_0}{RT})$$

$$\frac{d\theta}{(1-\theta)} + \frac{\theta d\theta}{(1-\theta)^2} = c_A K \frac{-zF}{RT} exp(-\frac{zF(\varphi-\varphi_0}{RT})d\varphi$$

$$\frac{d\theta}{d\varphi}\left(\frac{1}{(1-\theta)} + \frac{\theta}{(1-\theta)^2}\right) = c_A K \frac{-zF}{RT} exp(-\frac{zF(\varphi-\varphi_0}{RT})$$

$$\frac{\frac{d\theta}{d\varphi}}{(1-\theta)}\left(1 + \frac{\theta}{(1-\theta)}\right) = c_A K \frac{-zF}{RT} exp(-\frac{zF(\varphi-\varphi_0}{RT})$$

$$\frac{\frac{d\theta}{d\varphi}}{(1-\theta)}\left(1 + c_A K\, exp(-\frac{zF(\varphi-\varphi_0}{RT})\right) = c_A K \frac{-zF}{RT} exp(-\frac{zF(\varphi-\varphi_0}{RT})$$

$$\frac{\frac{d\theta}{d\varphi}}{(1-\theta)} = \frac{c_A K \frac{-zF}{RT} exp(-\frac{zF(\varphi-\varphi_0}{RT})}{1 + c_A K\, exp(-\frac{zF(\varphi-\varphi_0}{RT})} = \frac{zF}{RT}\theta$$

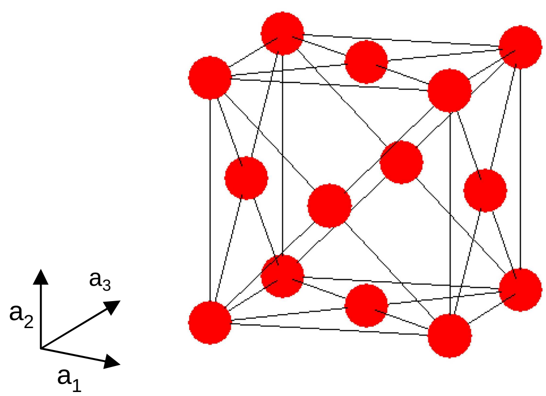
$$\frac{d\theta}{d\varphi} = \frac{-zF}{RT}\theta(1-\theta)$$

Replacing this equation into the equation for current we have

$$I = Q_0 \nu_s \frac{d\theta}{d\varphi} = Q_0 \nu_s \left(\frac{-zF}{RT}\right)\theta(1-\theta)$$

The structure of single crystal surface

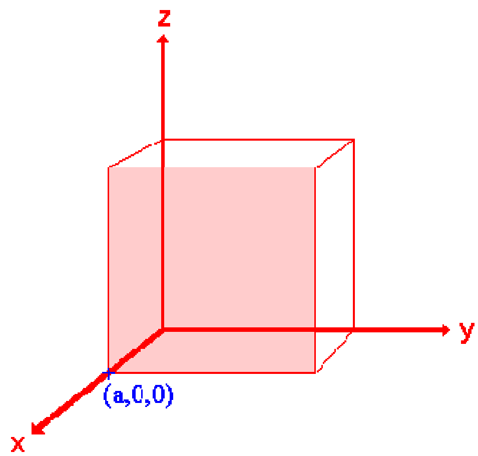
Most of the important metals in electrochemistry have fcc structure e.g. Au, Ag, Pt, Pd…



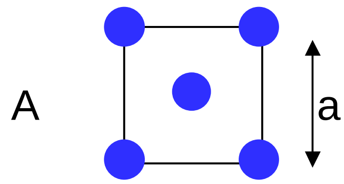
How can we specify a surface by having Miller indexes

Example: Specify the surface(100)

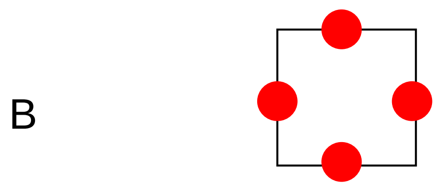
The index (100) shows that the surface crosses x-axes at 1xa (a is the lattice constant) and it is parallel to y and z axes



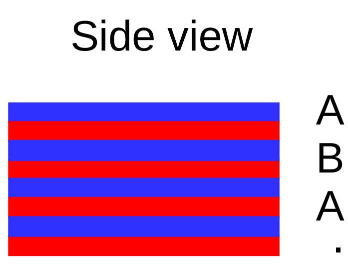
The atom positions in this layer for one unit cell are shown below.



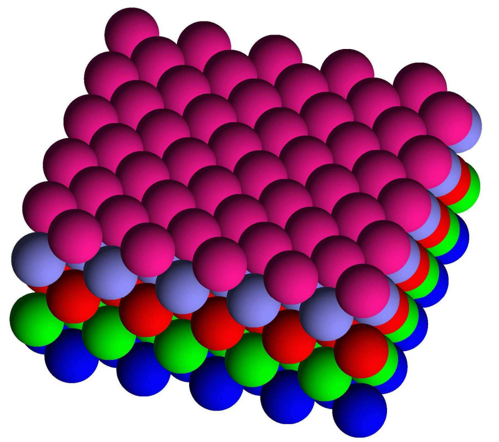
If you are interested to know about the atom positions at the second layer we have to move along x up or down. Below you see the atom positions for the second layer

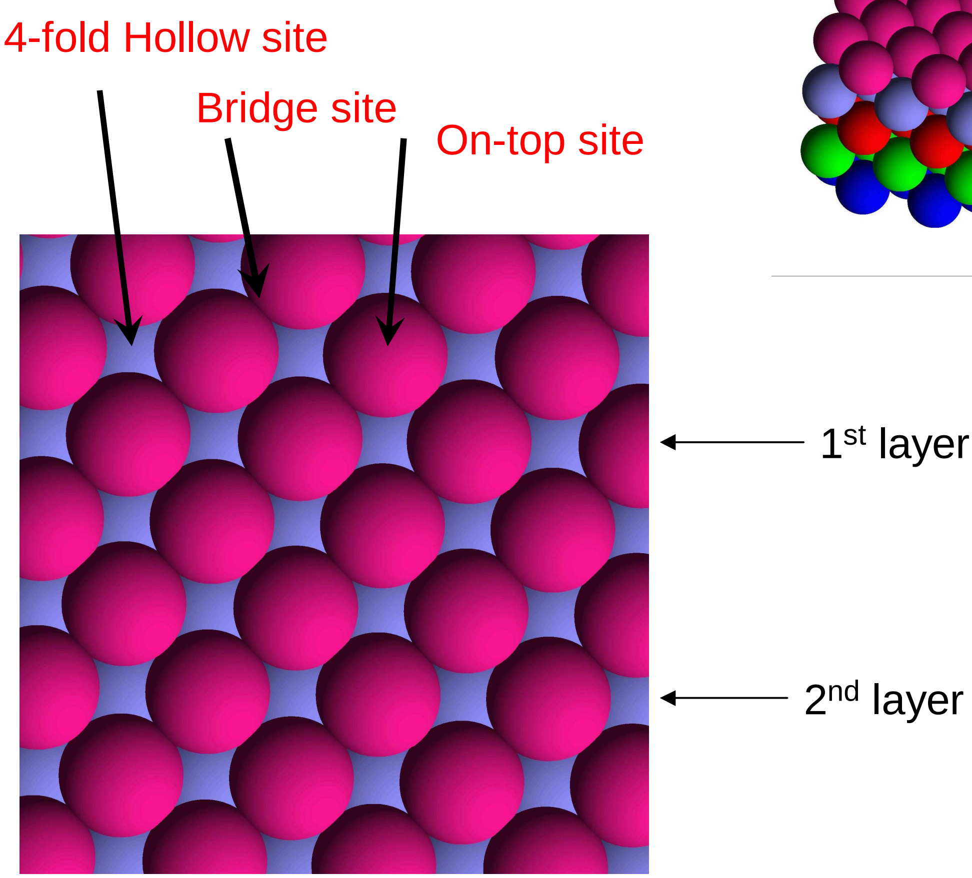


The atoms position in the third layers are the same as the first layer. Below you see how the layers stay on top of each other



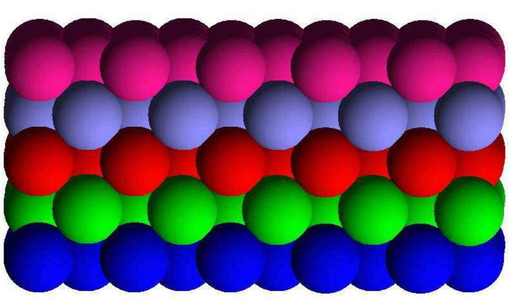
High symmetry sites for surface (100)





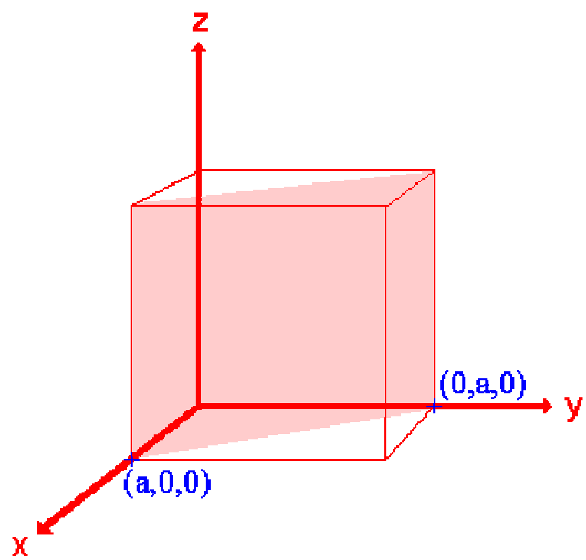
Top-view

Side-view

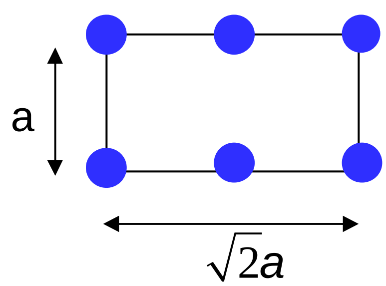


Example: Specify the Surface(110)

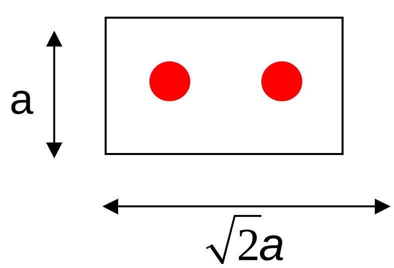
According to the definition, surface (110) crosses x and y axes at "a" and "a" and it is parallel to z axes.



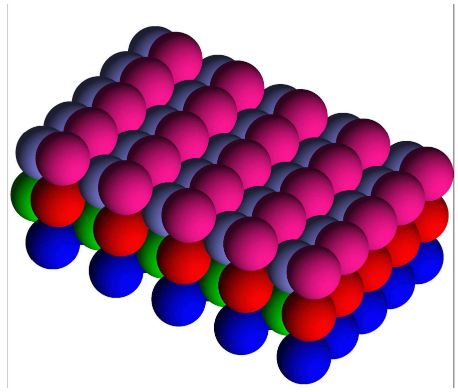
The atom positions for this surface is shown below

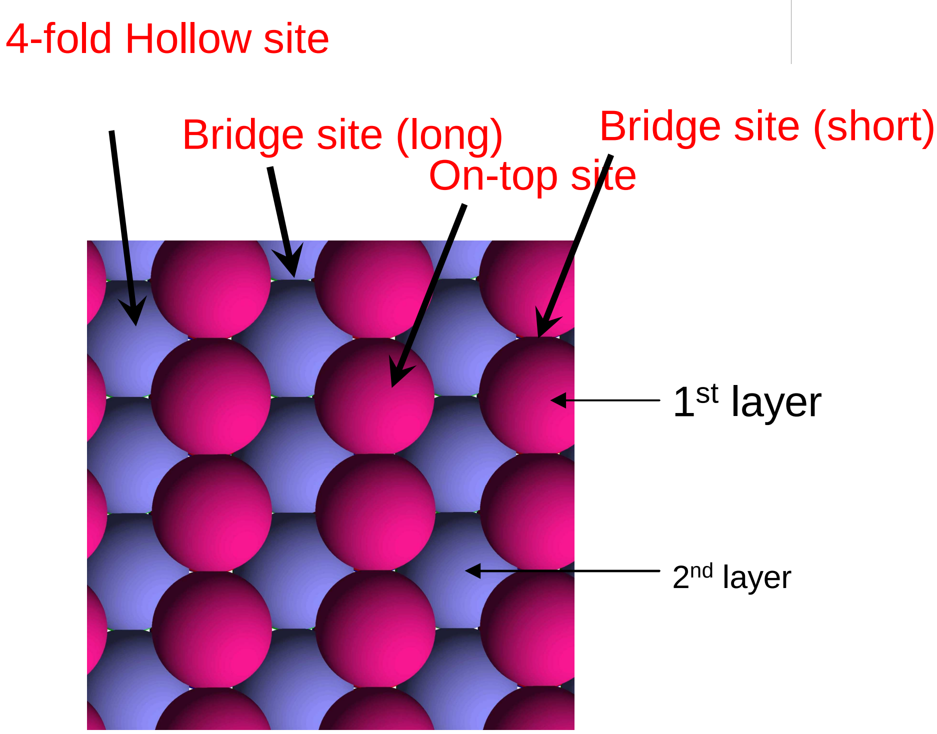


And atom positions for the second layer:



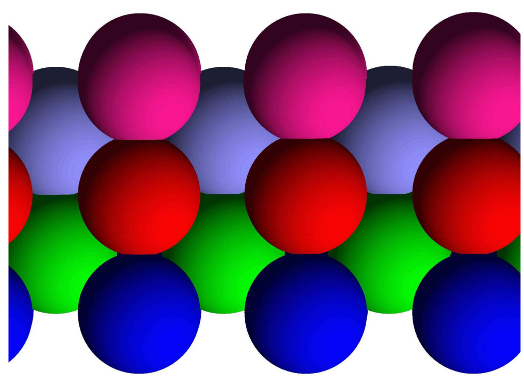
High symmetry sites in surface(110)





Top-view

Side-view



For surface (110) there are 4 high symmetry sites