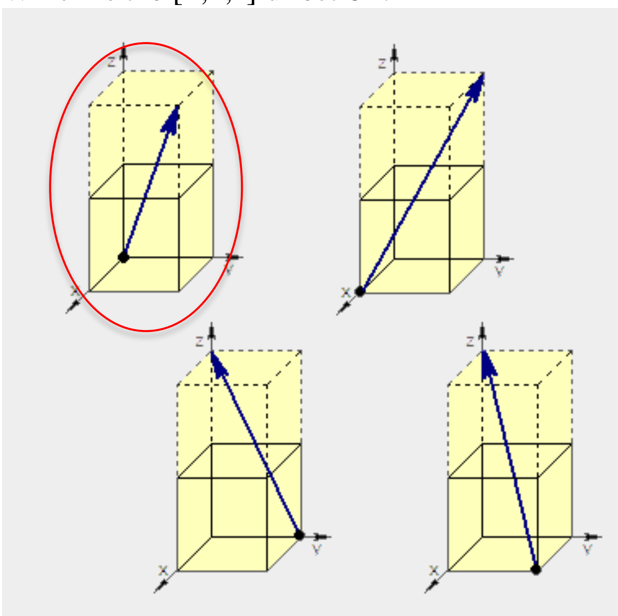
ChE-403 Problem Set 2.1

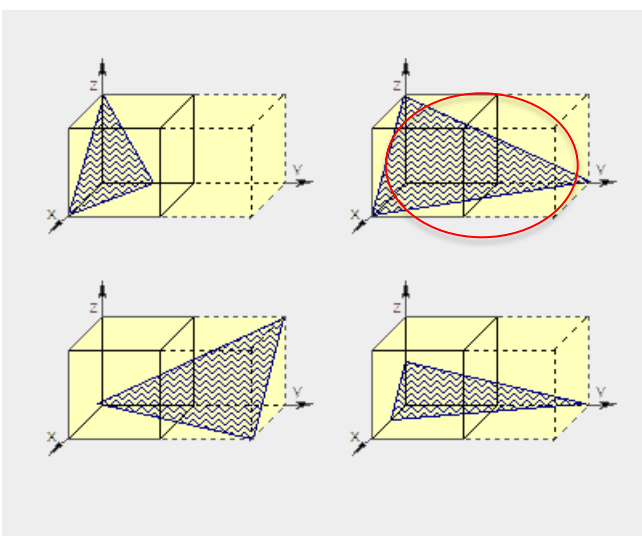
Week 5

Problem 1

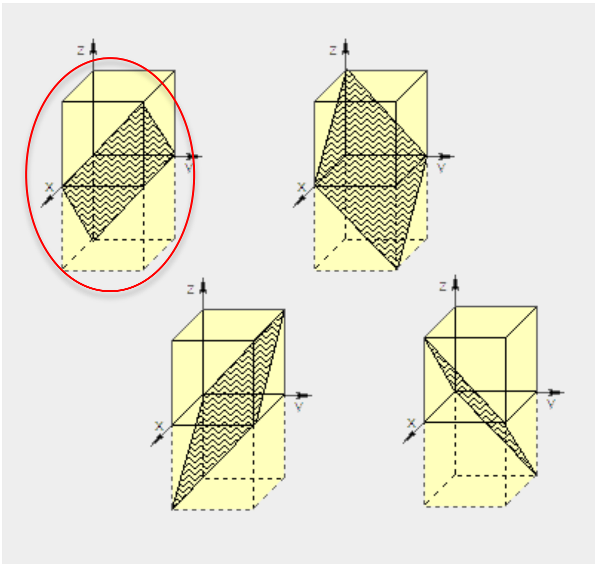
Which is the [1,1,2] direction?



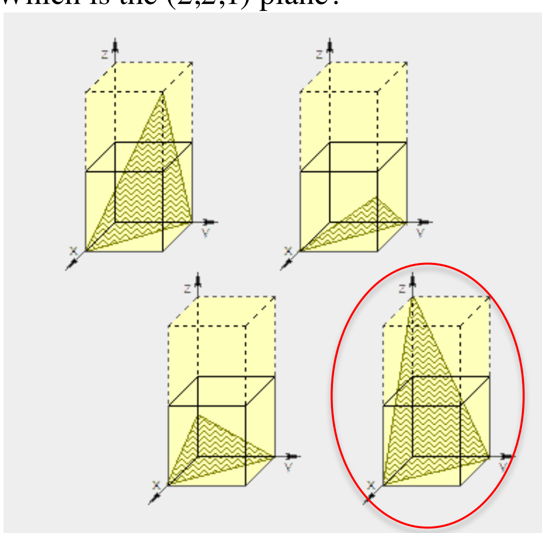
Which is the (2,1,2) plane?



Which is the (1,1,-1) (usually written as $(1,1,\bar{1})$) plane?



Which is the (2,2,1) plane?

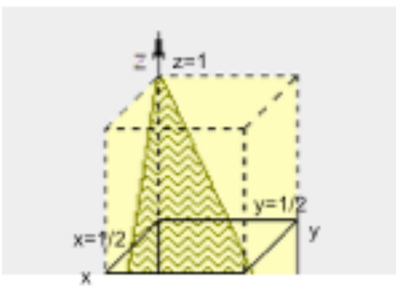


Problem 2

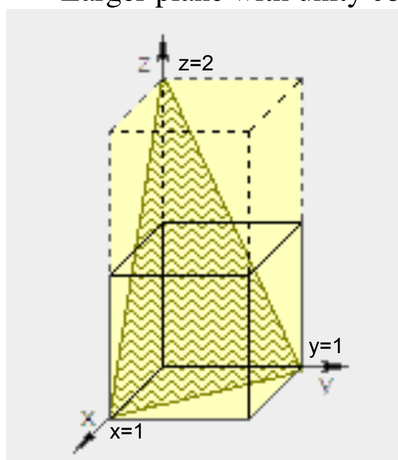
2.1 Can you draw a (1,2,1) plane both in a single (1,1,1) box and as a larger plane that only has unity coordinates (see example below)?

Example: for a plane (2,2,1) we have:

Single (1,1,1) box:



Larger plane with unity coordinates:

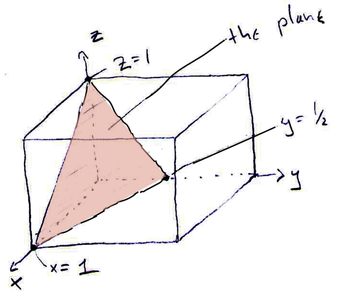


2.2 What would the larger plane (what is shown above to the right) with only unity coordinates be for a (2,1,3) vector? (Don’t draw it, just give the coordinates)

Solution:

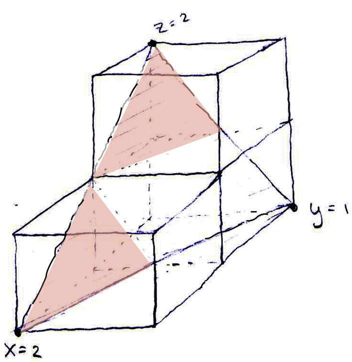
2.1.

2.1



For a (1,2,1) index we will cut the box in : (1, ½, 1)

If we have a surface that cuts the x, y, z planes in 1, ½, 1 than it will also form a surface that will connect at coordinates (2, 1, 2) :



Note that in the second drawing we show the same unit box planes from the first drawing in the larger surface.

2.2. In the unit box, this would form a surface that would cut the x,y,z planes at (1/2, 1 , 1/3). To make this whole we have to multiply by 3x2=6. The surface would connect the following coordinates: (3, 6, 2)

Problem 3
Determine the Miller Indices of a plane which is parallel to the x-axis and cuts the y axis at 2 and the z-axis at 1/2?

Solution:

3.1. The intercepts are:

$x=\infty$ $y=2$ $z=1/2$

The inverse of that is:

$1/x=0$ $y=1/2$ $z=2$

Miller indexes cannot have fractions, so we write:

(0,1,4)

Problem 4

Studies on model catalysts (flat metallic surface) revealed that catalytic activity is strongly dependent on which crystallographic plan (hkl) is exposed. For example, Ni(111) and Ni(100) convert ethane into methane, under reductive atmosphere, with different rate (see figure below). A simple geometric approach can help us understand why Ni(111) and Ni(100) have not the same reactivity.

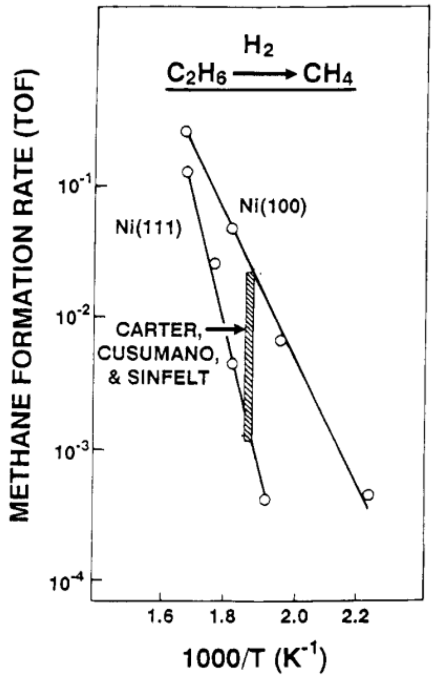
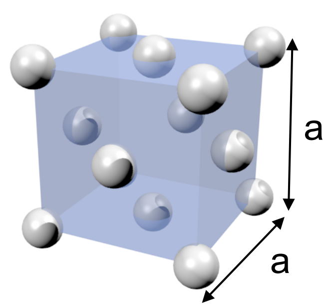


Figure 3. Arrhenius plot for ethane hydrogenolysis reaction on Ni(100) and Ni(111) surfaces at a total reactant pressure P_T of 100 Torr and $H_2/C_2H_6 = 100$.[12] Also shown is the result on supported nickel catalysts at P_T of 175 Torr and $H_2/C_2H_6 = 6.6$.[22]

Nickel has a face centered cubic crystal structure (FCC). Each atoms of nickel are equivalent in the bulk and surrounded by 12 neighbors. Now if we cut the unit cell along a plan like (100) a surface appear and Ni_{surf} are no longer equivalent to Ni_{bulk}.

Calculate the density of Ni atom per surface unit and number of neighbors (or lost neighbors) in case of a cut along the (100) and (111) planes.

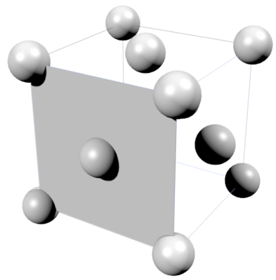
Hint: Try to find the number of atoms per area by calculating the surface area with *a* the cell parameter:

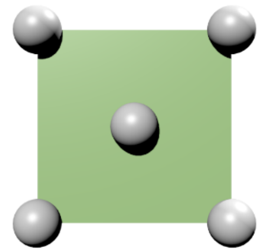


Solution

Let's consider surface atom density first.

Let's start with a cut along (100)

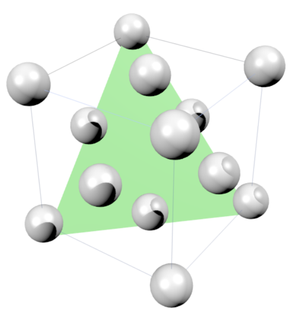


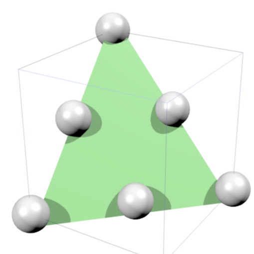


The surface density of atom can be calculated by considering a unit cell. If we only look at the face (100), we have:

On this square we count 2 atoms (1 + 4 x ¼). Note that each corner atom count for ¼ and not 1/8 because we are considering a plan in 2D and not a 3D cell anymore. The surface exposed can expressed with a, the cell parameter (the length of the cube). We end up with a surface atom density = 2 /a^2.

For (111) cut, the principle is the same





An equilateral triangle has according to Pythagoras a length equal to $\sqrt{2a^2} = a\sqrt{2}$ with 2 atoms on it (3x ½ +3x 1/6).

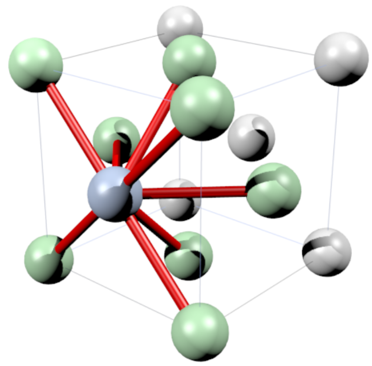
Area of eq triangle = $\frac{\sqrt{3}}{4}$ x L^2 with in our case L= $a\sqrt{2}$.

The atom density $= \frac{2}{\sqrt{3}}\frac{4}{2\,a^2} = \frac{2.3}{\mathrm{a}^2}$ which is higher than for (100).

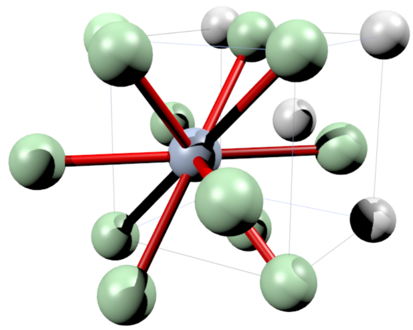
The atom density is different for (111) and (100). This difference can be critical for catalysis due to the surface reactivity and/or when the mechanism of reaction involves two metal atoms that are close to each other.

Let's also consider the number of nearest neighbors that are lost.

In order to count neighbors, it is easier to start with the atom at the center of the face. It has 4 direct neighbors in the same plane. It also has 4 more, which are at the center of the adjacent faces.

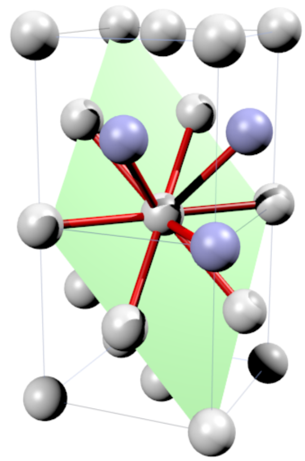


We know (and we can show it here) that in the bulk, each atom has 12 neighbors. To make them visible, you could draw a cell next to the first one.



If we cut along (100), we remove the 4 neighbors at the front. This means the surface energy created will be proportional to 4/12 (neighbors lost/coordination number).

Now let's consider cutting along (111). In this case, you see that we remove 3 atoms:



Here, we see clearly that there is a loss of 3 neighbors. This means the surface energy created will be proportional to 3/12 (neighbors lost/coordination number), which is lower.

The conclusion of this analysis is that the (111) surface has a higher atom density (which is more favorable) and a lower loss of neighbors (also favored). The consequence of this coordination frustration is an overall higher surface energy for the (100) plane and so a greater reactivity.

Side note: The stability difference between planes explain why crystals in nature (such as quartz) grow in anisotropic ways and expose well defined walls with the same angles between them (they are minimizing surface energy). In a same way, diamonds are always carved according to crystallographic planes.