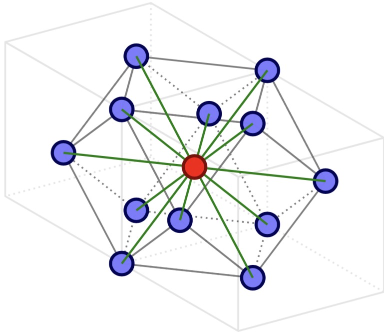
1. For **face centered cubic** crystal structure, the coordination number is 12, which means each atom can have a maximum of 12 nearest bonds, see the illustration below.



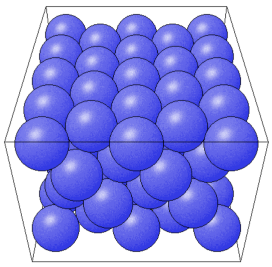
a) As you learn from the lecture, the generation of a surface is originated from broken interatomic/intermolecular bonds. Can you prove that in FCC structure, the surface energies of (111), (110) and (100) surfaces have a relation of: $\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)}$. (hint: count the number of broken bonds of nearest neighbors for atoms on different surfaces. There are many tools you can use to have a visualization of atomistic arrangement, here is a simple one you can use http://surfexp.fhi-berlin.mpg.de/)

b) Below is a table of calculated surface energies/(J/m^2) of FCC metals platinum and gold from publication: https://doi.org/10.1016/S0039-6028(02)01547-9 From the question above, you know that for FCC structure each surface orientation has a different number of broken bonds. Why do the surface energies of the same surface orientation different between Au and Pt even though they have the same crystallography structure? What are the reasons you can think of?

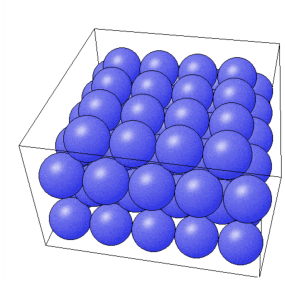
(hkl)	Pt	Au
(111)	2.31	1.39
(100)	2.65	1.62
(110)	2.91	1.75

Solution:

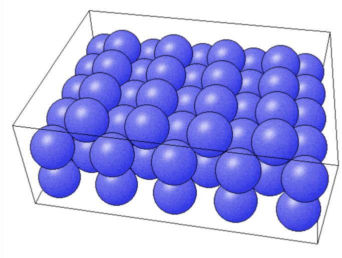
a) For atoms on (111) surface, each has 6 nearest neighbors on the surface and 3 below the surface, compare to atoms in the bulk, there are 3 missing bonds



For atoms on (100) surface, each has 4 nearest neighbors on the surface and 4 below the surface, compare to atoms in the bulk, there are 4 missing bonds



For atoms on (110) surface, each has 2 nearest neighbors on the surface and 5 below the surface, compare to atoms in the bulk, there are 5 missing bonds



The surface energy is proportional to the number of broken bonds, as the number of broken bonds $N_{(111)} = 3$, $N_{(100)} = 4$, $N_{(110)} = 5$, so

$$\gamma_{(111)} < \gamma_{(100)} < \gamma_{(110)}$$

b) Surface energy is proportional to the number of broken bonds and energy of sublimation of atoms (interaction energy), while it is inversely proportional to the equilibrium inter-atomic distance. So even though both gold and platinum have the same number of broken bonds(first nearest neighbors), their interaction energy and equilibrium interatomic distance is different, which will lead to a difference in the surface energies of the same surface orientation between them.

2. Selenium is a non-metal that is often used in semiconductor devices, in particular in photocells. Selenium crystal habit is an elongated prism, as shown in the sample below:

Figure 1 Selenium crystals, from www.periodictable.ru

Selenium has a low melting point, just above 200°C, and it can be processed using fiber technology, giving the possibility to integrate optoelectronic devices inside an optical fiber. To this aim, in the laboratory of Prof. Fabien Sorin at EPFL, researchers are experimenting on the re-crystallization of the Se core of the fiber (that emerges from the process in an amorphous form) into selenium nanowires. It turns out that, by soaking the tip of the fiber in alcohol (specifically, isopropanol), the material spontaneously forms nanowires, that appear as below under a scanning electron microscope. Read more about this at following publication: https://doi.org/10.1002/adma.201700681

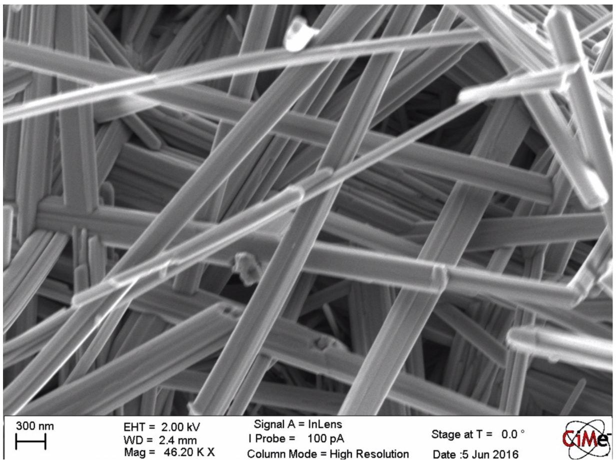


Figure 2 Se nanowires formed by recrystallization of the amorphous selenium fiber in the presence of isopropanol, from W. Yan (FIMAP).

a) Discuss with your classmates a few possible explanations for this observation. Which proper- ties of selenium could play a role? How could the presence of isopropanol play a role?

b) Selenium crystallizes in a trigonal space group, and is characterized by the presence of polymer-like 1D chains stretching along the [001] direction. Can you explain qualitatively why Se crystals typically have an elongated crystal shape? Hint: think about the crystal structure, and the energetic cost of breaking a covalent bond within the polymer chains.

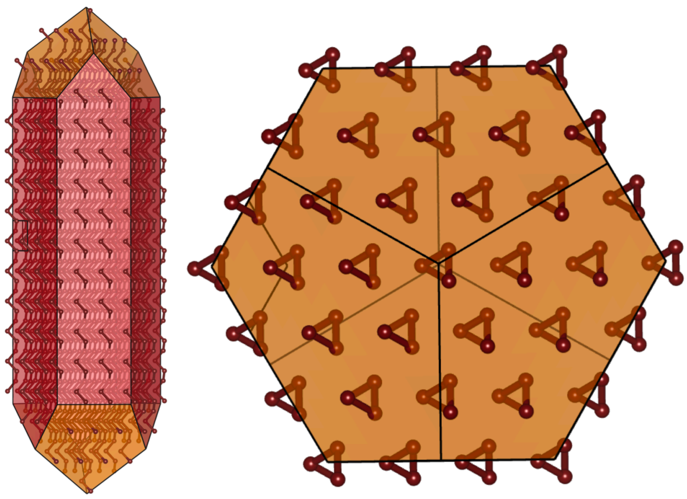


Figure 3 Observed crystal habit of trigonal selenium, together with a representation of its molecular structure.

Solutions:

a) The interfacial free energy between selenium and the surrounding may play a role, especially the anisotropy. The interface between isopropanol and selenium may have a different area specific free energy compared with the one between selenium and air.

b) The interfacial free energy along the [001] direction is particularly large, such that the crystal tries to minimize the surface area along this direction. The large interfacial free energy along the [001] direction stems from the energy cost of breaking the polymer covalent bonds.

3. Graphene is the two-dimensional form of carbon and it is widely studied because of its peculiar properties. The Nobel prize in Physics of 2010 was awarded for the discovery and study of this material. Graphene has a planar, hexagonal arrangement of carbon atoms (the so-called "honeycomb lattice") corresponding to a single plane taken from a graphite structure.
Consider now a graphene lattice, as the one shown in the following Fig. 4. Consider the vectors $\mathbf{a}_{1,2}$ and $\mathbf{b}_{1,2}$.

   a) Which pair of vectors corresponds to a unit cell for the 2D Bravais lattice of graphene? How many atoms are contained within each unit cell?

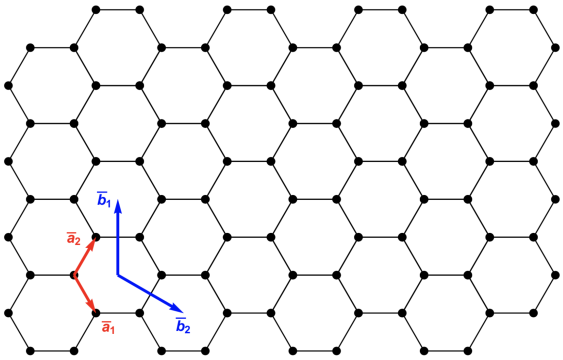


Figure 4 The "honeycomb" lattice of graphene. One should imagine that this lattice extends infinitely in both directions.

   b) Now suppose to cut the lattice along the direction indicated by the continuous red line (see Fig. 5). How is the "line energy" energy associated with this cut similar to a surface energy? Determine the energy per unit length created due to this cut, assuming the energy per bond to be ε.

   c) Now consider a cut along the dashed black line. What is the surface energy along this direction?

   d) Cutting along the dotted green line, which is parallel to the dashed one, would give a surface energy twice as large. Which of the two should be used in the construction of a γ plot? Why does graphene have two different surface energies along the same direction?

   e) With the results obtained in points (b) and (c), draw the γ plot for graphene, and derive from it the equilibrium shape a two-dimensional graphene flake. *Hint: Only consider the surface energy for high-symmetry directions. Each of the surfaces you evaluated leads to six symmetry-equivalent singular surfaces.*

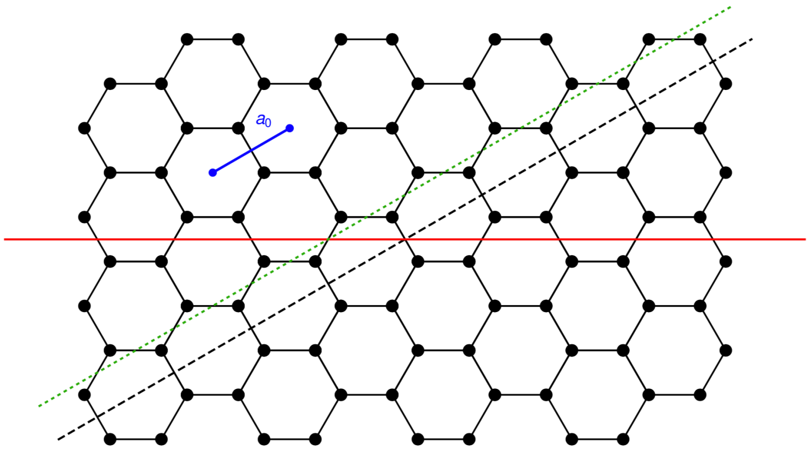


Figure 5 The cutting directions considered for the graphene lattice and the unit length a_0.

Solutions:

a) The unit cell vectors are b_1 and b_2, and the unit cell contains two atoms.

b) Let a_0 be the lattice parameter length, namely $a_0 = |b_1| = |b_2|$. In a similar manner to the surface energy, we can write the "line energy", γ, as

$$\gamma = \frac{w}{l}$$

where W is the work done to break the bonds along the given direction and l is the length of the vector along the cut. In this case, the length is $l = \sqrt{3}a_0/_2$ and the work, which is given by the sum of the energies of the broken bonds, is w = ε. Inserting W and l in the equation above, we get

$$\gamma^b = \frac{2\epsilon}{\sqrt{3}a_0}$$

c) Along the dashed line, the length is a_0 and the work is ε. Thus, we get

$$\gamma^c = \frac{\epsilon}{a_0}$$

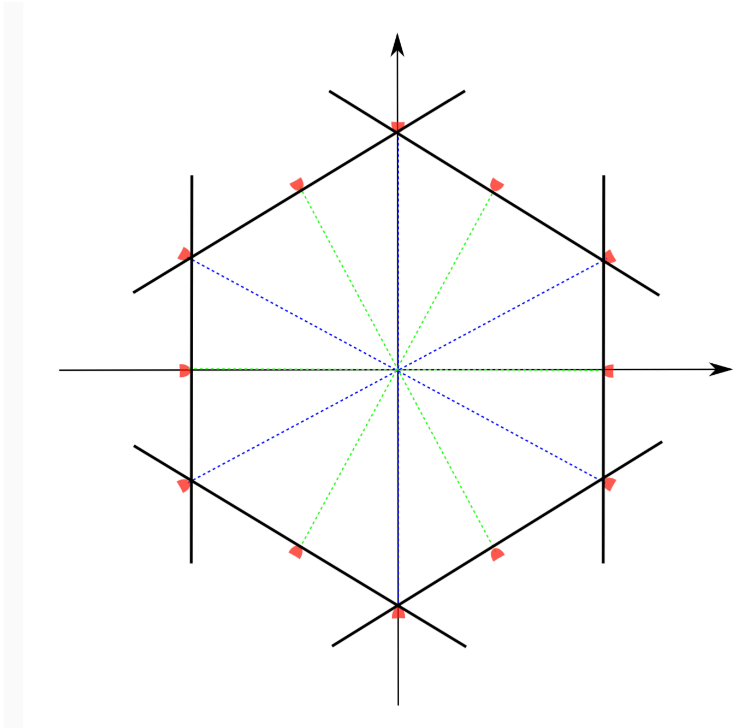
d) Since the two directions are equivalent, one should take the smallest between the two energies to construct the γ-plot. The reason why graphene has two surface energies for the same direction is the fact that its structure is actually a "lattice with a basis": the underlying lattice is the hexagonal Bravais lattice and the basis is composed of two carbon atoms placed at (1/3, 2/3) and (2/3, 1/3). For each direction one can obtain different surfaces depending on the point of the unit cell at which the structure is cut.

e) From (b) and (c), let's define $\gamma^c = \gamma(\theta = 0)$ and $\gamma^b = \gamma\left(\theta = \frac{\pi}{6}\right)$. If we impose the hexagonal symmetry, we have:

$$\gamma(0) = \gamma\left(\frac{\pi}{3}\right) = \gamma\left(\frac{2\pi}{3}\right) = \gamma(\pi) = \gamma\left(\frac{3\pi}{4}\right) = \gamma\left(\frac{5\pi}{3}\right) = \frac{\epsilon}{a_0}$$

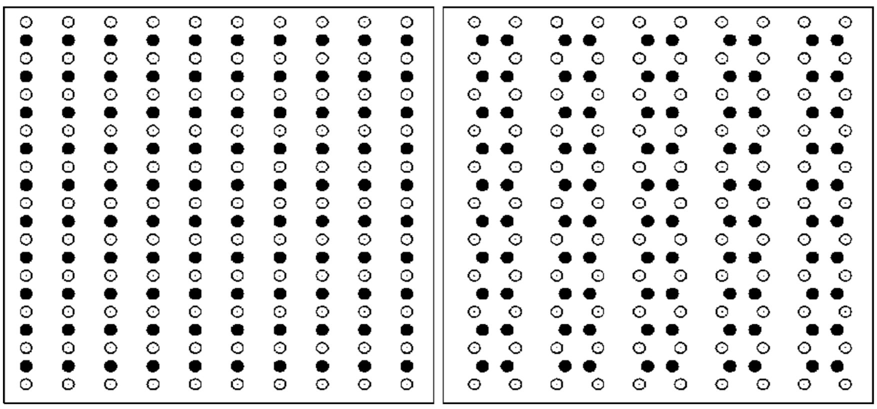
$$\gamma\left(\frac{\pi}{6}\right) = \gamma\left(\frac{\pi}{2}\right) = \gamma\left(\frac{5\pi}{6}\right) = \gamma\left(\frac{7\pi}{6}\right) = \gamma\left(\frac{3\pi}{2}\right) = \gamma\left(\frac{11\pi}{6}\right) = \frac{2\epsilon}{\sqrt{3}a_0}$$

From the previous results, we can derive the γ-plot and then the equilibrium shape of this crystal by Wulff construction:



4. The following illustrations show two types of reconstructions on the (100) surface of Si (black dots indicate Si atoms lying below the white Si atoms), read more on publication: https://doi.org/10.1002/adma.201700681 Draw the unit cell and determine which type of reconstruction (?x? reconstruction) each of them belongs, and give the reconstruction matrix G:

$$\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} g_{11} & g_{12} \\ g_{21} & g_{22} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix}$$



Solutions:

Left: 1x1 reconstruction of Si(001), with a reconstruction matrix: $\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$

Right: 2x1 reconstruction of Si(001), with a reconstruction matrix: $\begin{bmatrix} 2 & 0 \\ 0 & 1 \end{bmatrix}$