*** Exercise 1 Growth of Selenium Nanowires

Part 2

Recall the last two questions for Part 1 from the previous week's exercise:

1. Write the expression of the total surface energy G_{surf} (with the values for the interfacial free energy left as γ_{001} and γ_{010}).
2. The crystal shape is determined by the minimization of G_{surf} at constant volume. Use the relation between volume, a and c to write c as a function of a and V.

Take the results you got and try to go a bit further in the understanding of this surface science problem. Let the following points guide you.

(a) Plug the result for G_{surf} to obtain an expression that depends only on a and V. Derive with respect to a to find the value of a that corresponds to the energy minimum at constant V.

(b) Use this expression to write the aspect ratio as a function of $\gamma_{001}/\gamma_{010}$. By means of *ab initio* calculations, one can compute the values of γ_{001} – which is equal to 39 meV/Å^2 – and that of γ_{010} – which is equal to 9 meV/Å^2.

(c) What is the aspect ratio? Does it compare well with the crystals observed in air? And what about the nanowires? Think again of your initial hypothesis on why the nanowires assume the elongated shape: is it still valid?

Now you probably start to see that the habit of the crystals is determined by the surface energies of different facets. Nanowires can be regarded as crystals with a very large aspect ratio, so perhaps the thermodynamic drive towards nanowire growth can be explained by the changes in interface energy when the crystal is immersed in isopropanol. Unfortunately it is hard to grow large crystals of selenium so as to measure the interface energy on different surfaces. Instead, we'll try to see how it can be estimated by simple *ab initio* calculations.

(d) Write the Dupré equation for the surface energy between selenium and isopropanol. What terms enter it? A quick Google search (and some units conversion!) will tell you that the surface tension of isopropanol is 1.35 meV/Å^2. Which is the missing term?

(e) Consider two materials A and B separated from each other. Write the internal energy between the two materials in terms of pair interactions V_{AA} and V_{BB} between their atoms (not necessarily the first neighbors).

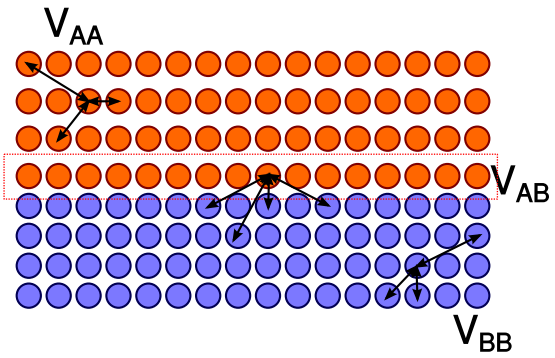


Figure 1: A scheme of the adhesion between the two materials in terms of pair interactions. It is assumed that only the first layer of A interacts with (all) the molecules in B.

(f) Now put into contact the two materials, and write the total energy including also the interactions between the two materials V_{AB}. We will make the approximations that (1) only the first layer of molecules in A interacts with B and (2) that the conformation and interactions between molecules in the two materials don't change upon joining the materials.

(g) Explain how this approximation allows us to estimate the work of adhesion based only on the adsorption energy of a single molecule of isopropanol on a selenium surface.

(h) The adsorption energy of an isopropanol molecule on selenium {001} can be computed to be $E_{001} = -0.28$ eV, and on {010} $E_{010} = -0.30$ eV. Assume that the area occupied by a molecule at the interface is of the order of 30Å^2. Estimate the interface energies $\gamma_{010,\text{iso}}$ and $\gamma_{001,\text{iso}}$.

(i) What aspect ratio do you predict for a crystal growing in isopropanol? Does this help explain the experimental findings? Did your initial hypothesis match with what you discovered in this exercise?

Solution to Exercise 1

Question (a).

$$G_{\text{surf}} = 3\sqrt{3}a^2\gamma_{001} + 6a(\frac{2V}{3\sqrt{3}a^2})\gamma_{010} = 3\sqrt{3}a^2\gamma_{001} + \frac{4V}{\sqrt{3}a}\gamma_{010}$$

After taking the derivative with respect to a,

$$0 = \frac{\partial G_{\text{surf}}}{\partial a} = 6\sqrt{3}a\gamma_{001} - \frac{4V}{\sqrt{3}a^2}\gamma_{010}$$

so

$$a = \left(\frac{2V\gamma_{010}}{9\gamma_{001}}\right)^{\frac{1}{3}}.$$

Question (b).

$$r = \frac{c}{a} = \frac{2V}{3\sqrt{3}a^3} = \sqrt{3}\frac{\gamma_{001}}{\gamma_{010}}$$

Cont.

Question (c). The aspect ratio is computed to be:

$$\sqrt{3}\,\frac{39\,\mathrm{meV\,\AA^{-2}}}{9\,\mathrm{meV\,\AA^{-2}}} \approx 7.5.$$

Question (d). The Dupré equation for the surface energy between selenium and isopropanol is

$$\gamma_{si} = \gamma_{ss} + \gamma_{ii} - W_{si},$$

where γ_{ss} is the surface free energy of selenium, γ_{ii} is the surface tension of isopropanol, and W_{si} is the work of adhesion between selenium and isopropanol. We know about γ_{ss} and γ_{ii}, so W_{si} is the missing term.

Question (e). The internal energy for material A can be expressed as

$$E_A = \sum_i \sum_{j<i} V_{AA}(\mathbf{r}_{ij}),$$

where the sum is looped over every pair of molecules i and j in material A, and $\mathbf{r}_{ij}$ denoted the displacement between the two molecules.

Similarly, the internal energy for material B can be expressed as

$$E_B = \sum_m \sum_{n<m} V_{BB}(\mathbf{r}_{mn}),$$

where the sum is looped over every pair of molecules m and n in material B.

Question (f). The cohesion energy between material A and B can be expressed as

$$E_{AB} = -W_{AB} = \sum_i \sum_m V_{AB}(\mathbf{r}_{im}),$$

where i denotes a molecule belongs to material A in the first layer of the interface, and m denotes a molecule belongs to material B in the first layer of the interface.

Question (g). The adsorption energy of a single molecule i of material A on a surface of material B can be expressed as

$$E_{\mathrm{abs}} = \sum_m V_{AB}(\mathbf{r}_{im}).$$

So it is easy to see that $E_{AB} = E_{\mathrm{abs}} \times N$, where N is the number of molecules of material A in the first layer of the interface.

Question (h).

$$\gamma_{001,\mathrm{iso}} = \gamma_{010} + \gamma_{ii} - W_{si} = \gamma_{010} + \gamma_{ii} + E_{\mathrm{abs},\,001}/A,$$

so

$$\gamma_{001,\mathrm{iso}} = 39\,\mathrm{meV\,\AA^{-2}} + 1.35\,\mathrm{meV\,\AA^{-2}} - 280/30\,\mathrm{meV\,\AA^{-2}} = 31\,\mathrm{meV\,\AA^{-2}}.$$

Similarly,

$$\gamma_{010,\mathrm{iso}} = 9\,\mathrm{meV\,\AA^{-2}} + 1.35\,\mathrm{meV\,\AA^{-2}} - 300/30\,\mathrm{meV\,\AA^{-2}} = 0.4\,\mathrm{meV\,\AA^{-2}}.$$

Cont.

Question (i). The aspect ratio is

$$r = \sqrt{3}\frac{\gamma_{001,\mathrm{iso}}}{\gamma_{010,\mathrm{iso}}} \simeq 134.$$

** Exercise 2 Surface free energy of a graphene flake

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 Fig. 2. 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?

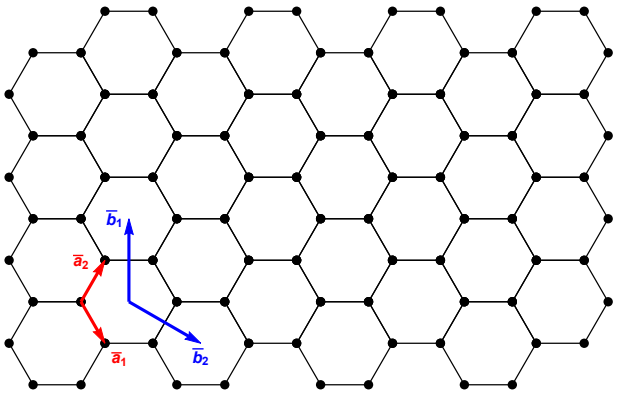


Figure 2: The "honeycomb" lattice of graphene. One should imagine that this lattice extends infinitely in both directions.

(b) Now suppose to cut the lattice along the direction indicated by the continuous line (see Fig. 3). 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 line. What is the surface energy along this direction?

(d) Cutting along the *dotted* 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.*

Cont.

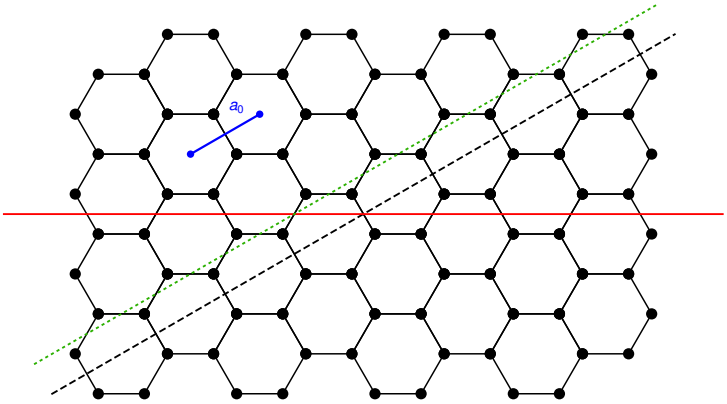


Figure 3: The cutting directions considered for the graphene lattice and the unit length a_0.

Solution to Exercise 2

1. The unit cell vectors are $\mathbf{b}_1$ and $\mathbf{b}_2$, and the unit cell contains two atoms.

2. Let a_0 be the lattice parameter length, namely $a_0 = \|\mathbf{b}_1\| = \|\mathbf{b}_2\|$. In a similar manner to the surface energy, we can write the "line energy", γ, as

$$\gamma = \frac{W}{2l},$$

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 $l = \sqrt{3}a_0$ and the work, which is given by the sum of the energies of the broken bonds, is $W = 2\epsilon$. Inserting W and l in the equation above, we get

$$\gamma^{(b)} = \frac{\epsilon}{\sqrt{3}a_0}.$$

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

$$\gamma^{(c)} = \frac{\epsilon}{2a_0}.$$

4. 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 $(\frac{1}{3}, \frac{2}{3})$ and $(\frac{2}{3}, \frac{1}{3})$. For each direction one can obtain different surfaces depending on the point of the unit cell at which the structure is cut.

5. From the points (b) and (c), we know $\gamma^{(c)} \equiv \gamma(\theta = 0)$ and $\gamma^{(b)} \equiv \gamma(\theta = \pi/6)$. If we impose the hexagonal symmetry (i.e. C6 symmetry), we have:

$$\gamma(0) = \gamma(\pi/3) = \gamma(2\pi/3) = \gamma(\pi) = \gamma(4\pi/3) = \gamma(5\pi/3),$$
$$\gamma(\pi/6) = \gamma(\pi/2) = \gamma(5\pi/6) = \gamma(7\pi/6) = \gamma(3\pi/2) = \gamma(11\pi/6).$$

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

Cont.

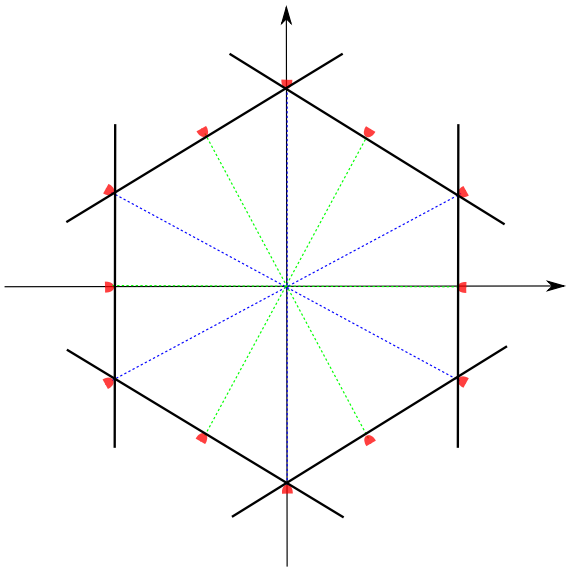


Figure 4: γ–plot of graphene at the cusp points and its respective Wulff construction.

The End.