Exercise 1 The free energy as the "maximum work"

This brief theoretical exercise aims to recall the importance of the free energy in thermodynamics. Suppose that we have a system (for example, a vessel in which a chemical reaction occurs) held at constant temperature and pressure.

(a) Give a proof that the Gibbs free energy ($G = H - TS$) is exactly equal to the maximum amount of non–expansion work the system can do, i.e. $w_{\max} = \Delta G$.

(b) In a similar way, the Helmholtz free energy ($A = U - TS$) is a thermodynamic quantity defined at constant volume and temperature. One can prove that a change in the Helmholtz function is equal to the maximum mechanical work accompanying a process, that is $dw_{\max} = dA$. As a result, A is sometimes called "maximum work function". Can you justify this statement? *Hints: Think of the molecular interpretation of work and heat.*

Solution to Exercise 1

Question (a). Start from the definition of enthalpy $H = U + pV$. Its change is

$$dH = dU + d(pV).$$

The corresponding change in Gibbs energy is

$$dG = dH - TdS - SdT = dU + d(pV) - TdS - SdT.$$

Now, recall the First Law of thermodynamics: $dU = dw + dq$. Substituting this in the equation above, with the requirement that the change occurs at constant temperature ($dT = 0$), we have

$$dG = dq + dw + d(pV) - TdS.$$

When the change is also reversible, we have $dw = dw_{\text{rev}}$ and we can use the Second Law of thermodynamics in the form of the Clausius inequality, namely

$$dS \geq \frac{dq}{T}.$$

In the above equation, the equal sign holds only for a reversible transformation. So for a reversible, isothermal process, we can write

$$dG = TdS + dw_{\text{rev}} + d(pV) - TdS = dw_{\text{rev}} + d(pV).$$

The work consists of expansion work, which for a reversible change is given by $-pdV$, and possibly some other kind of work (for instance, the electrical work of pushing electrons through a circuit); this additional work we denote dw_{add}. Writing explicitly the total differential $d(pV) = pdV + Vdp$,

$$dG = (-pdV + dw_{\text{add,rev}}) + pdV + Vdp = dw_{\text{add,rev}} + Vdp.$$

If the change occurs at constant pressure (as well as constant temperature), we can set $dp = 0$ and obtain $dG = dw_{\text{add,rev}}$. Therefore, at constant pressure and temperature, $dw_{\text{add,rev}} = dG$. However, since the process is reversible, the work done must now have its maximum value.

Question (b). The relation between the work that a system can do and the Helmholtz energy is obtained by recalling that work is energy transferred to the surroundings as the uniform motion of atoms. We can interpret the expression $A = U - TS$ as showing that A is the total internal energy of the system (U) less a contribution that is stored as energy of thermal motion (the quantity TS). Because energy stored in random thermal motion cannot be used to achieve uniform motion in the surroundings (i.e. work), only the part of U that is not stored in that way, the quantity $U - TS$, is available for conversion into work.

Exercise 2 Growth of Selenium Nanowires

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: **10.1002/adma.201700681**.

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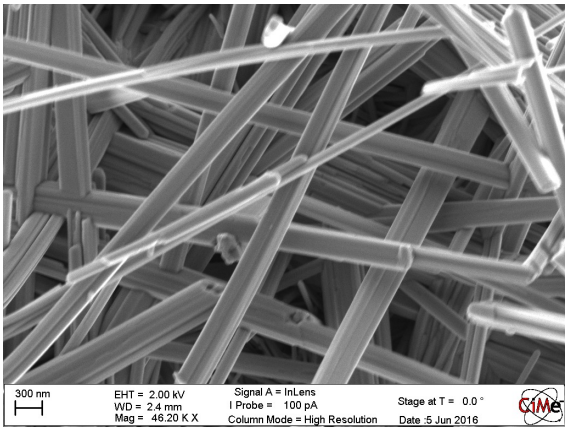


Figure 2: Se nanowires formed by recrystallization of the amorphous selenium fiber in the presence of isopropanol, from W. Yan (FIMAP).

(a) Discuss with your colleagues a few possible explanations for this observation. Which properties of selenium could play a role? How could the presence of isopropanol play a role? Make a hypothesis - in the following exercises we will collect more data that will allow you to verify it, disprove it, or formulate an alternative one.

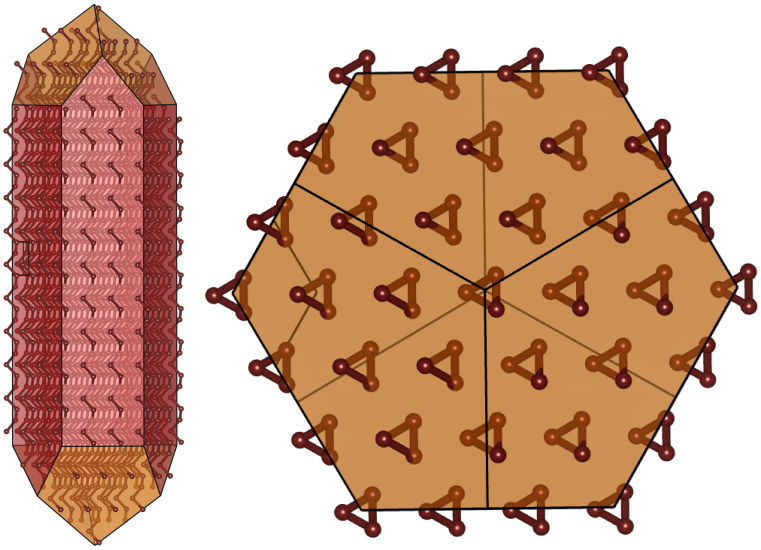


Figure 3: Observed crystal habit of trigonal selenium, together with a representation of its molecular structure.

Selenium crystallizes in a trigonal space group, and is characterized by the presence of polymer-like 1D chains stretching along the [001] direction.

(b) 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*

For simplicity, we will assume that the crystal has a prismatic shape, with the side of the hexagon labelled by a and the height of the prism labelled by c. We will work out the relation between the

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aspect ratio $r = c/a$ and the ratio between the surface energies $\gamma_{001}/\gamma_{010}$.

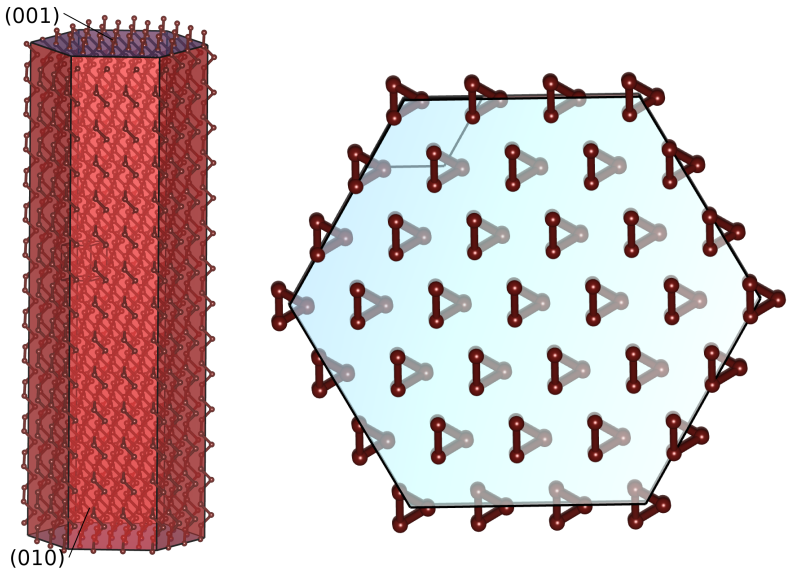


Figure 4: A simplified model of the crystal shape of Se.

(c) Write the expression of the volume of the prism and of its surface area as a function of c and a.

(d) Write the expression of the total surface energy G_{surf} leaving the energy of the basal and prismatic planes expressed as γ_{001} and γ_{010}, respectively.

(e) The crystal shape is determined by the minimization of G_{surf} at constant volume. To do so, use the relation between volume, a and c to write c as a function of a and V.

Solution to Exercise 2

Question (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.

Question (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.

Question (c). The area of each hexagonal basal plan equals $\frac{3\sqrt{3}}{2}a^2$, and the area of each rectangular prismatic plan equals ac, so the total surface area of the prism is $3\sqrt{3}a^2 + 6ac$, and the volume is $V = \frac{3\sqrt{3}}{2}a^2c$.

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Question (d).

$$G_{\text{surf}} = 3\sqrt{3}a^2\gamma_{001} + 6ac\gamma_{010}$$

Question (e).

$$c = \frac{2V}{3\sqrt{3}a^2}$$

The End.