1. Consider a surface with a step (ledge) and terraces. We have seen how to calculate the equilibrium concentration of vacancies (n_v) on a terrace. The argument was based purely on the calculation and minimization of the Gibbs free energy associated with the defect's formation. Do you expect that the energy required for the formation of a ledge vacancy is greater or smaller than that of a simple surface vacancy? Justify your answer.

2. Consider a step with the edge along the ⟨100⟩, on the (100) surface of a simple cubic crystal, at zero temperature. At finite temperature the step edge fluctuates (this is called roughening transition) as a result of the formation of kinks. We can consider the step's edge line L as made up of N segments of length equal to the lattice parameter (L = Na). On each of these segments we may find a positive kink (i.e. an atom that sticks from the step), a negative kink (a missing atom on the step) or no kink at all.

   a) Assuming that the temperature is low enough so that only kinks of atomic size occur, show that the average distance λ_0 between kinks is

   $$\lambda_0 = a\frac{1+2\zeta}{2\zeta} \qquad \text{with} \qquad \zeta = e^{\frac{-\epsilon_{kink}}{kT}}$$

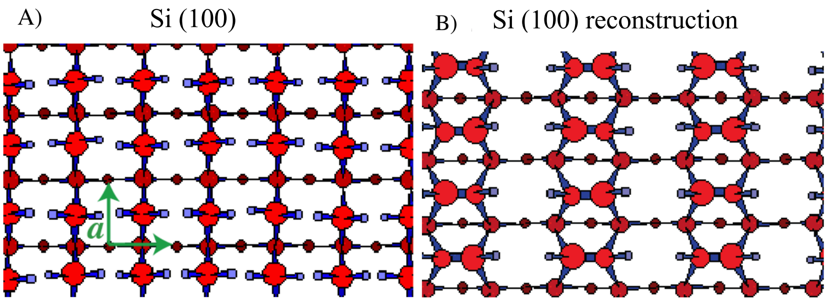
   Where a is the lattice parameter, and ϵ is the formation energy of a kink.

   Hints:

   - *Write down the "constraints" on the number of positive and negative kinks per unit length of the step (you can denote them as p_- and p_+). Take into account that in a segment of the step no kink p_0 is also possible!*
   - *By minimizing the free energy F, one can prove the following relation:* $\frac{p_- p_+}{p_0^2} = \zeta^2$

   b) Sketch a rough plot of $1/\lambda_0$ as a function of temperature with ϵ fixed. Interpret it from a physical point of view. Does it make sense?

3. Figure A) is an illustration of unreconstructed silicon (100) surface A silicon atom in the structure of a silicon crystal can form four bonds with the four nearest neighboring atoms. In the bulk of a silicon crystal, viewed from the (100) plane, two of these bonds reach to the level below and two reach to the next level above. In the figure A) three successive planes of silicon are represented with dots of different shades of red (each shade represent atoms on different levels). Cleaving a crystal along a (100) plane leaves the surface atoms with only two bonds intact and the other two dangling (blue dots in Fig. A). The surface atoms then swing toward neighboring atoms to form pairs, known as dimers. Figure B) shows the same Si (100) plane reconstructed to form rows of dimers along the surface.

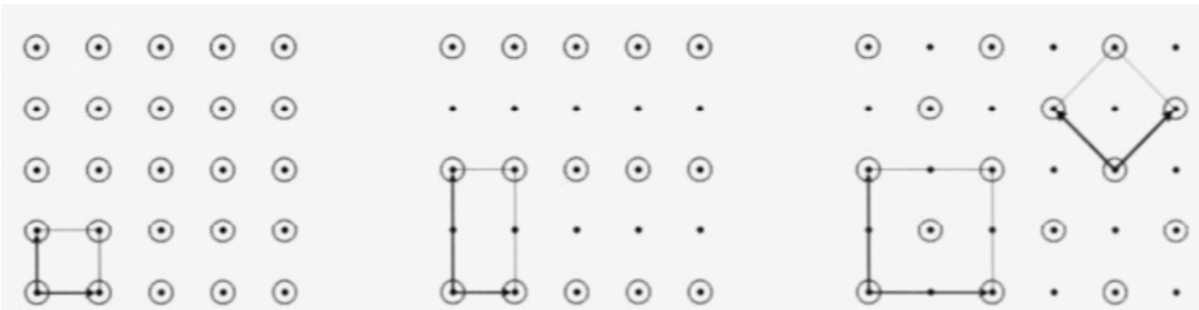


a) Determine the unit cell of the reconstructed Si(100) surface.

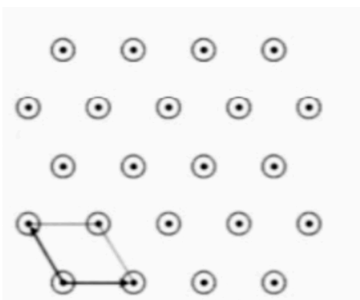
b) Using exclusively the broken bond model in the first nearest neighbor approximation, determine the surface energies of the surface reconstructed and unreconstructed, as a function of ε(bond energy) and a (lattice parameter of the unconstructed surface).

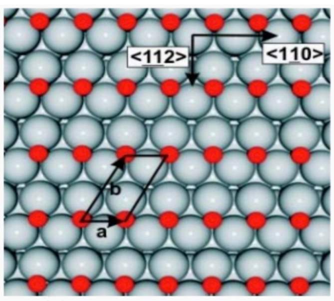
c) What is the gain in energy due to the reconstruction with this approximation?

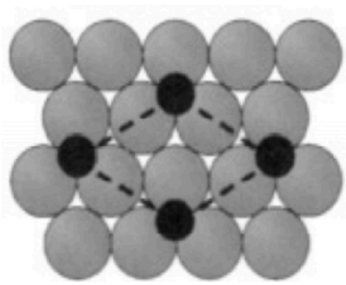
4. For the following surface structures, determine for each the Wood's notation



Unreconstructed reconstructed reconstructed

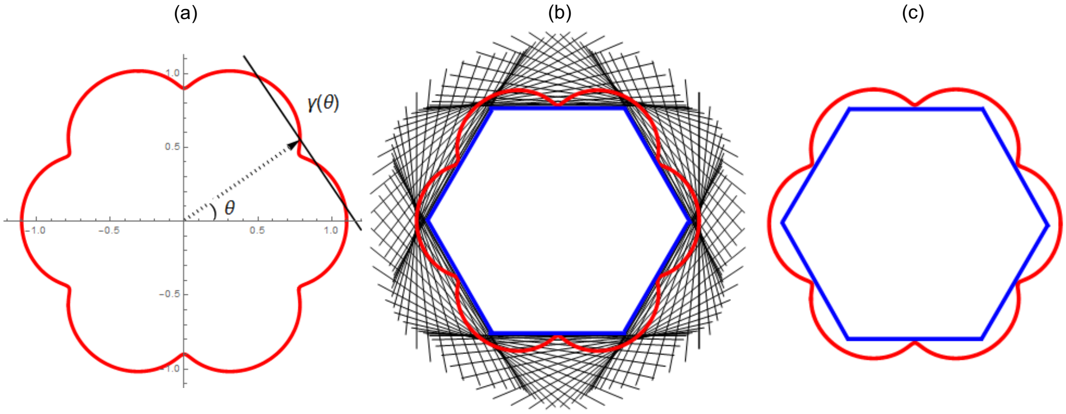






Unreconstructed reconstructed reconstructed

5. The following figures are a 2D illustration of Wulff construction. As you learned from the lecture, the Wulff shape is the envelope shape enclosed by the tangent lines of surface energy vectors in the $\gamma - plot$ in polar coordinates, which is the red shape below. The enclosed faceted blue shape, which is the equilibrium crystal shape for this specific $\gamma - plot$, depends largely on the cusps, lowest surface energy orientations, from the $\gamma - plot$.



This is also true for 3D shapes, the facets indicate the lowest surface energy orientations. Below is a high resolution SEM micrograph of 3D equilibrium crystal shape (ECS) of gold supported on Yttria Stabilized Zirconia (YSZ), read more on publication: 10.1007/s10853-019-03436-5. Determine what are the facet families you can see from this shape. Use the Wulffmaker Mathematica file and try to reproduce a 3D carton shape of this experimental ECS of gold. Write down the values of surface energies you insert and recall what you did in the first problem in exercise 1. Do these values apply to the result you got from the broken bond model?