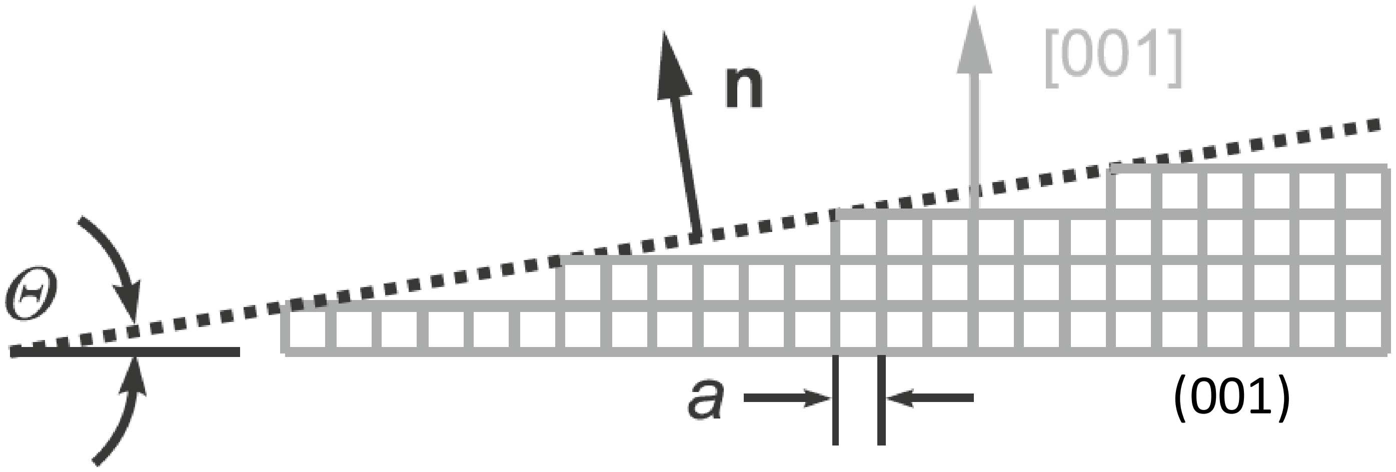
5.1 Vicinal surfaces (stepped)

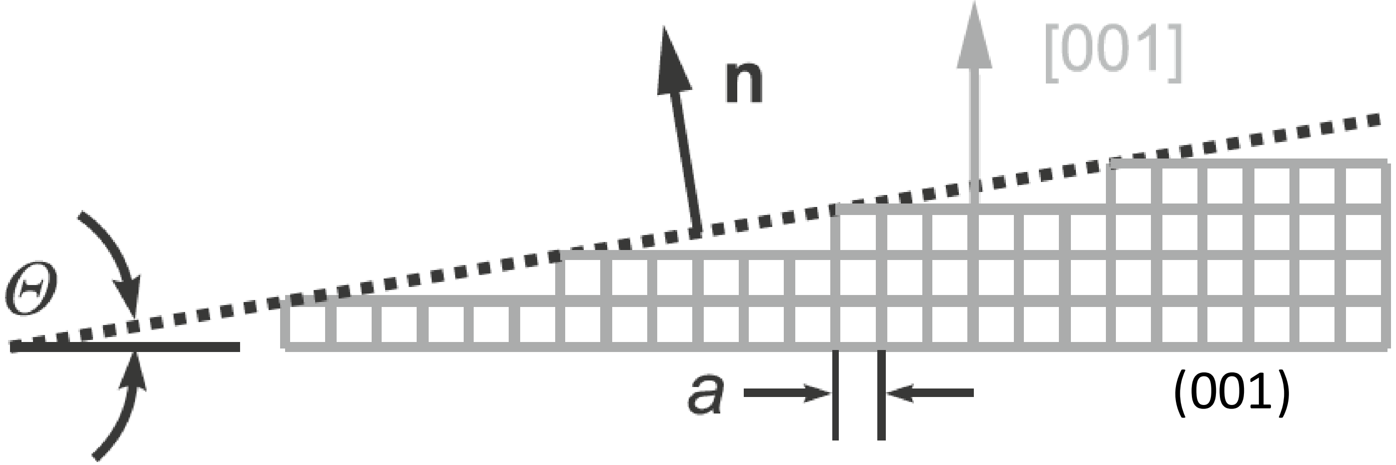
The sketch below represents a vicinal surface.

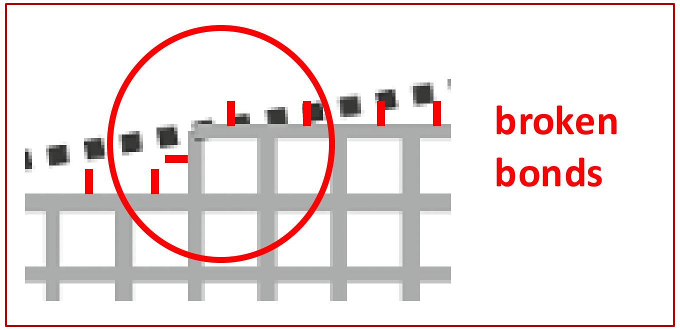
Can you explain qualitatively why the surface energy of the vicinal surface is higher than the corresponding singular (low Miller-index) surface?



5.1 Vicinal surfaces (stepped)

On the vicinal surface there are more broken bonds than on the singular (low Miller-index) surface: atoms at steps have two broken bonds instead of one.
This is a general result.

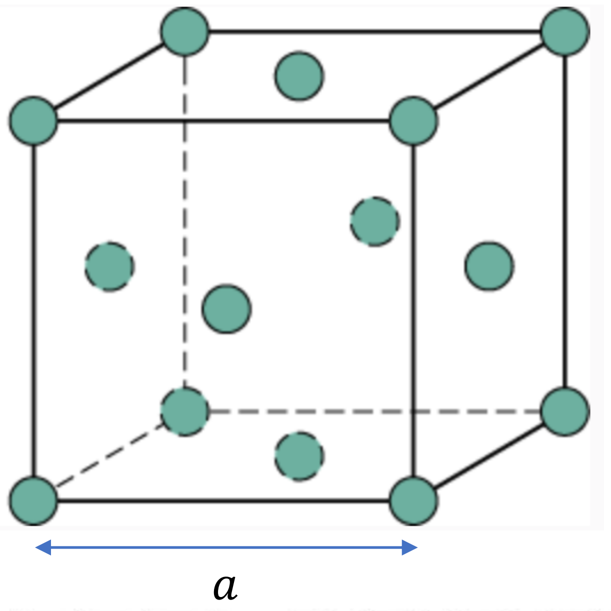




5.2 fcc crystal, surface energy

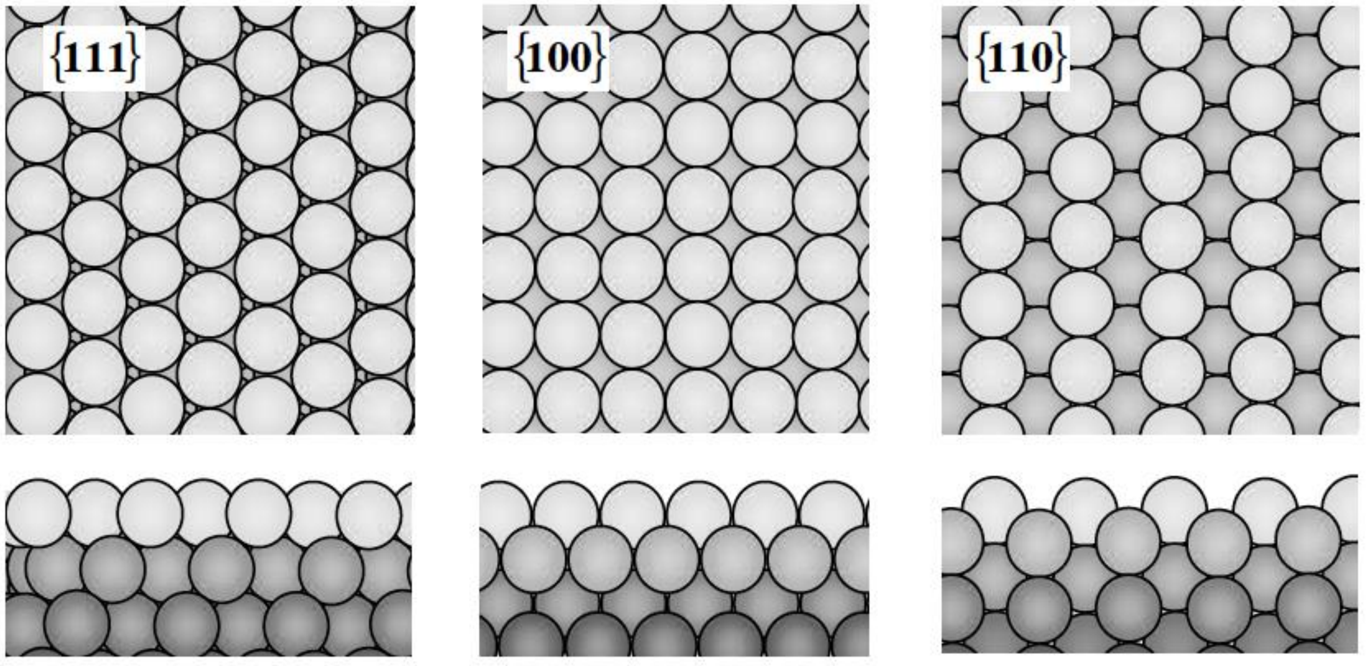
We want to verify the result presented in the lecture about the surface energy per unit surface (surface tension) for the three low-Miller index surfaces of a fcc elemental crystal.

We consider only the interaction between nn (nearest neighbors).
The number of nn in the bulk is 12.
The energy of a broken bond E_b= $E_c/12$ with E_c the bulk cohesive energy.
a is the fcc bulk lattice constant.



For each surface

- find the surface unit cell in terms of a;
- find the number of broken bonds per surface unit cell. Warning: the {110} is tricky!
- express the surface energy per unit surface, γ_{hkl}, in terms of E_c and a;
- compare the values of γ_{hkl} found for the three crystal orientations.

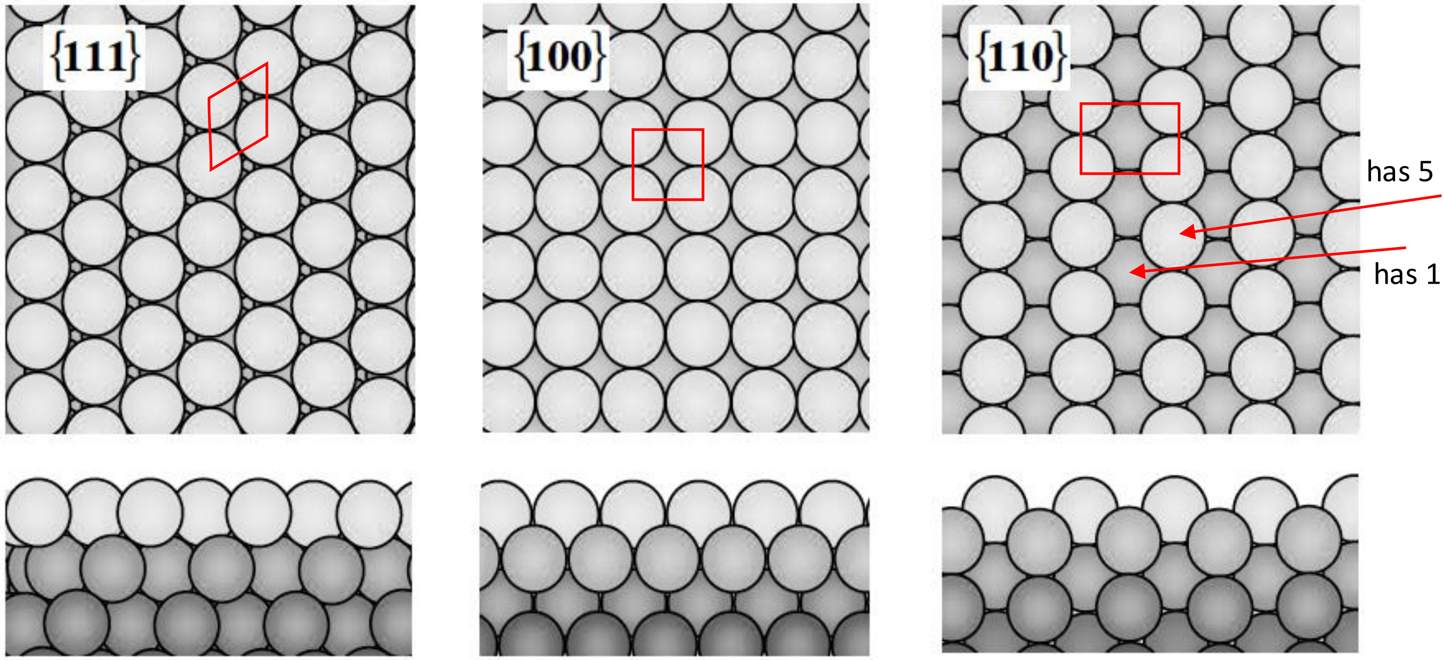


5.2 fcc crystal, surface energy - Solution

hkl	111	100	110
area surface unit cell	$a^2\sqrt{3}/4$	$a^2/2$	$a^2/\sqrt{2}$
n_b (broken bonds, out of 12)	3	4	5+1=6
surf. energy per surf. unit cell	$E_c/4$	$E_c/3$	$E_c/2$
γ_{hkl} (surface energy per unit surface)	$\frac{E_c}{4}\frac{1}{\frac{a^2\sqrt{3}}{4}} = \frac{E_c}{a^2\sqrt{3}} = 0.577\,\frac{E_c}{a^2}$	$\frac{E_c}{3}\frac{1}{\frac{a^2}{2}} = \frac{2E_c}{3a^2} = 0.666\,\frac{E_c}{a^2}$	$\frac{E_c}{2}\frac{1}{\frac{a^2}{\sqrt{2}}} = \frac{E_c}{\sqrt{2}a^2} = 0.707\,\frac{E_c}{a^2}$

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

the surface unit cells are indicated in red

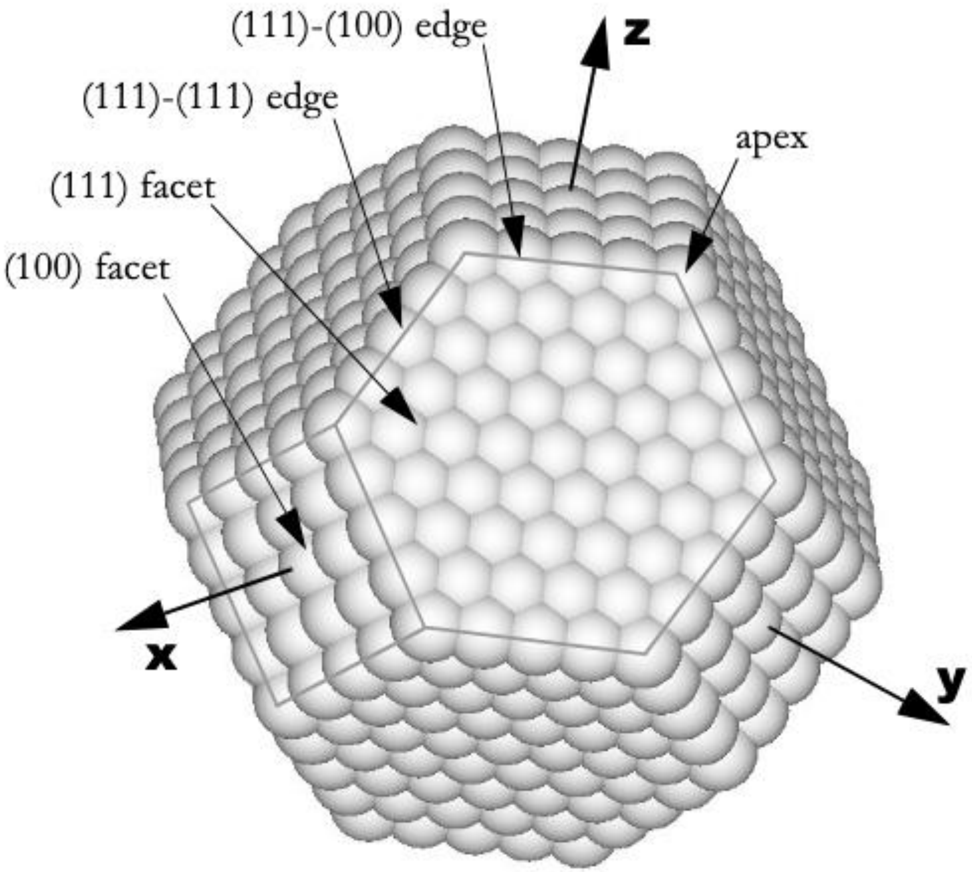


has 5 broken bonds

has 1 broken bond!

5.3 Equilibrium shape of a nanocrystal

Consider the nanocrystal shown below.
By looking at the existing surface facets, determine if the material bulk structure is simple cubic (sc), body-centered cubic (bcc) or face-centred cubic (fcc)

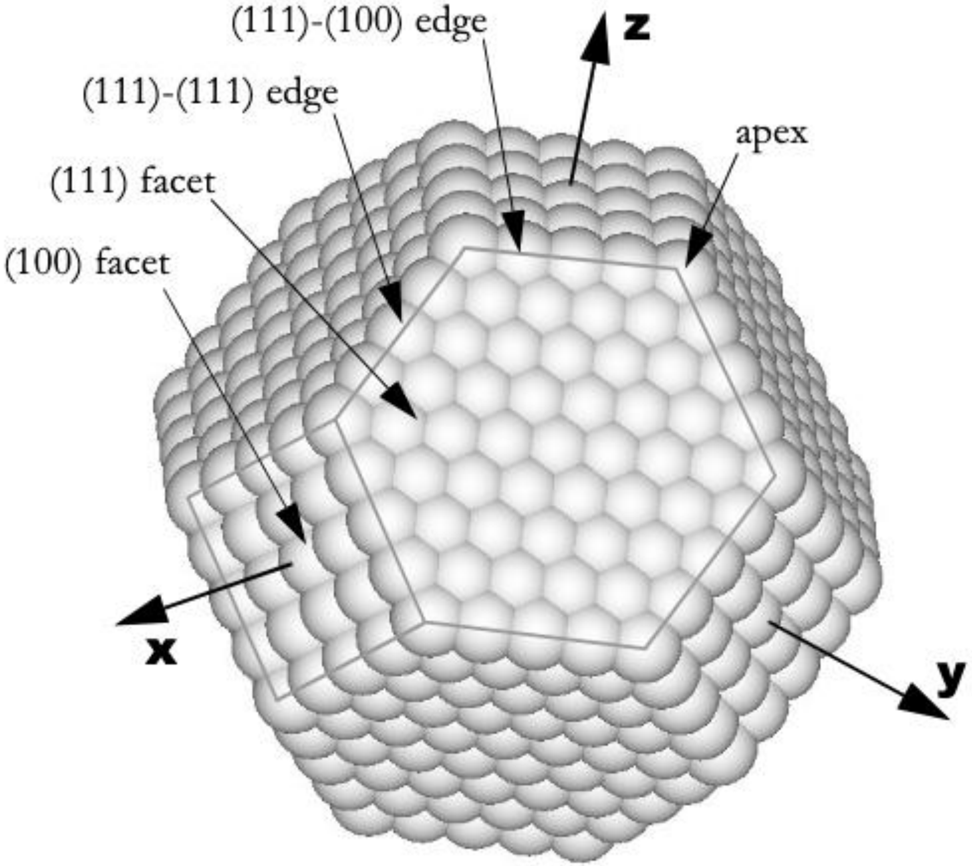


Facts and Figures:

- 482 surface atoms
- 8 (111)-facets
- 6 (100)-facets
- 24 apex positions
- 54 atoms on a (100)-surface (excluding edges)
- 296 atoms on a (111)-surface (excluding edges)
- 36 atoms form a (111)-(111) edge
- 72 atoms form a (100)-(111) edge

5.3 Equilibrium shape of a nanocrystal - Solution

The nanocrystal surface is composed of (111) and (100) facets, which have the lowest and second lowest surface energy in fcc crystals. Therefore, we can deduce that the material has a fcc structure.



Facts and Figures:

- 482 surface atoms
- 8 (111)-facets
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- 24 apex positions
- 54 atoms on a (100)-surface (excluding edges)
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- 36 atoms form a (111)-(111) edge
- 72 atoms form a (100)-(111) edge

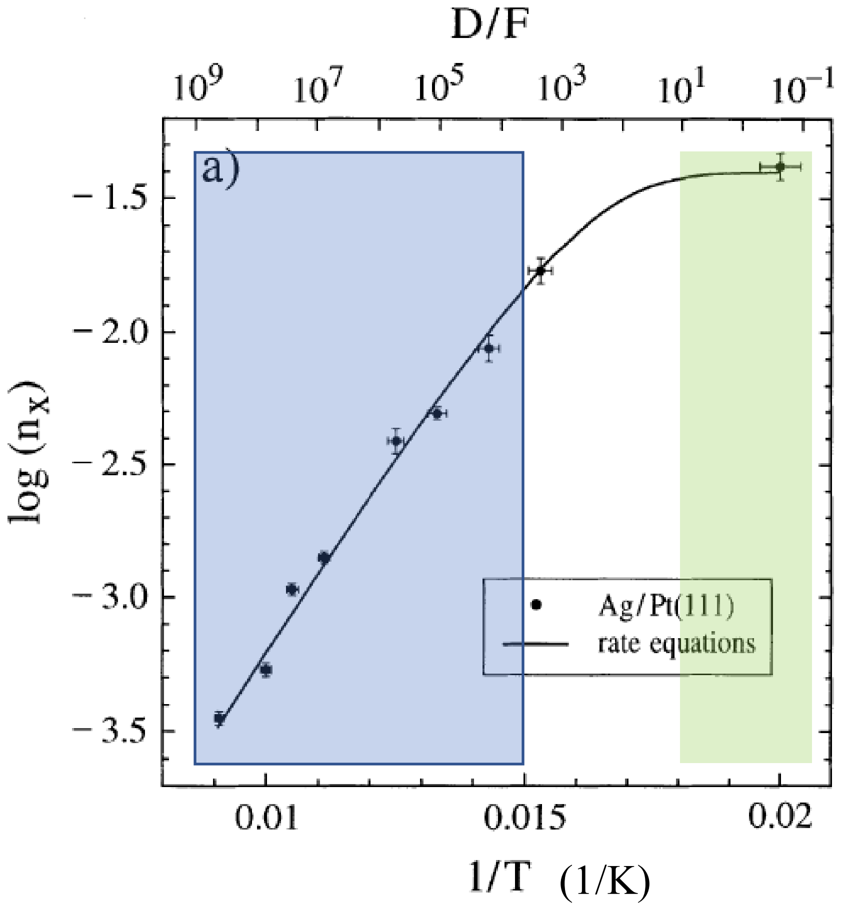
5.4 Ag/ Pt(111)

Researchers want to measure the diffusion barrier of Ag monomers on the Pt(111) surface. To this purpose they deposit 0.2 ML of Ag on Pt(111) at different substrate temperatures and measure the corresponding island density (n_x), as reported in the Arrhenius plot.

We can easily recognize two different regimes, corresponding to the blue- and green-shaded areas, separated by a transient.

1) Describe qualitatively the island growth in the two regimes.

2) Assuming that only monomers can diffuse on the surface (critical nucleus size $i = 1$), calculate the energy barrier for adatom diffusion.



H. Brune Surf. Sci. Rep. **31**, 121 (1998)

5.4 Ag/ Pt(111) - Solution

1) In the green-shaded area the island density is constant, meaning that the adatoms do not diffuse (statistical growth). In the blue-shaded area, the Arrhenius plot for the island density has a linear behavior. This regime corresponds to adatom diffusion and nucleation to form islands

2) For $i = 1$, the island density (n_x), as a function of temperature T is described by:

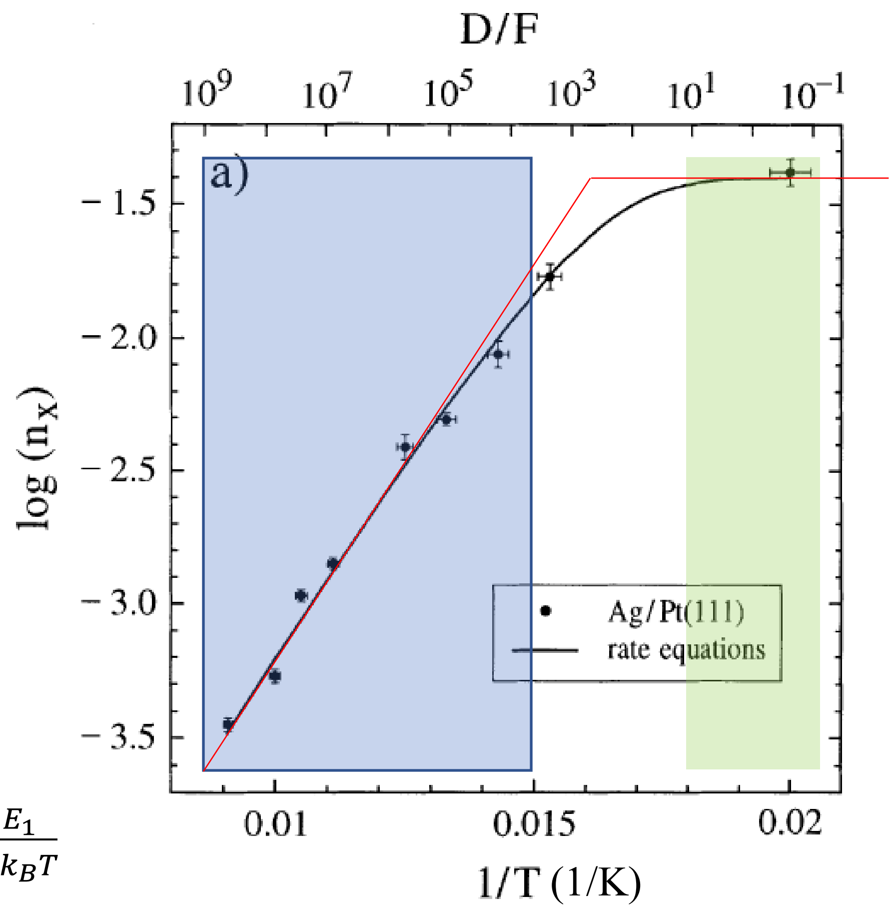
$$n_x = \eta(\theta, 1)\left(\frac{D_0}{F}\right)^{-1/3} \exp\left(\frac{E_1}{3k_B T}\right)$$

where E_1 is the energy barrier for adatom diffusion.
We can see that:

$$\log(n_x) = \log[\eta(\theta, 1)\left(\frac{D_0}{F}\right)^{-1/3}] + \log(\exp\left(\frac{E_1}{3k_B T}\right)) = \log[\eta(\theta, 1)\left(\frac{D_0}{F}\right)^{-1/3}] + \log(e) * \frac{E_1}{3k_B T}$$

and then:

$$E_1 = 3k_B \frac{\Delta(\log(n_x))}{\Delta(\frac{1}{T})} \frac{1}{\log(e)}$$ ≈ 3 * 0.086 meV/K * 1.4/(0.005 1/K) * 1/0.436 = 165 meV



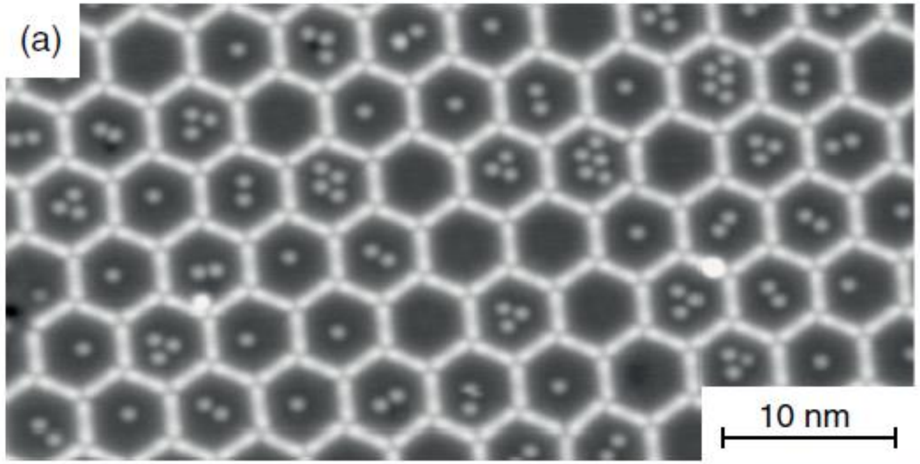
5.5 Self assembly and templated growth

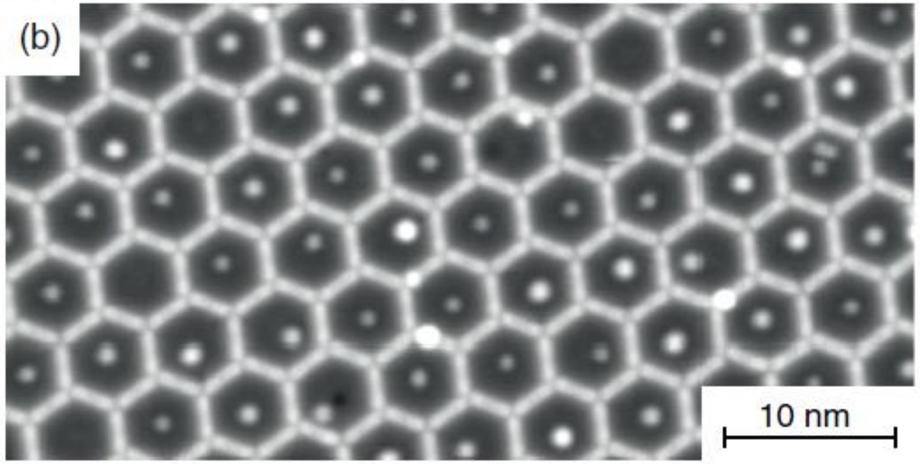
Consider the following observations on the STM images:

- for single occupancy of the hexagonal cells, adatoms or clusters sit in the center;
- for multiple adatom occupancy, the adatoms show well defined distances.

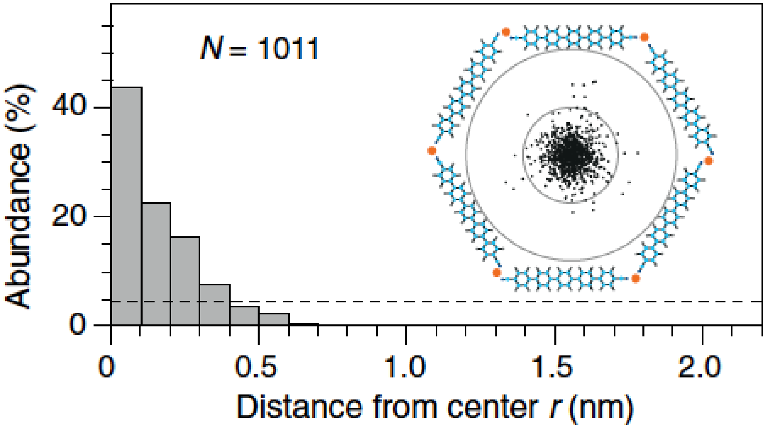
Can you explain qualitatively these behaviors?

a) Fe deposition at T = 10K





b) cluster formation after annealing to T_{ann} = 18K



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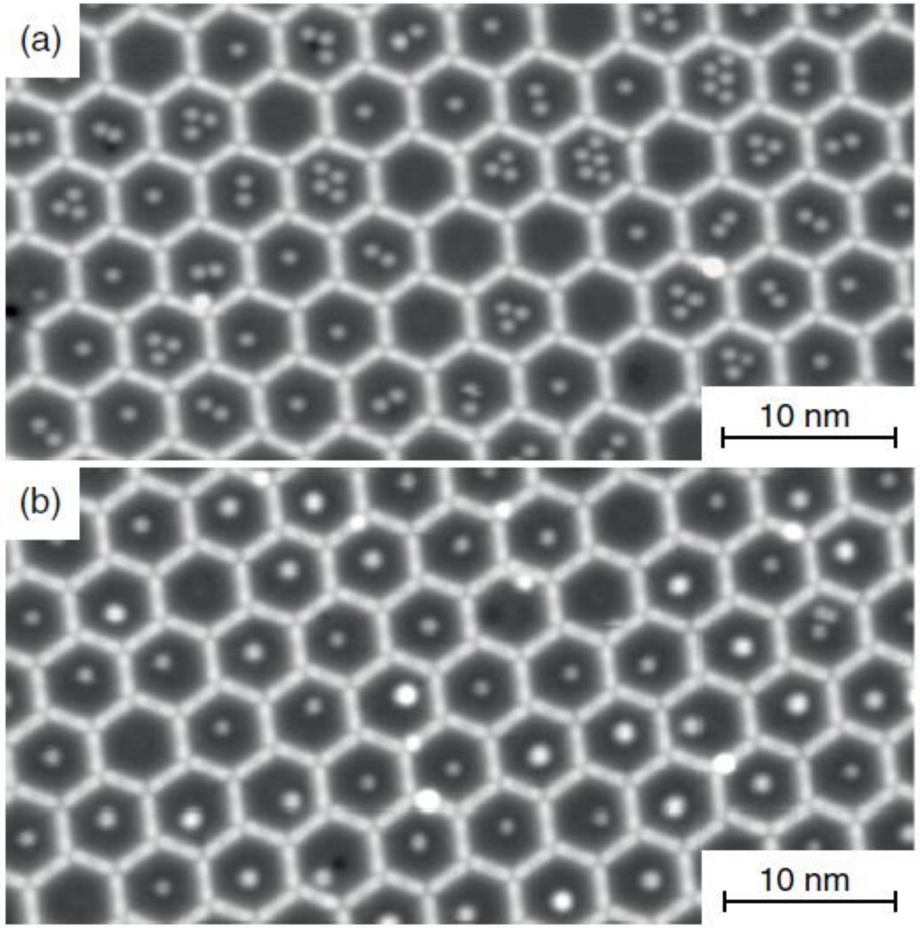
5.5 Self assembly and templated growth - Solution

- The LDOS at E_F originating from confinement of the surface state shows a local maximum. The adsorption of adatoms and clusters is favorable where the LDOS at E_F is higher.

- Each adatom scatters the surface state electrons; additional adatoms will adsorb at a distance from the first one that correspond to the first maximum of the LDOS. This mechanism can give rise to ordered adatom superlattices thanks to surface-state mediated interactions.

a) Fe deposition at T = 10K



b) cluster formation after annealing to T_{ann} = 18K