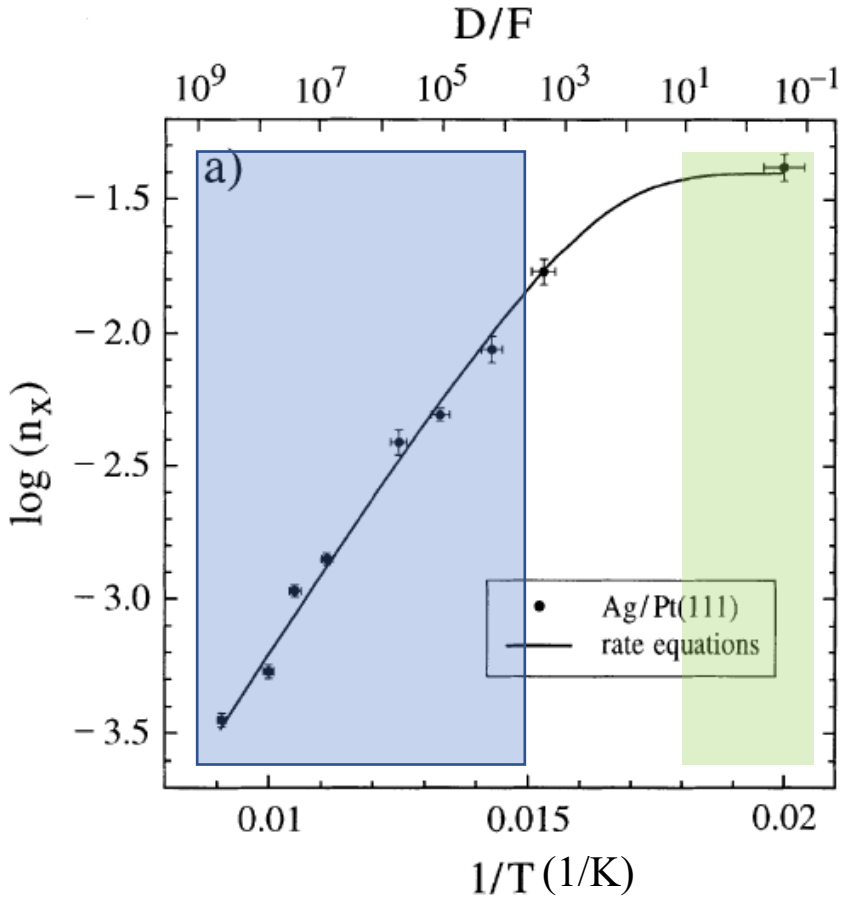
Exercise 1: Ag/Pt(111)

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.

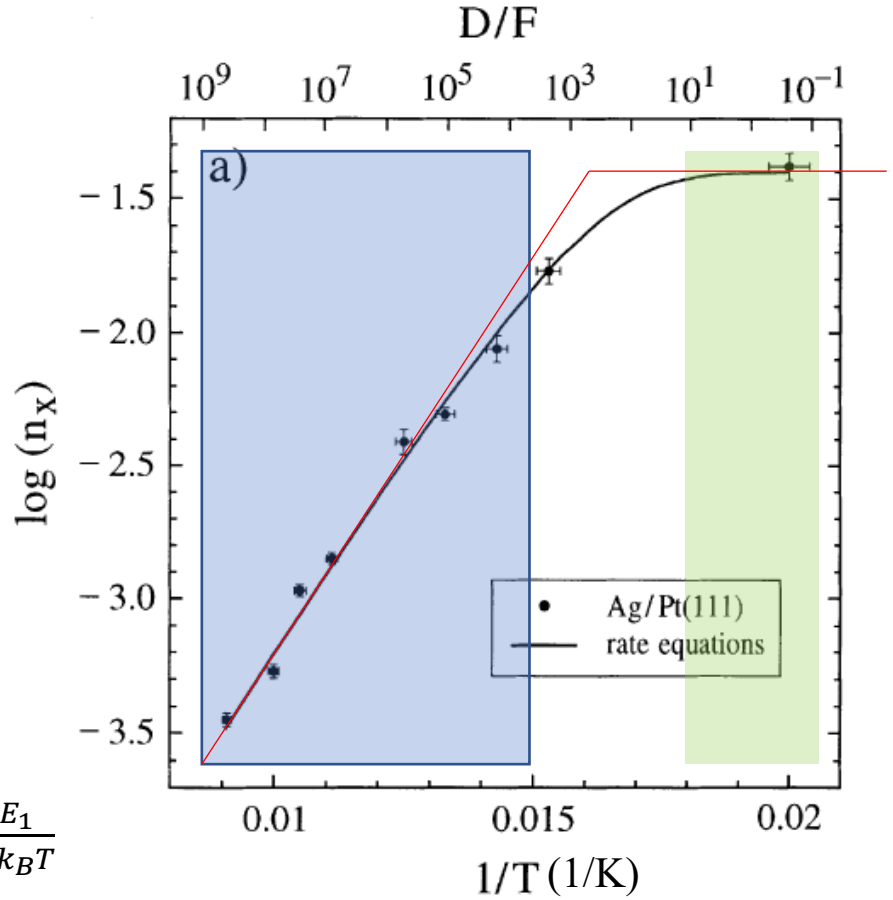
2) Assuming that only monomers can diffuse on the surface (critical nucleus size $i = 1$), calculate the energy barrier for adatom diffusion.



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

Solution: Ag/Pt(111)

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 easily see that:

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

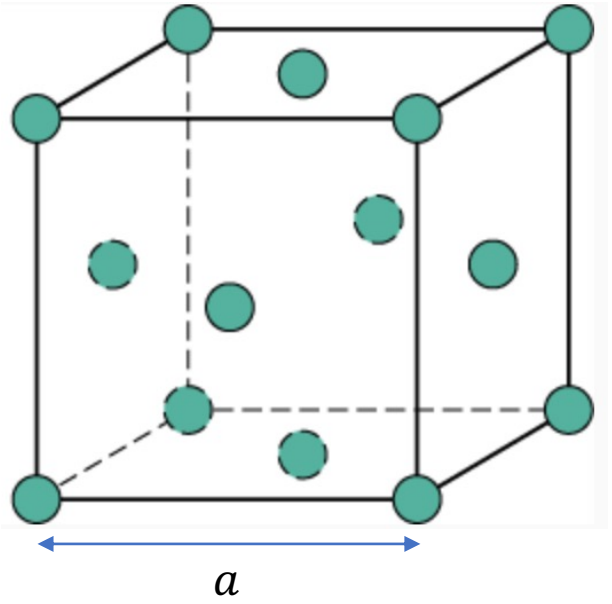
and then:

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

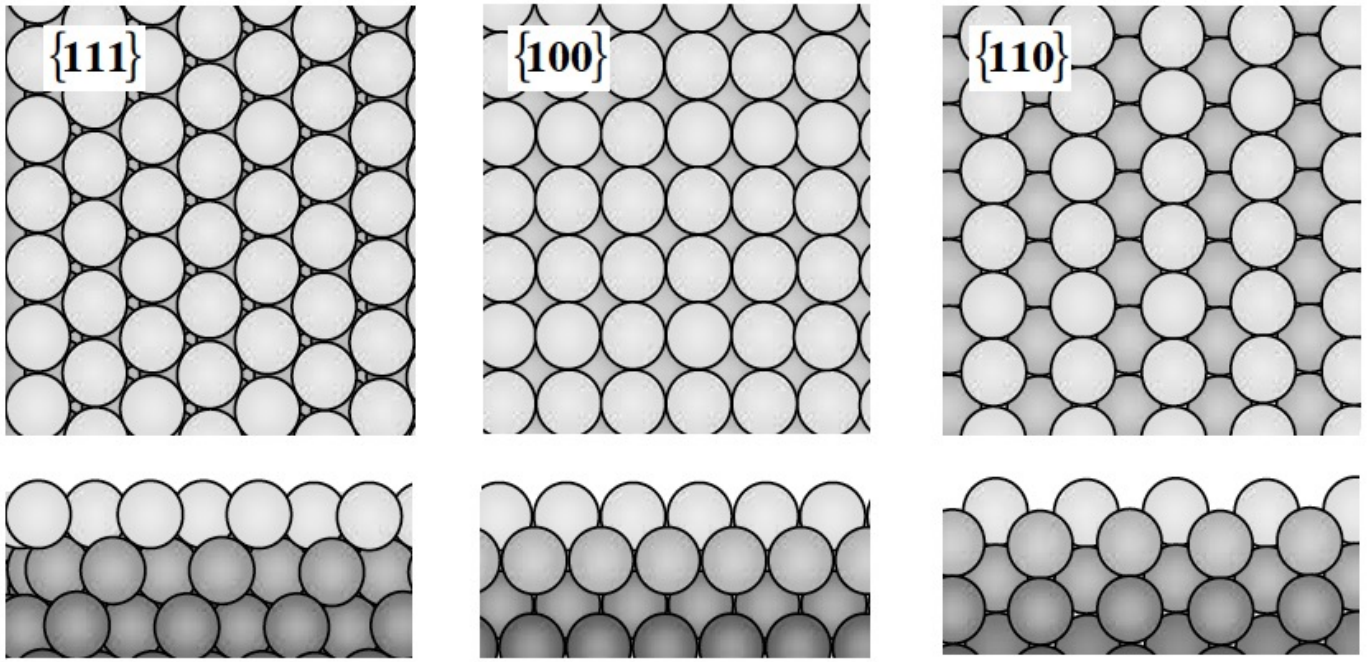
Exercise 2: fcc crystal, surface energy

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.
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.

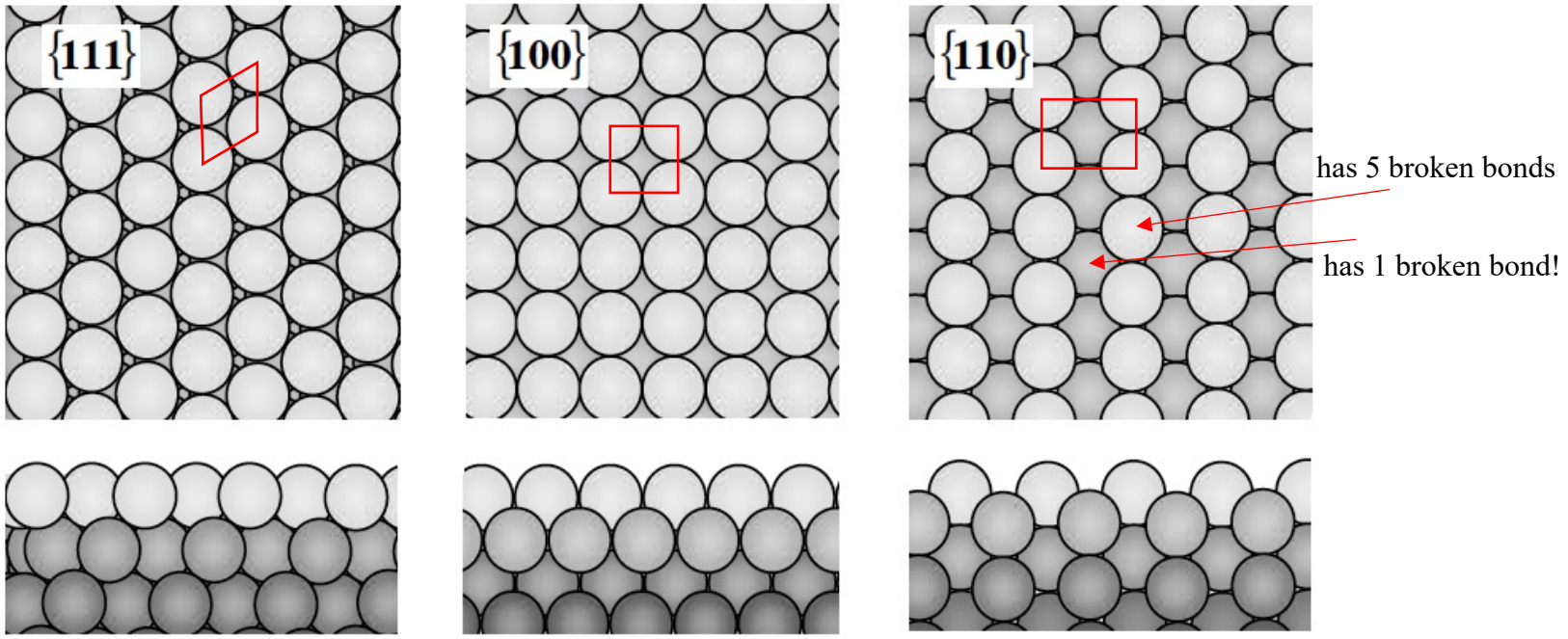


Solution: fcc crystal, surface energy

hkl	111	100	110
area surface unit cell	$a^2\sqrt{3}/4$	$a^2/2$	$a^2/\sqrt{2}$
n_b (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

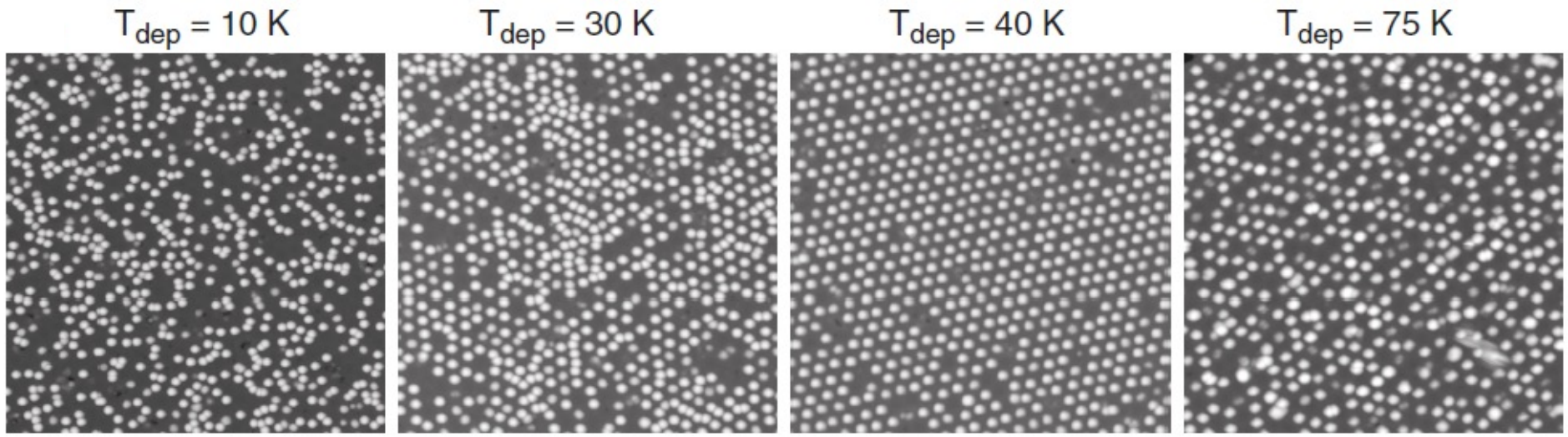


Exercise 3: Dy on graphene/Ir(111)

An STM study of the Dy deposition on graphene/Ir(111) shows different morphology depending on the substrate temperature, as reported in the figure below.

1) Explain qualitatively what happens at each temperature.

2) Give your best estimation of the different energy barriers for adatom diffusion characterizing the system. The deposition process takes 300 s. Then we assume that a diffusion process is activated if the diffusion frequency ν is equal or larger than 1 Hz



Remember that adatoms diffuse according to:

$D = D_0 \exp\left(-\frac{E_1}{k_B T}\right)$; $D_0 = a\,\nu_0$ with $\nu_0 = 10^{13}$ Hz

where a is the lattice parameter and $\nu_0 \exp\left(-\frac{E_1}{k_B T}\right)$ is the diffusion frequency

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Solution: Dy on graphene/Ir(111)

1)
- 10 K: adatoms do not diffuse (statistical growth)
- 30 K: adatoms starts to diffuse which results in partial order
- 40 K: adatoms are free to diffuse inside the moiré cell, but they can not escape the cell
- 75 K: the adatoms can move from one cell to the other, resulting in disorder, but they cannot overcome the Coulomb repulsion (only a very few islands are seen)

2) The diffusion frequency ν is given by

$$\nu = \nu_0 \exp\left(-\frac{E_1}{k_B T}\right)$$

then, with ν = 1Hz

$$E_1 = -k_B T\big(ln(\nu) - ln(\nu_0)\big) = k_B T\ ln(\nu_0)$$

Adatom start to diffuse at 30 K -> E_d = 0.086 * 30 * 29.9 = 77 meV
Adatom overcome the limits of the moiré cell at 75 K -> E_m = 0.086 * 75 * 29.9 = 192 meV
Since a little number of islands is observed the Coulomb repulsion E_q must satisfy $E_q > E_m$