EPFL
École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering

sunmil.epfl.ch

SuNMIL
Supramolecular NanoMaterials and Interfaces Laboratory

Real Surfaces
Lesson 3

MSE 304

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桑缪 썬밀 सानमिल ΣouNMιΛ سنمل CaHMПЛ

Key Topics in the Previous Class

Surface generation is associated

with an energy → γ

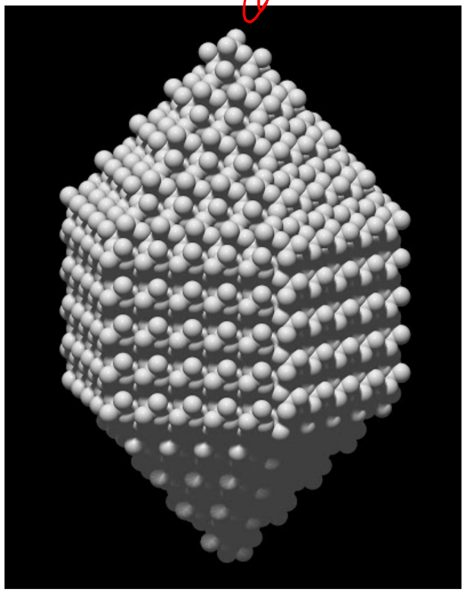
with a force (stretching bonds) → σ

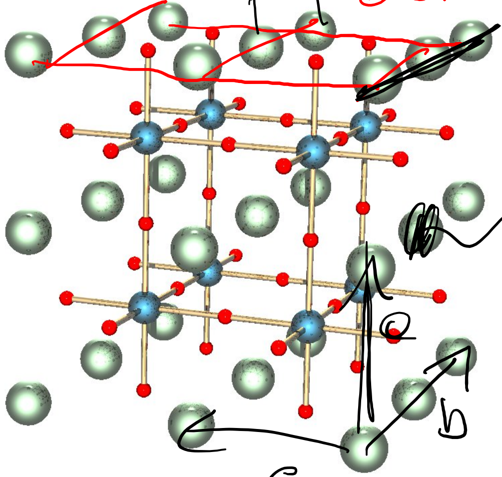
> excess surface free energy $\tilde{\gamma}(hkl)$

> surface stress f_{ij}

shape of an object → $\tilde{\gamma}(hkl)$

Difference between an Ideal and a Real surface





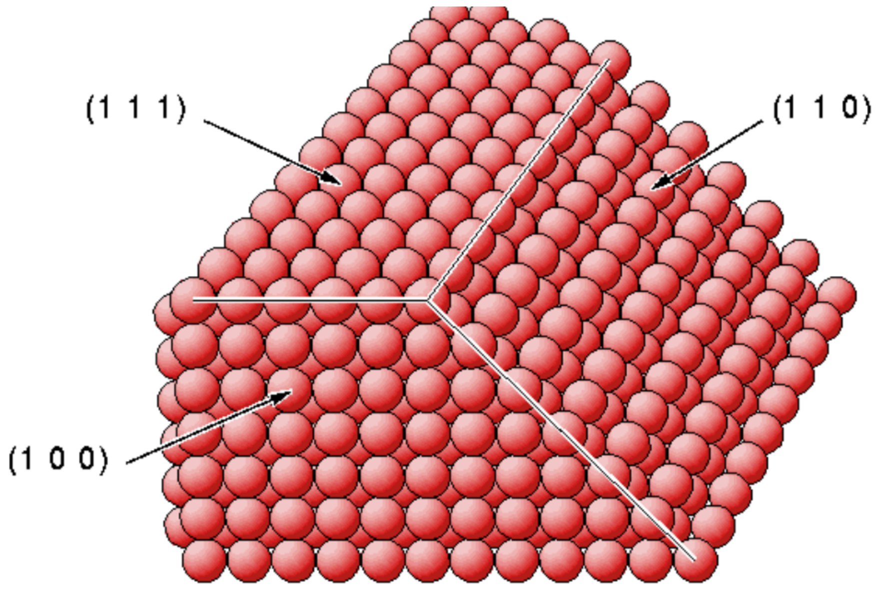
single crystal

polycristalline

1) Point defects 1D
2) Line defects 2D
3) Surface
   Plane defects 3D

4) Residual stress
5) Impurities

Difference between an Ideal and a Real surface



fcc lattice : different net planes

- Point Defects
- Line Defects
- Defects from the Bulk
- Reconstructions

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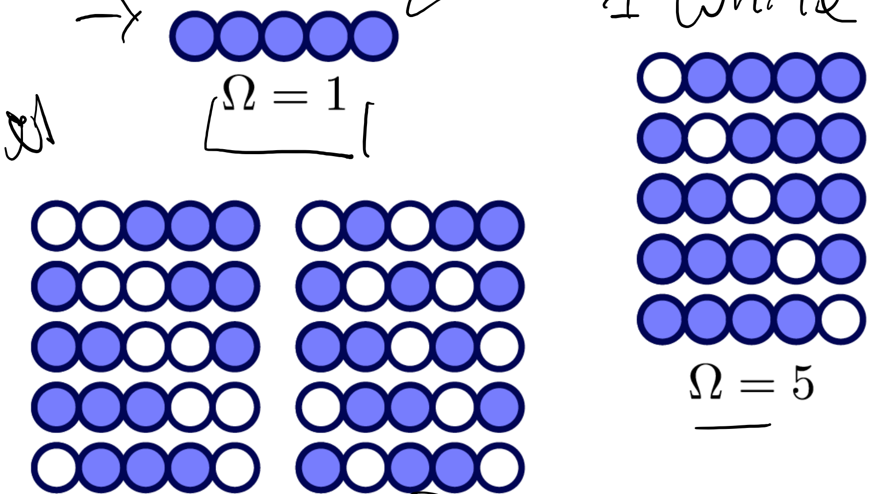
Point Defects in Real Surfaces

- Entropy is a counter of the number of ways you can realize a thermodynamic state: $S = k_B \ln \Omega$
- n_v vacancies in N states - *Stirling approximation* ($\ln N! \approx N \ln N$)

$$S(n_v) = k_B \ln \frac{N!}{(N-n_v)!n_v!} = k_B \left[N \ln N - (N-n_v)\ln(N-n_v) - n_v \ln n_v \right]$$

1 white

2 whites



$\Omega = 1$

$\Omega = 5$

$\Omega = 5 \cdot 4/2 = 10$

Point Defects in Real Surfaces

- Gibbs free energy for a solid with N sites containing n_v vacancies:

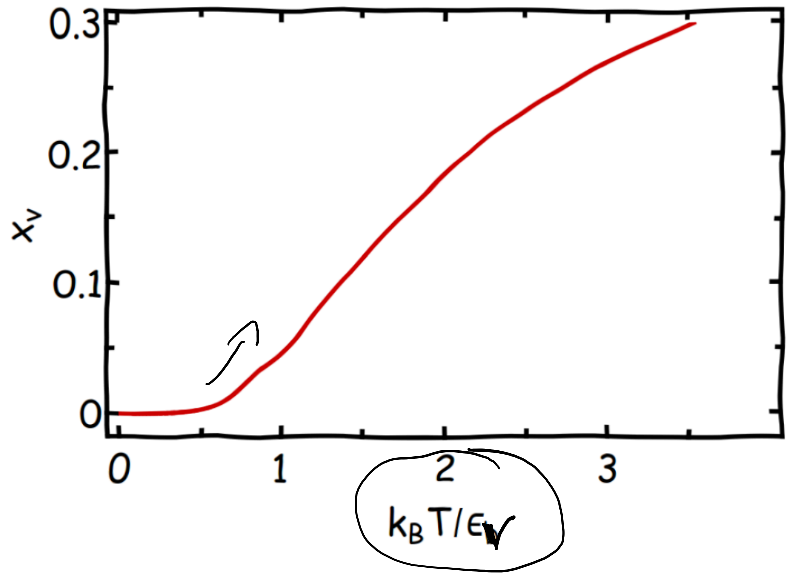
$$G = G_0 + n_v \epsilon_v - k_B T \underbrace{\left[N \ln N - (N - n_v) \ln (N - n_v) - n_v \ln n_v \right]}$$

- At equilibrium $\partial G / \partial n_v = 0$

$$\left(\frac{\delta G}{\delta n_v} \right)_{T,P,n_i} = 0$$

T, P, n_i

$$\frac{n_v}{N - n_v} = \exp\left(- \frac{\epsilon_v}{k_B T} \right) \longrightarrow \boxed{\frac{n_v}{N} \approx \frac{1}{1 + \exp\left(\frac{\epsilon_v}{k_B T} \right)}}$$



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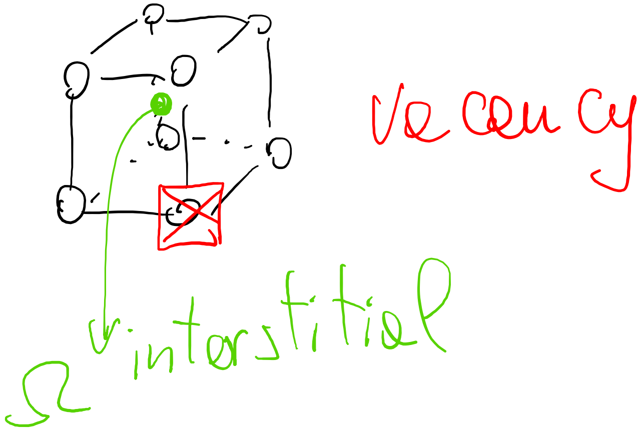
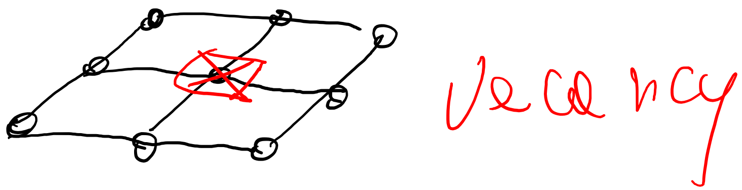
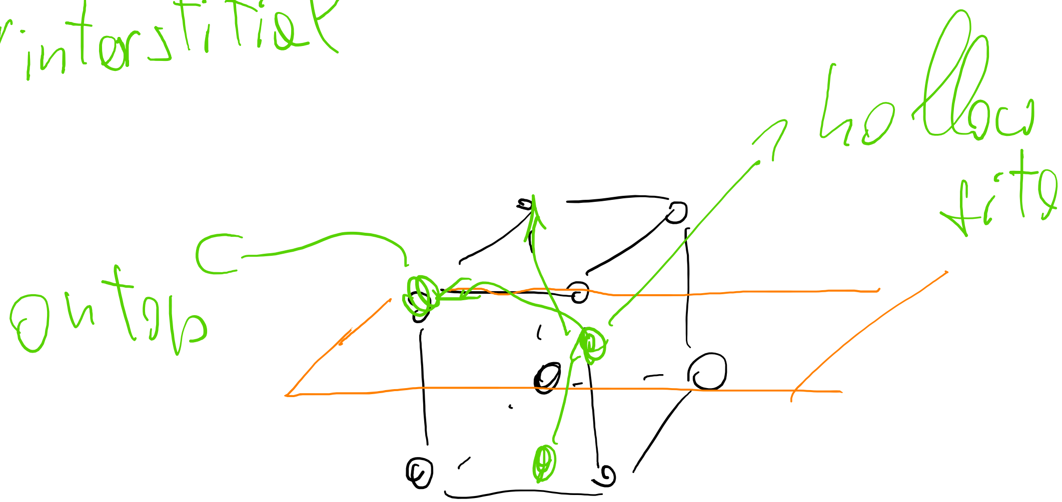
Point Defects in Real Surfaces

Point Defects in 3D



Point Defects in 2D





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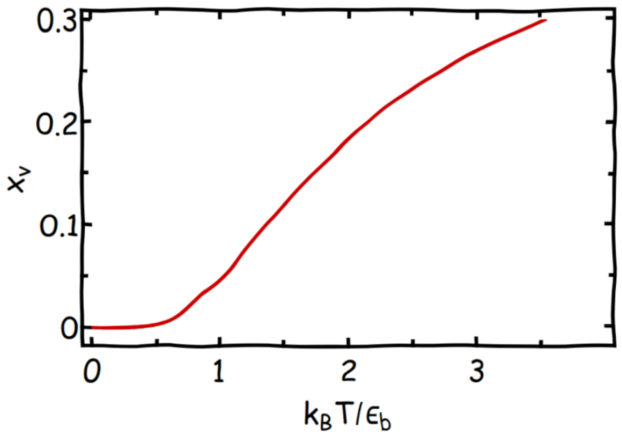
Point Defects in Real Surfaces

- Gibbs free energy for a solid with N sites containing n_v vacancies:
$$G = G_0 + n_v \epsilon_v - k_B T \left[N \ln N - (N - n_v) \ln (N - n_v) - n_v \ln n_v \right]$$
- Energy for creating a vacancy: bulk→kink $\epsilon_v \approx (12\epsilon_b - 6\epsilon_b) = 6\epsilon_b$
surf.→kink $\epsilon_v \approx (9\epsilon_b - 6\epsilon_b) = 3\epsilon_b$
- At equilibrium $\partial G / \partial n_v = 0$
$$\frac{n_v}{N - n_v} = \exp\left(-\frac{\epsilon_v}{k_B T}\right) \longrightarrow \frac{n_v}{N} \approx \frac{1}{1 + \exp\left(\frac{\epsilon_v}{k_B T}\right)}$$

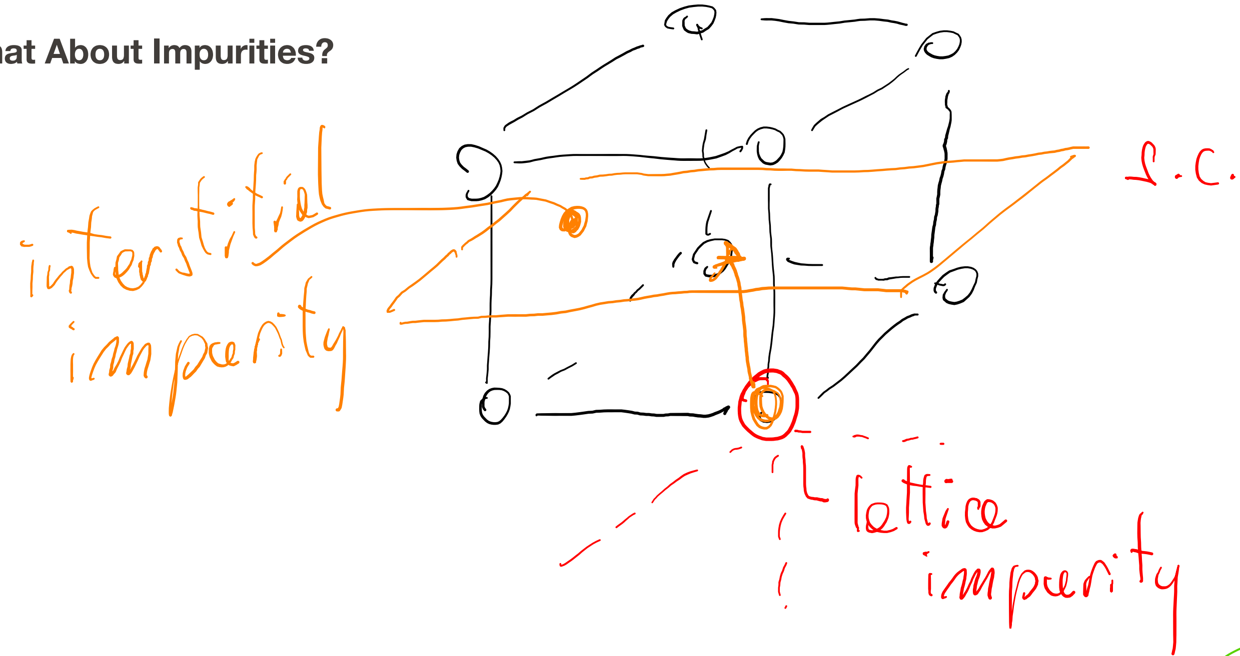


$$\frac{n_v^s}{N_s + \alpha n_v^s - \beta n_a^s} \simeq \frac{1}{1 + \exp\left(\frac{\epsilon_v^s}{k_B T}\right)}$$

$$\alpha, \beta \to f(h, k, l)$$

Point Defects in Real Surfaces

What About Impurities?



$$6h_B^p - 6h_B^i = 6\Delta h$$

$$5h_B^p - 5h_B^i = 5\Delta h$$

blossoming → impurities with time tend to segregate on surfaces

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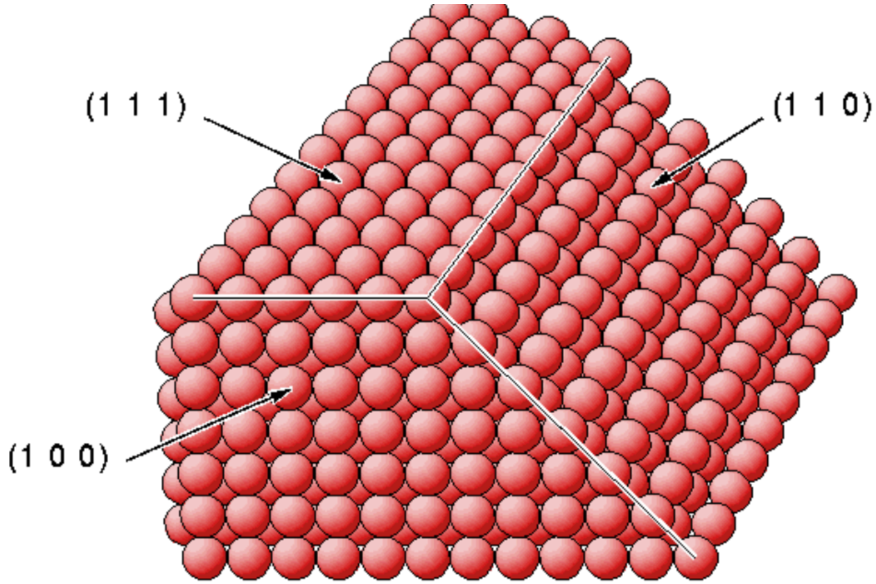
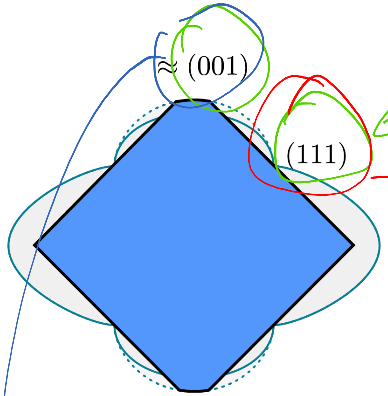
Difference between an Ideal and a Real surface



fcc lattice : different net planes

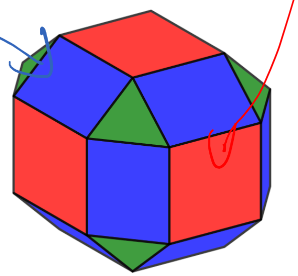
- **Point Defects**
- **Line Defects**
- **Defects from the Bulk**
- **Reconstructions**

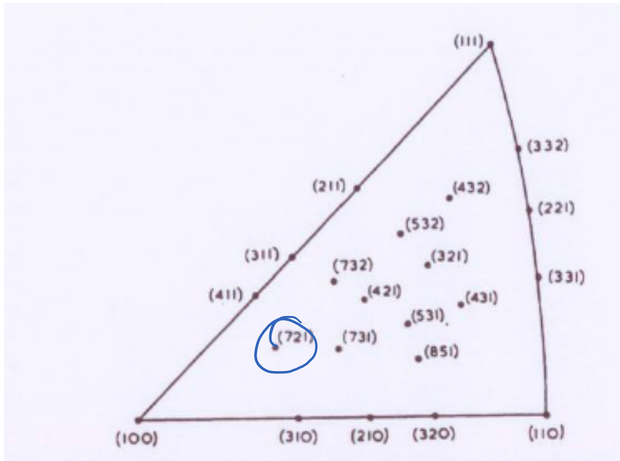
Line Defects in Real Surfaces

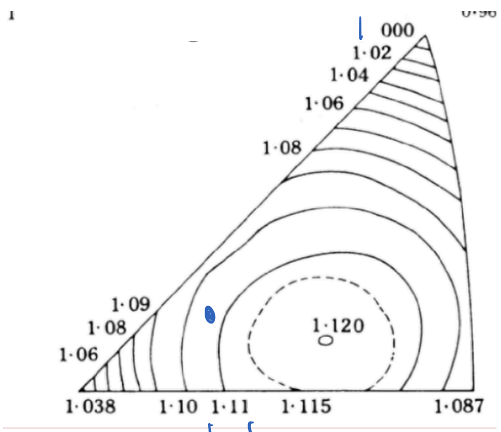


- In a liquid, γ is constant, so the system just want to minimize area at fixed volume $\longrightarrow$ spherical droplets
- In a solid, the surface energy γ is orientation-dependent. Minimize total surface energy at constant volume

$$\boxed{\min \int \gamma\left(\hat{\mathbf{n}}\right) dA}$$



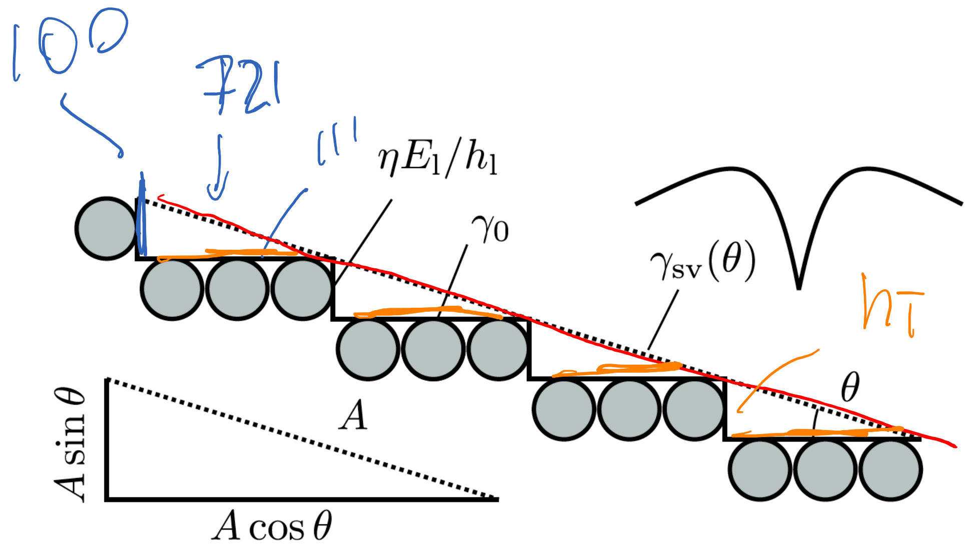




Line Defects in Real Surfaces

- Surfaces that correspond to cusps in the Wulff plot are very stable, and atomically flat (“singular surfaces”)
- Surfaces that are slightly tilted (“vicinal surfaces”) exhibit faceting: flat, singular-orientation **terraces** separated by **ledges**
- Surface energy can be worked out as a function of the angle θ

$$\gamma_{\mathsf{sv}}\left(\theta\right) = \gamma_0 \cos\theta + \frac{\eta E_{\mathsf{l}}}{h_{\mathsf{l}}} \sin\theta$$



Line Defects in Real Surfaces

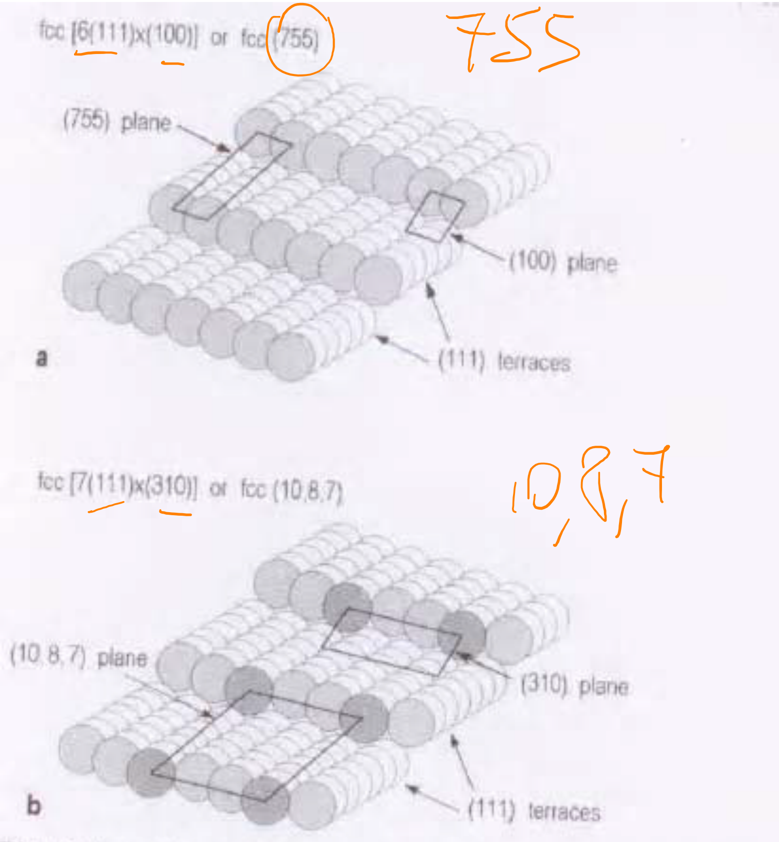
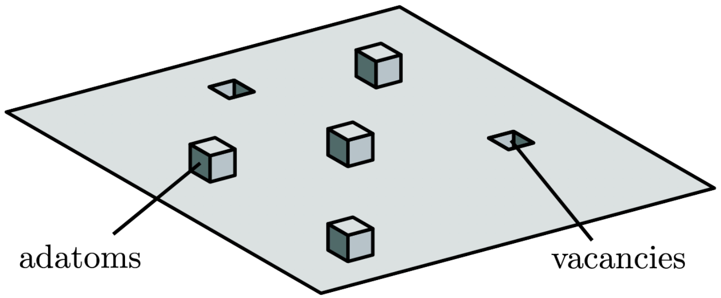


Fig. 2.11. (a) Stepped (755) and (b) kinked (10 8 7) fcc crystal faces

Line Defects in Real Surfaces



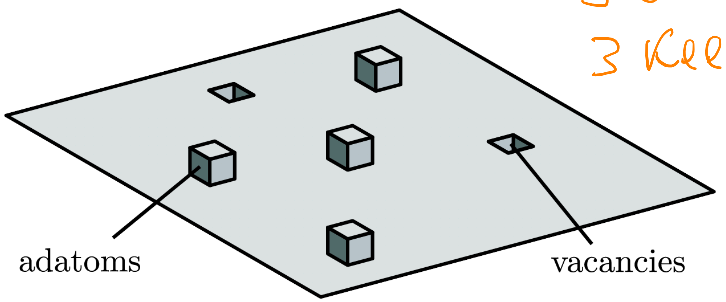
Line Defects in Real Surfaces

fcc

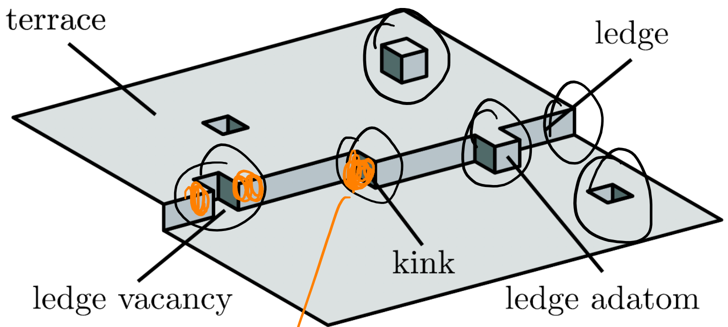
ledge 6 cut 6 keep

terrace 3 cut 9 keep

kink 9 cut 3 keep

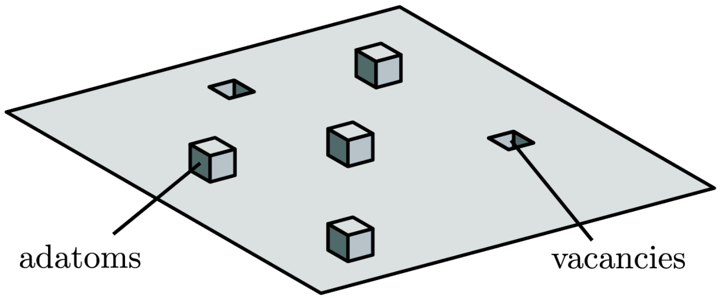


- In a real case, with ledges and kinks, the story is more complex
- Kinks are special, in that you can add an atom without changing the number of broken bonds



1 atom 9 cut 3 keep

Line Defects in Real Surfaces



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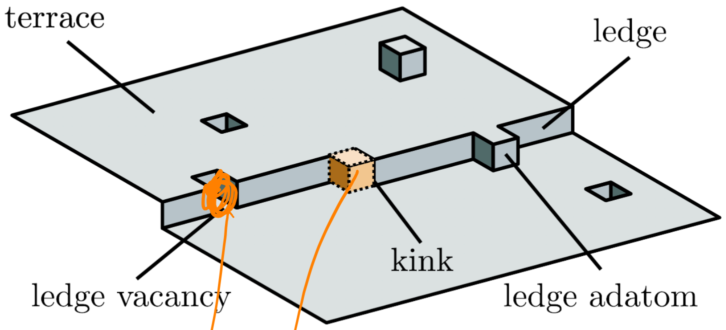
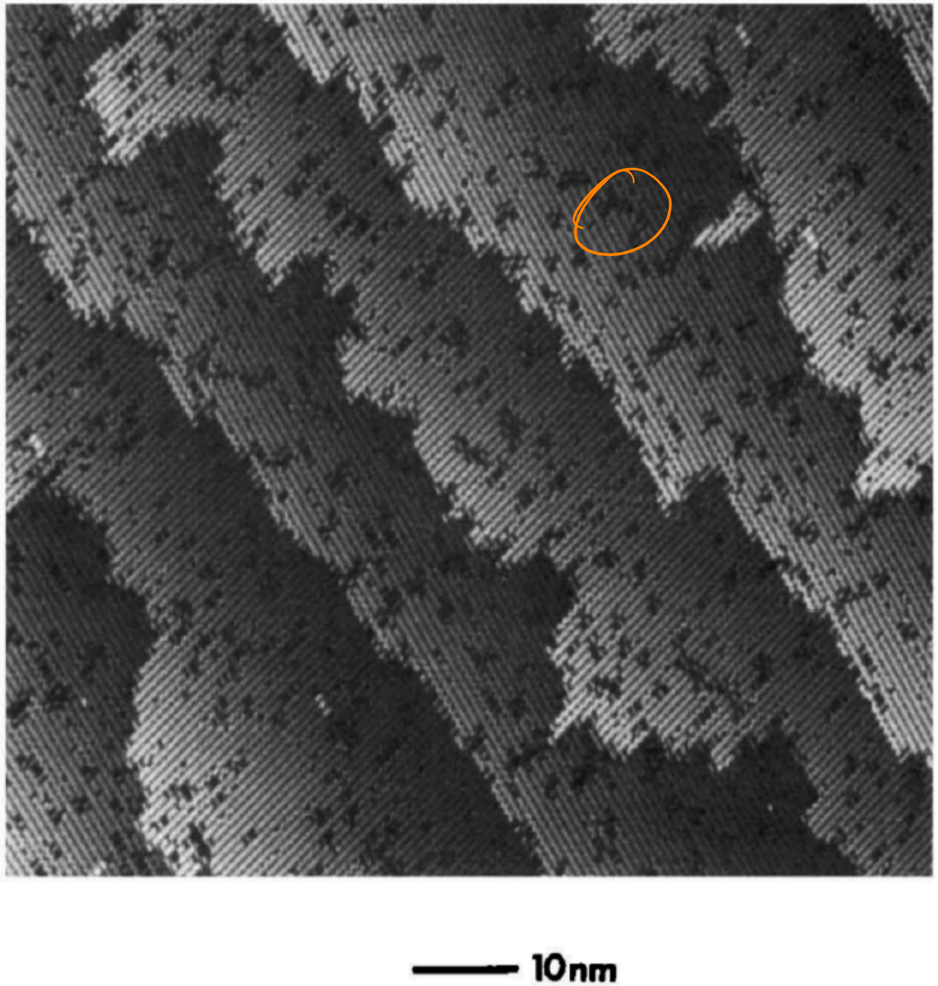


+ 8 cut
3 keep

Line Defects in Real Surfaces

very mobile



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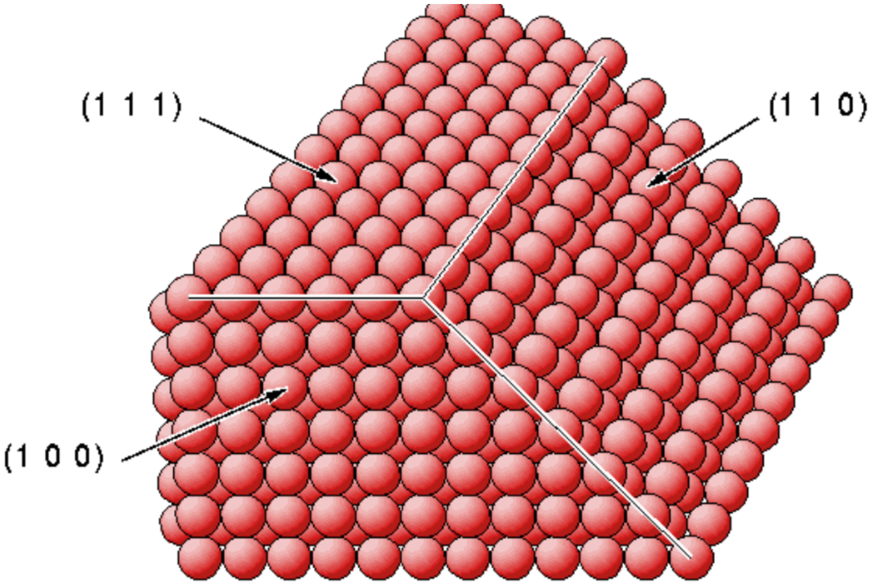
Difference between an Ideal and a Real surface

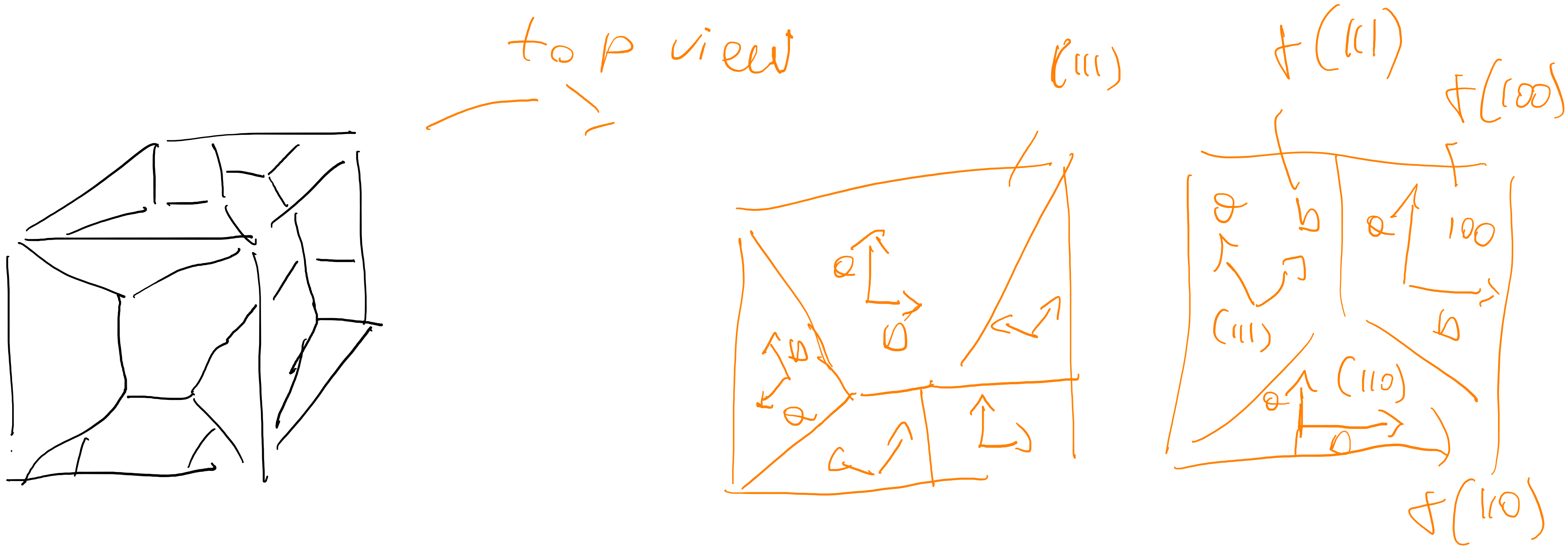


fcc lattice : different net planes

- Point Defects
- Line Defects
- Defects from the Bulk
- Reconstructions

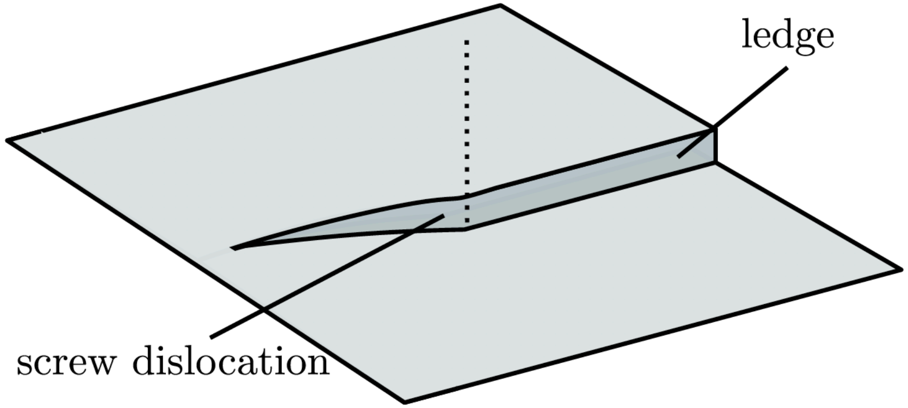
Defects from the Bulk in Real Surfaces

polycristalline

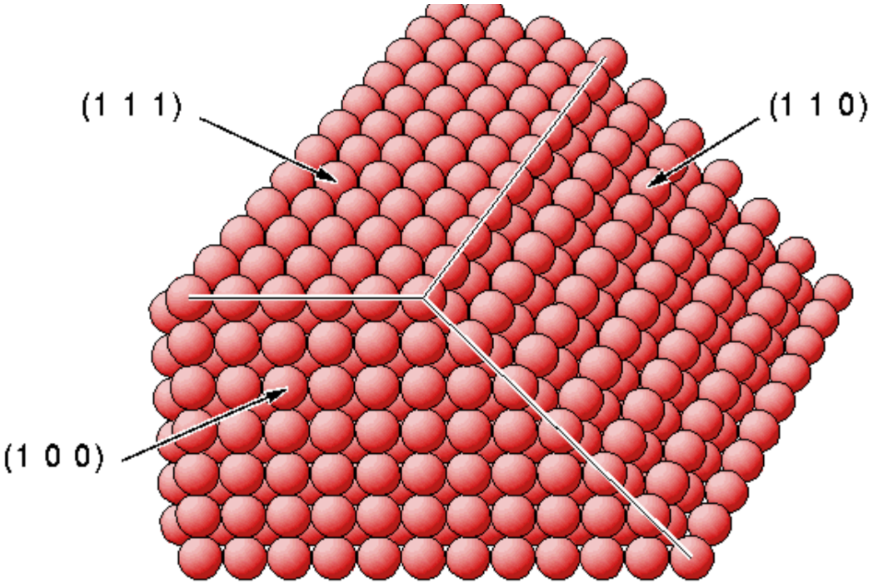


Defects from the Bulk in Real Surfaces

- Surfaces contain *kinetic* defects, that are typically connected to bulk defects (grain boundaries, dislocations)
- Surfacing dislocations can be seen by etching, or by decoration of the surface
- Screw dislocations can be a mechanism for crystal growth



Difference between an Ideal and a Real surface



fcc lattice :   different net planes

- Point Defects
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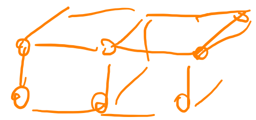
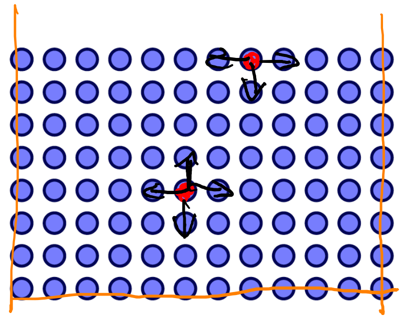
Reconstructions in Real Surfaces

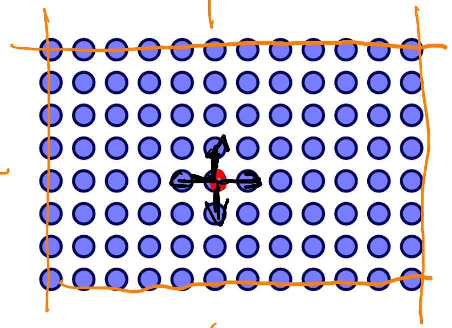
Cubic Crystal



Side View

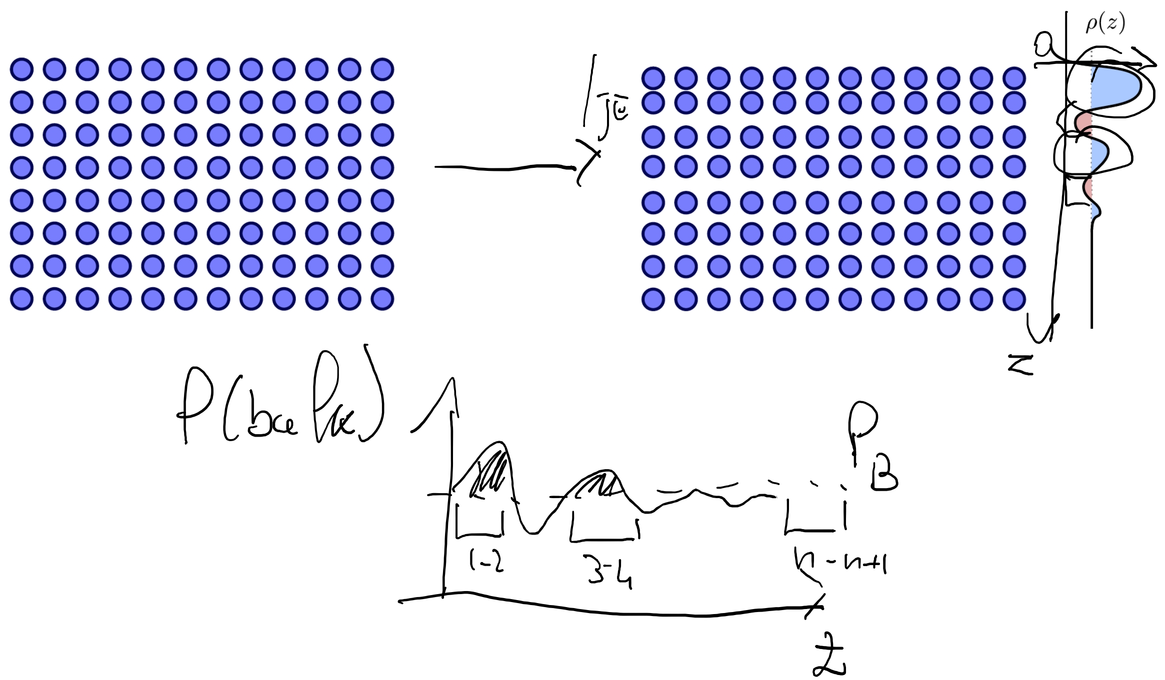


Top View

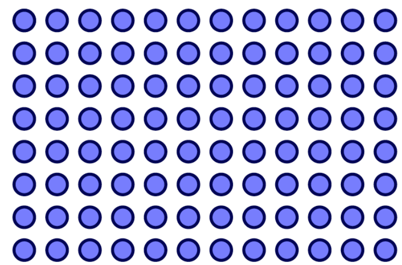


Reconstructions in Real Surfaces

Side View



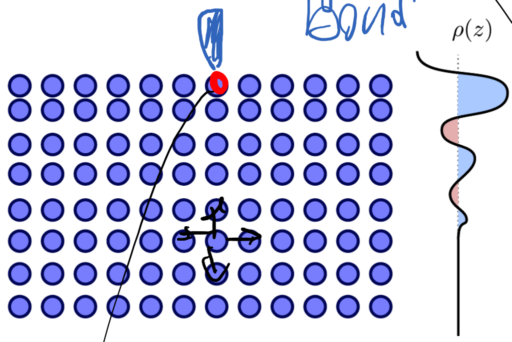
Top View



Reconstructions in Real Surfaces

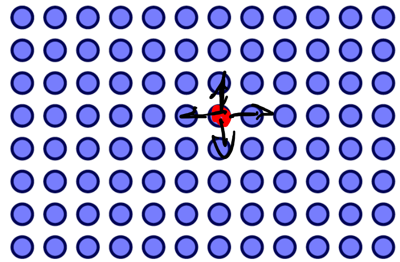
Side View

dangling bond



+1

Top View



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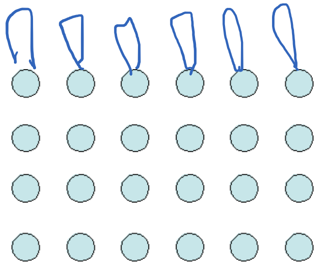
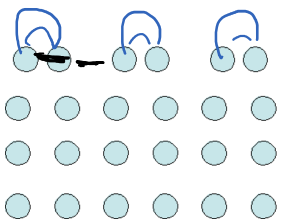
Reconstructions in Real Surfaces

Side View



dangling orbitals

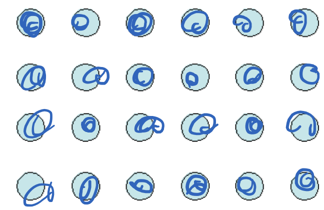
– surface bonds



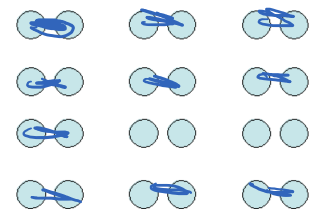
dangling bonds

the dangling bond is on top of the surface plane

Top View



d. orbitals

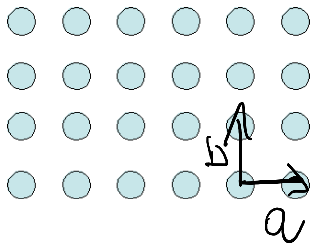


d. bonds

broken symmetry

Reconstructions in Real Surfaces

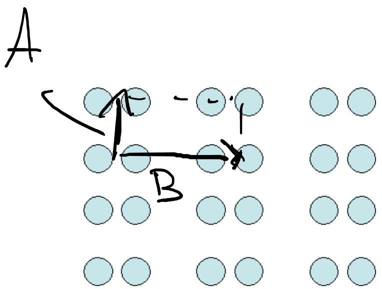
3D unit cells α, β, γ α β γ hkl a, b



$$\begin{bmatrix} A \\ B \end{bmatrix} = \begin{bmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{bmatrix} \begin{bmatrix} a \\ b \end{bmatrix}$$

* COMMENSURATE

$$G_{ij} \times \begin{bmatrix} a \\ b \end{bmatrix} = \begin{bmatrix} A \\ B \end{bmatrix}$$



if G_{ij} are all integers numbers

then the reconstruction is called *

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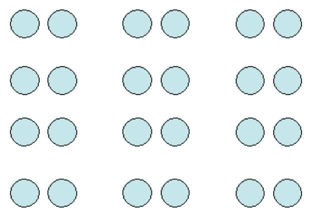
Reconstructions in Real Surfaces

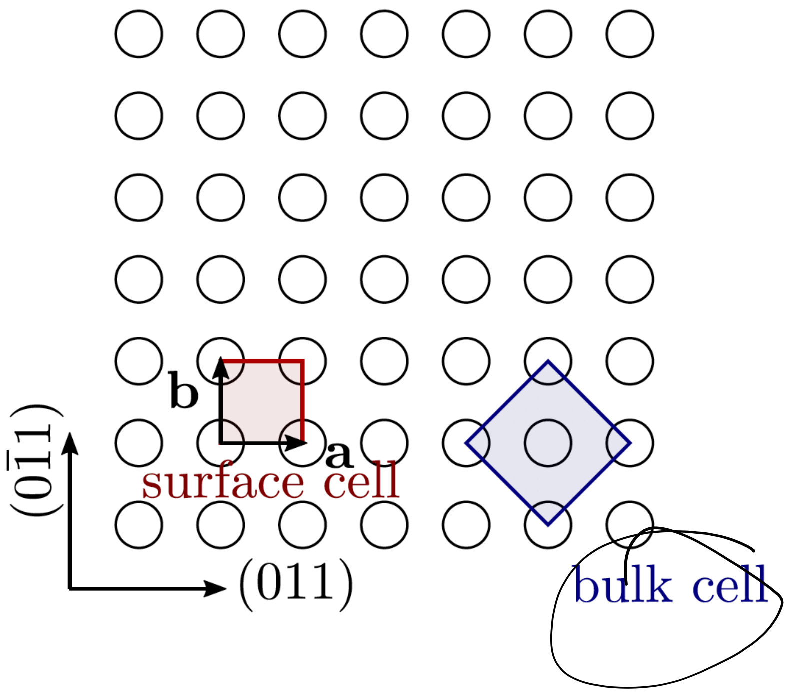


for commensurate reconstruction

Wood notation

- The unit cell of a (reconstructed) surface is often labeled relative to the clear-cut lattice vectors (Wood notation)

$$M\,(hkl) - [c|p]\,(m \times n)\,[R\alpha]$$



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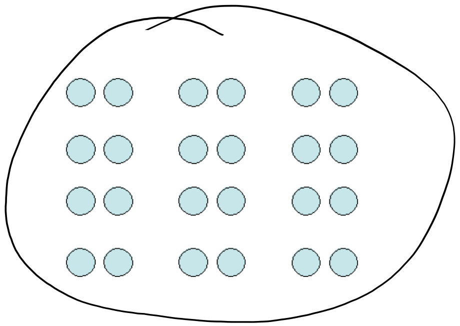
Reconstructions in Real Surfaces



- The unit cell of a (reconstructed) surface is often labeled relative to the clear-cut lattice vectors (Wood notation)

$$M\,(hkl) - [c|p]\,(m \times n)\,[R\alpha]$$

omition means $\alpha = 0$

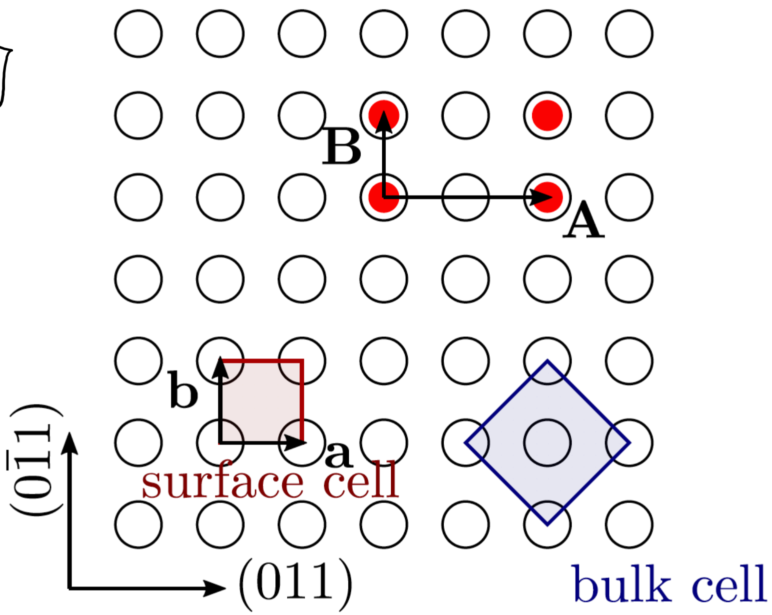
omition $[c|p]$ means p

$$m = \frac{|A|}{|a|}$$

$$n = \frac{|B|}{|b|}$$

α angle

Si(100)-(2 × 1)



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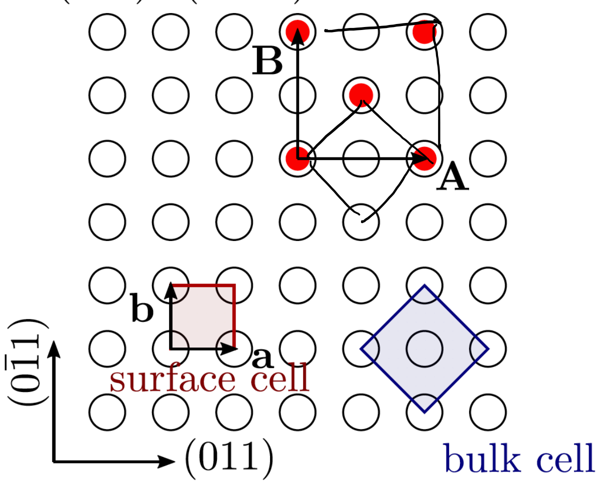
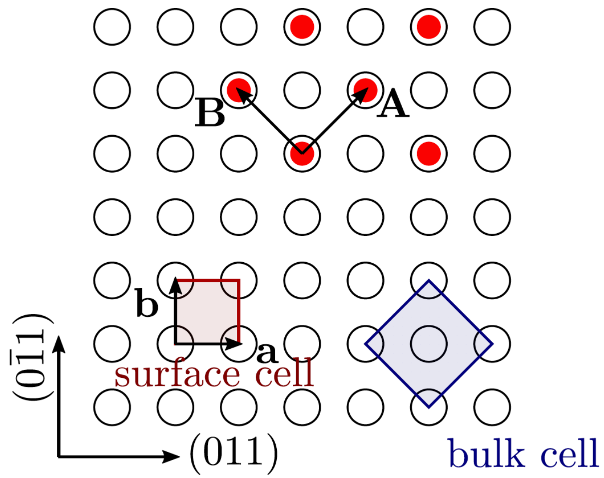
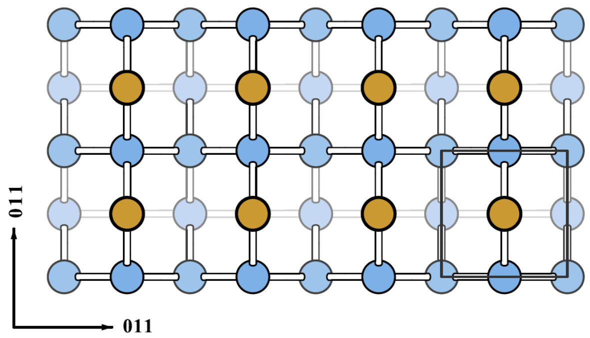
Reconstructions in Real Surfaces

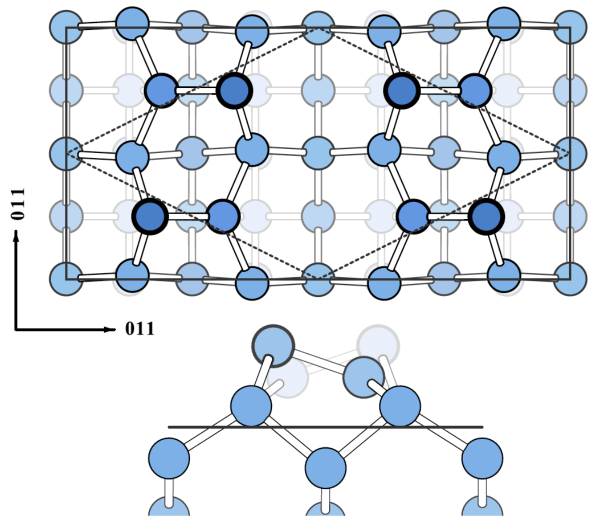
√2 x √2 R45





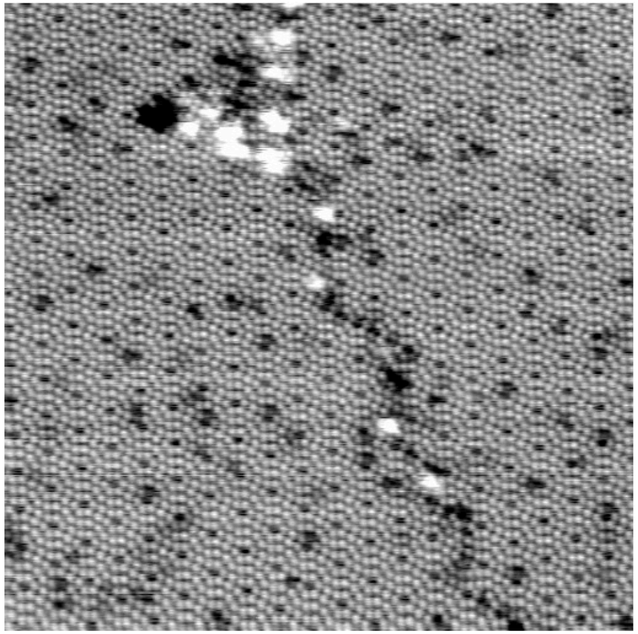
Reconstructions in Real Surfaces



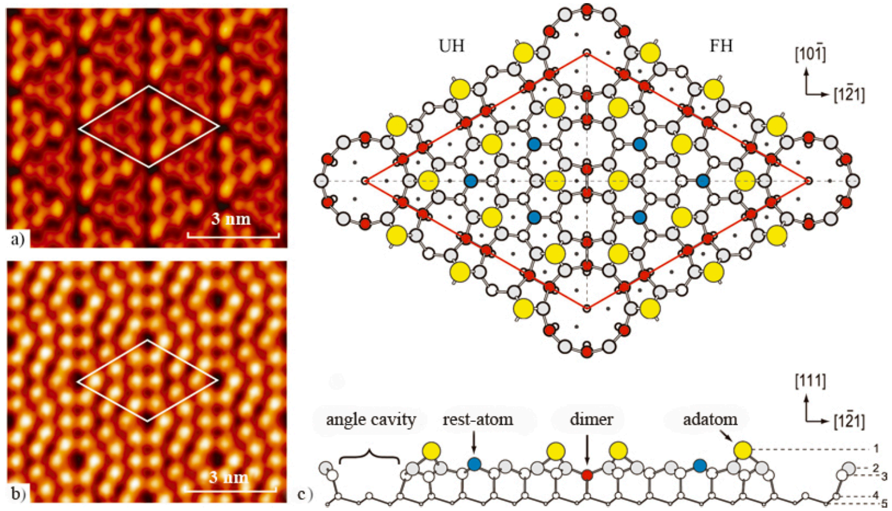


Si (111)

Reconstructions in Real Surfaces



Si(111)-(7 × 7)



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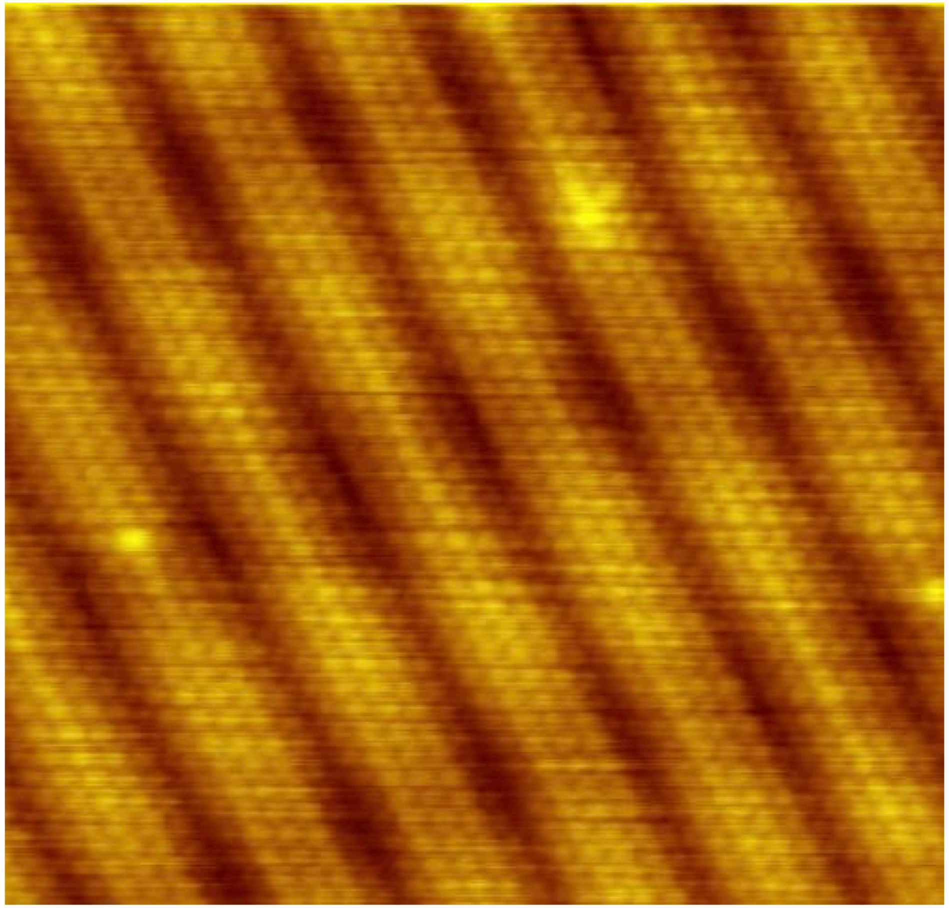
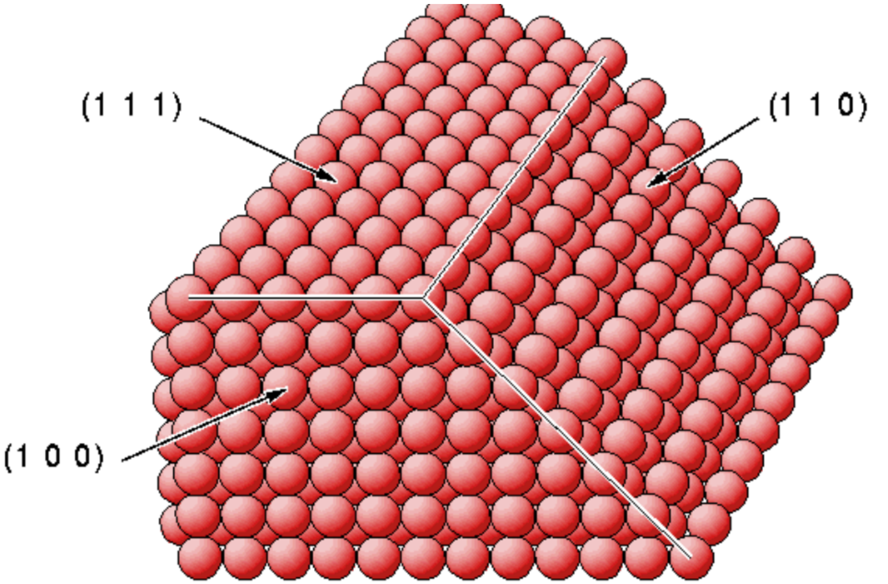
Reconstructions in Real Surfaces



$Au(100)\text{-}(28 \times 5)$

Conclusions



fcc lattice : different net planes

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