EPFL
École polytechnique fédérale de Lausanne

Institute of Materials - Institute of Bioengineering
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SuNMIL
Supramolecular NanoMaterials and Interfaces Laboratory

Real Surfaces
Lesson 3

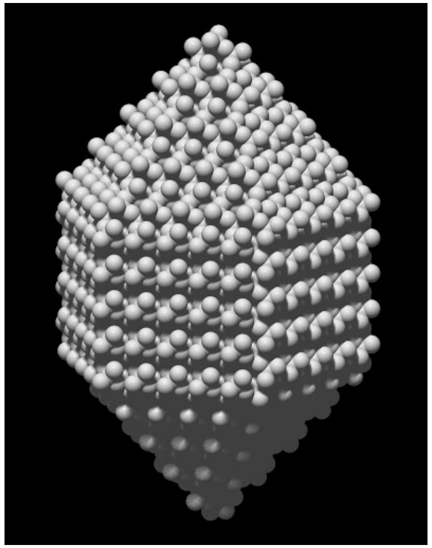
MSE 304

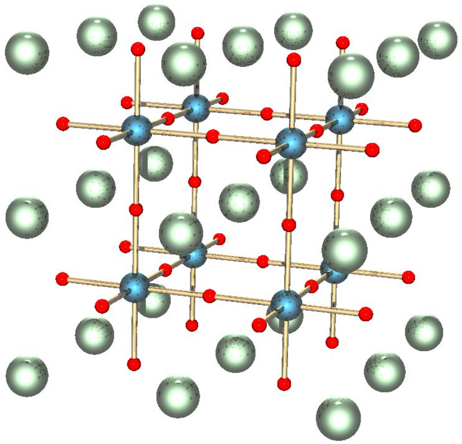
Francesco Stellacci

桑缪 썬밀 सानमिल ΣouNMιΛ سنمل CaHMПЛ

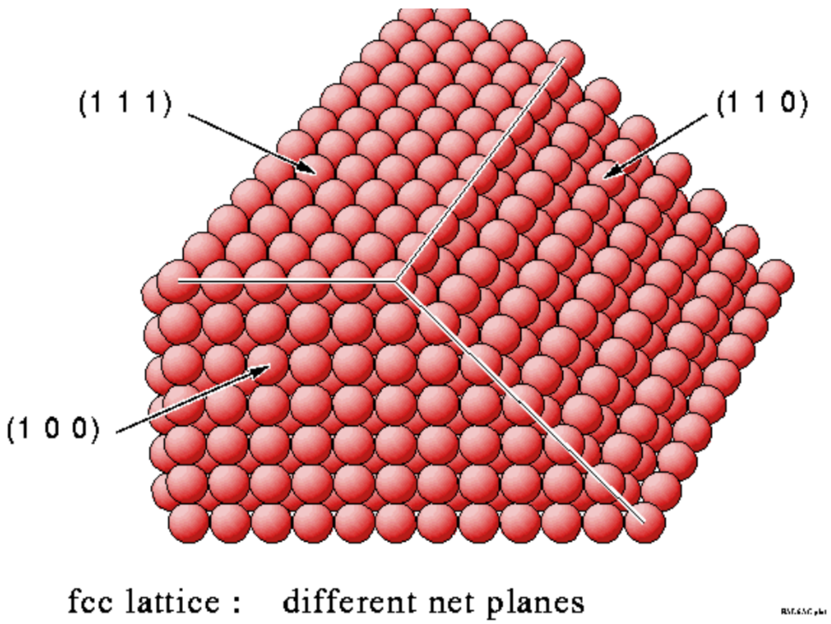
Key Topics in the Previous Class

Difference between an Ideal and a Real surface





Difference between an Ideal and a Real surface

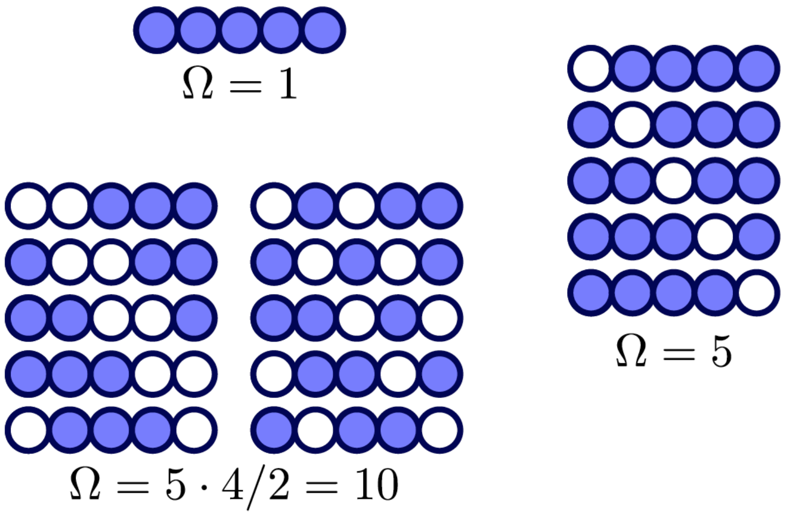


- **Point Defects**
- **Line Defects**
- **Defects from the Bulk**
- **Reconstructions**

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* ($\ln N! \approx N \ln N$)

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



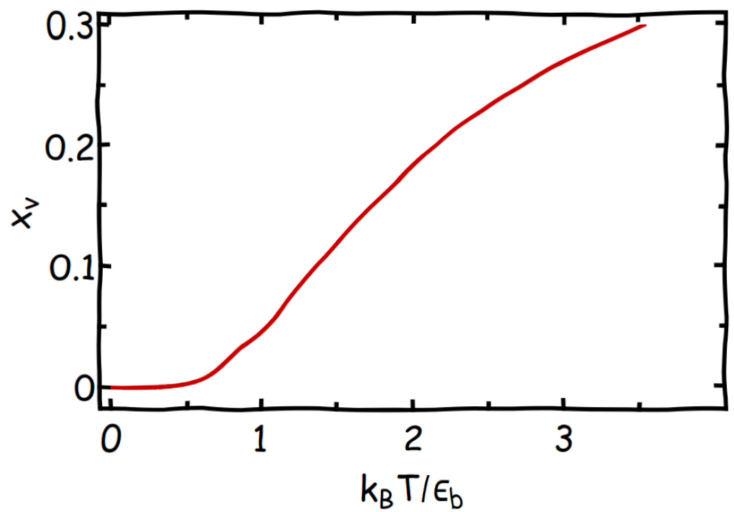
Point Defects in Real Surfaces

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

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

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

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



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Point Defects in Real Surfaces

Point Defects in 3D

Point Defects in 2D

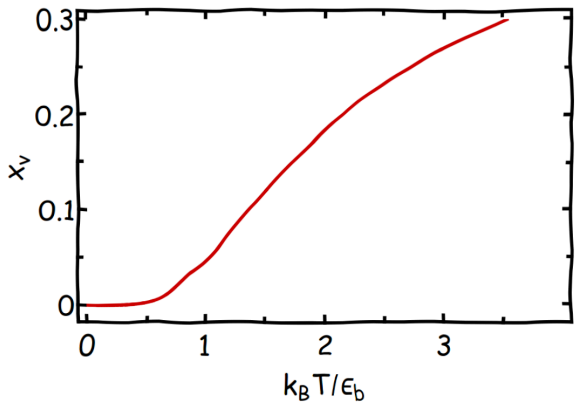
Point Defects in Real Surfaces

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

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



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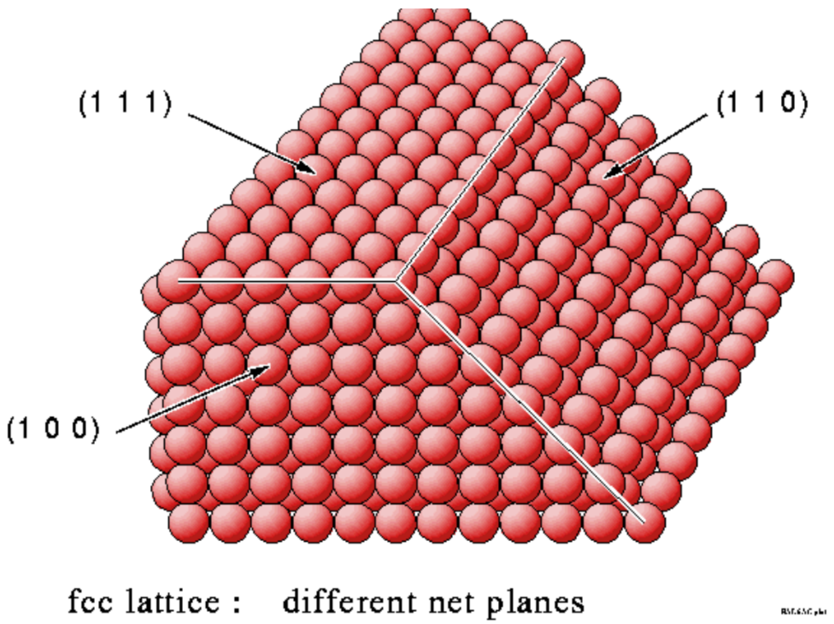
Point Defects in Real Surfaces

What About Impurities?

Difference between an Ideal and a Real surface



- **Point Defects**
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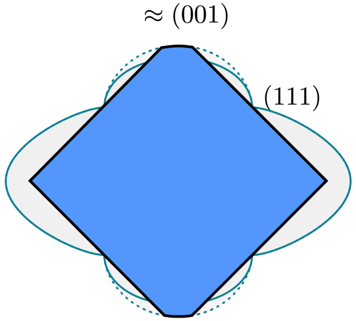
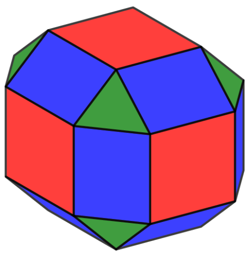
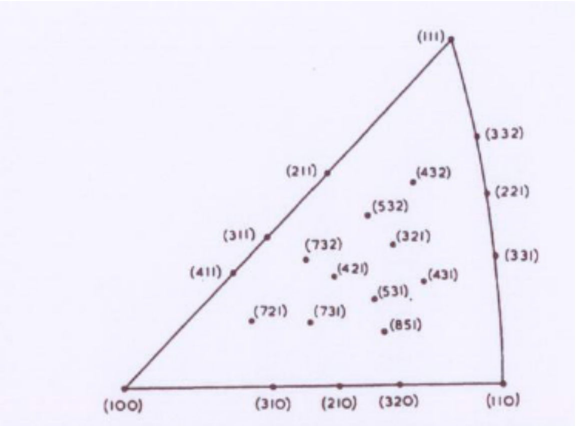
Line Defects in Real Surfaces

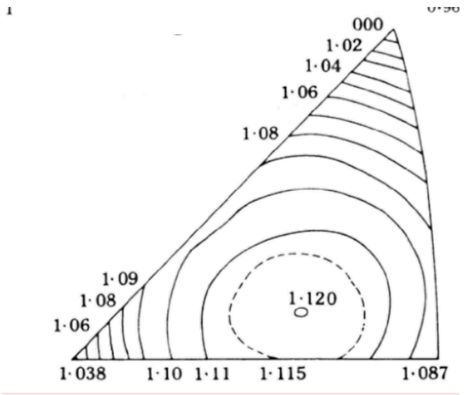


- In a liquid, γ is constant, so the system just want to minimize area at fixed volume $\longrightarrow$ spherical droplets
- In a solid, the surface energy γ is orientation-dependent. Minimize total surface energy at constant volume

$$\min \int \gamma(\hat{\mathbf{n}})\, dA$$



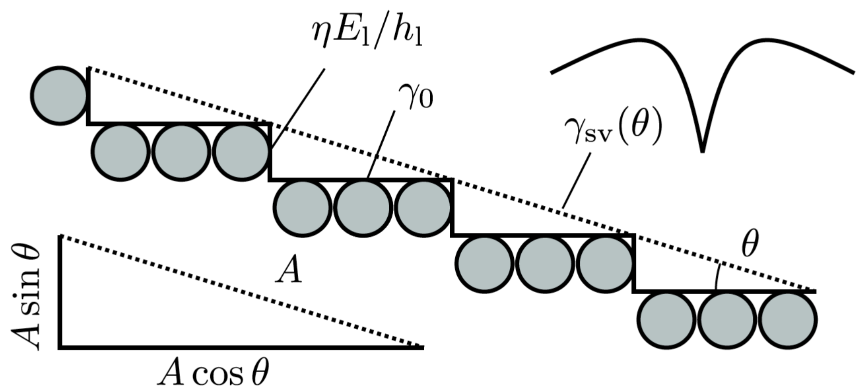




Line Defects in Real Surfaces

- 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

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



Line Defects in Real Surfaces

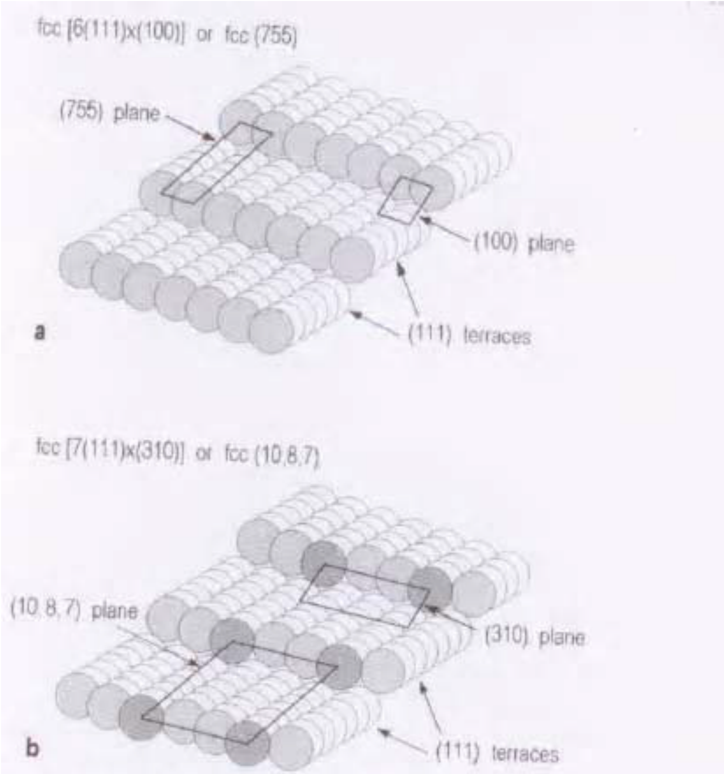
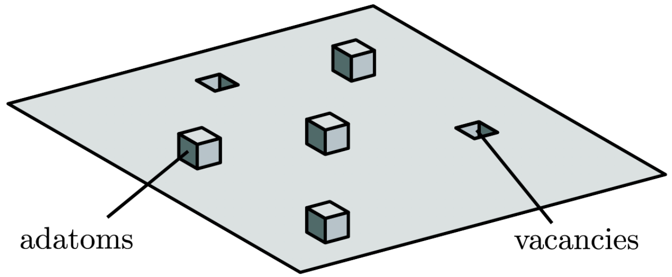
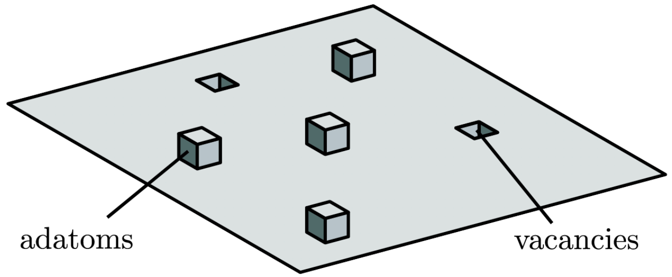


Fig. 2.11. (a) Stepped (755) and (b) kinked (10 8 7) fcc crystal faces

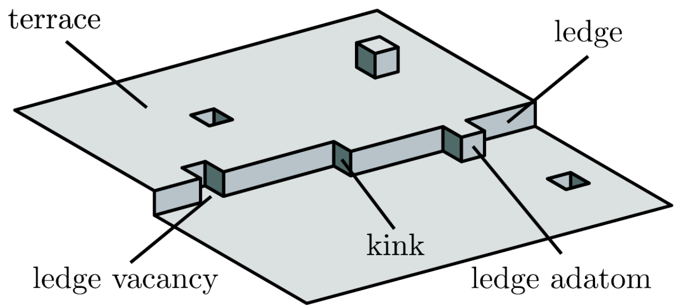
Line Defects in Real Surfaces



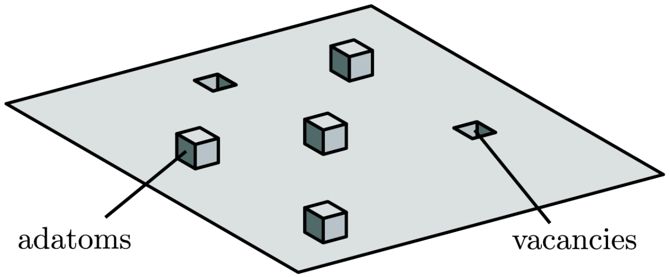
Line Defects in Real Surfaces



- 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



Line Defects in Real Surfaces



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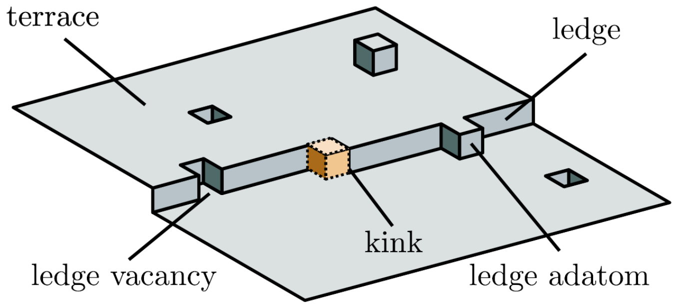
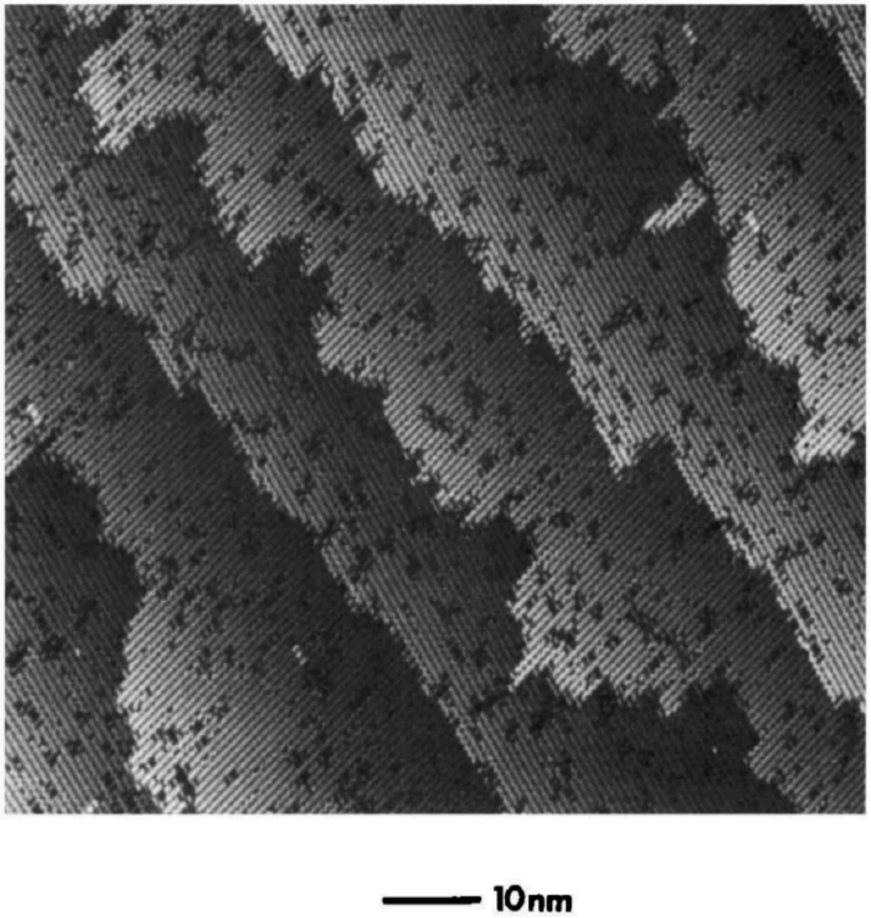
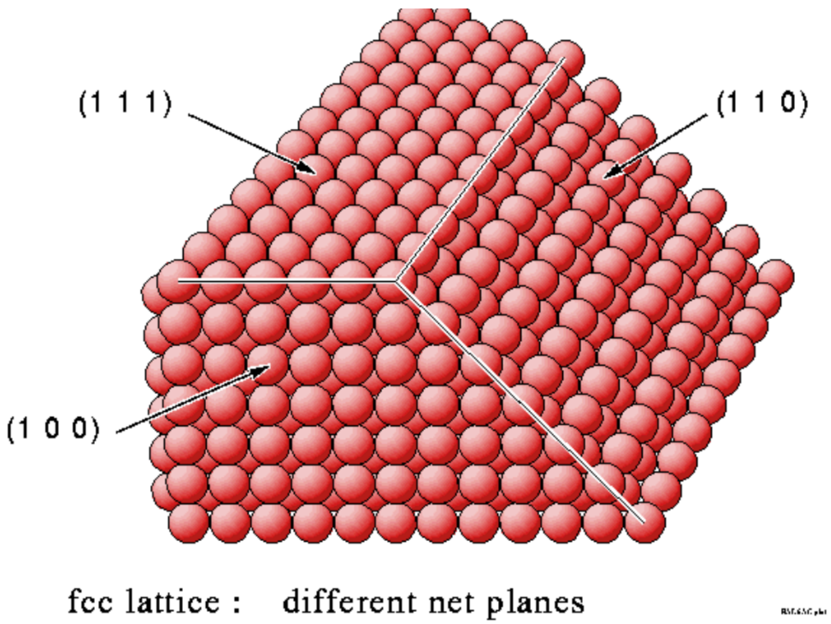


Line Defects in Real Surfaces



Difference between an Ideal and a Real surface

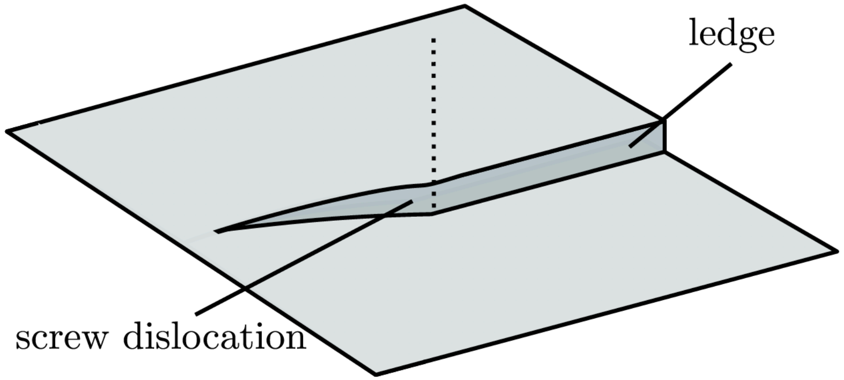


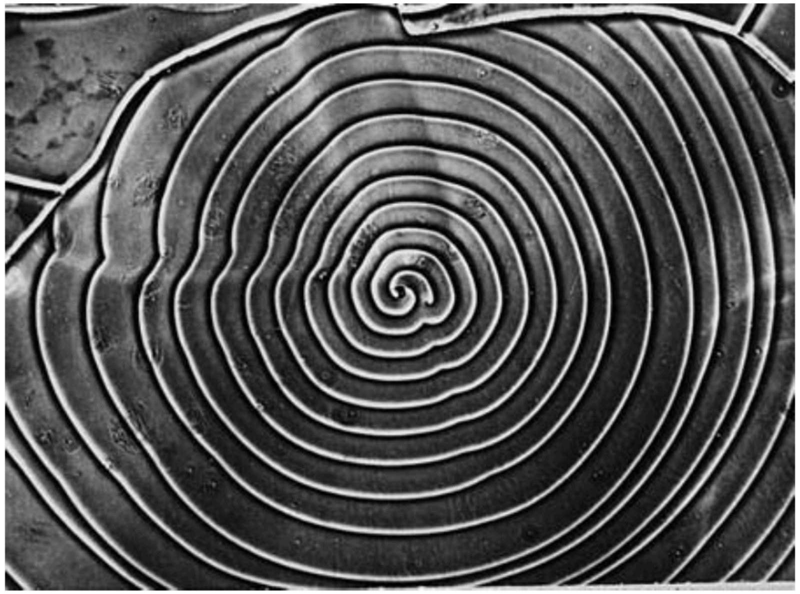
- **Point Defects**
- **Line Defects**
- **Defects from the Bulk**
- **Reconstructions**

Defects from the Bulk in Real Surfaces

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





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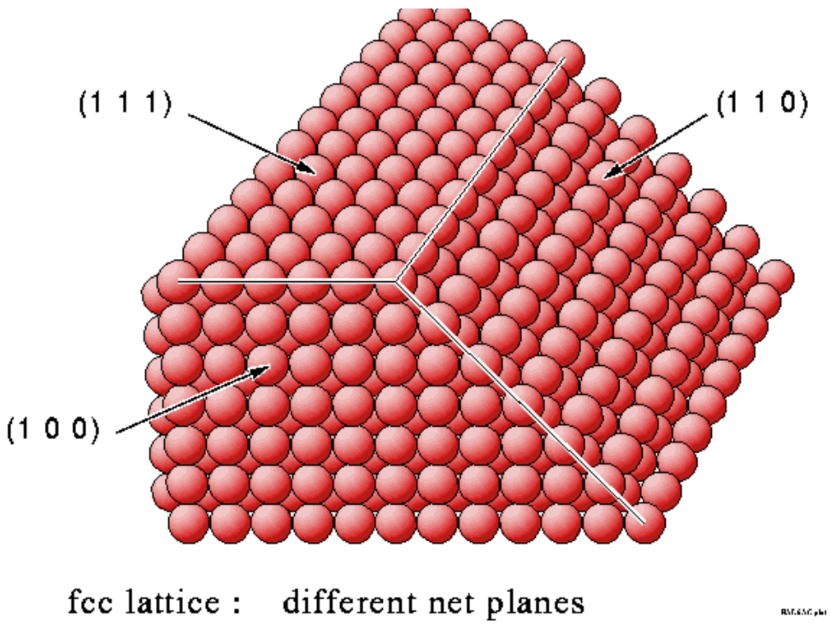
Difference between an Ideal and a Real surface



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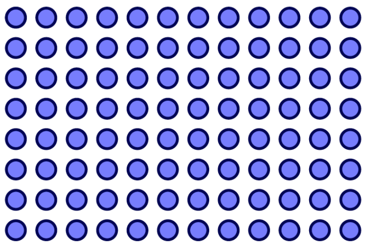
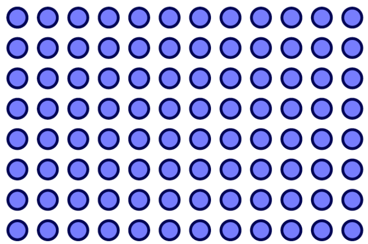
Reconstructions in Real Surfaces

Side View

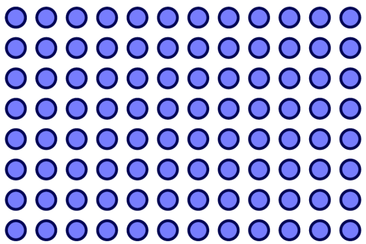


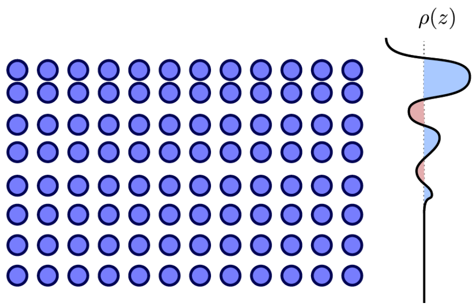
Top View



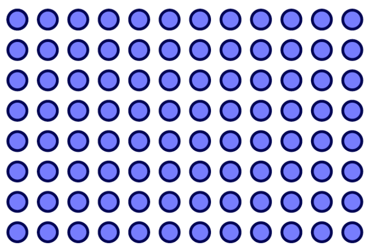
Reconstructions in Real Surfaces

Side View





Top View



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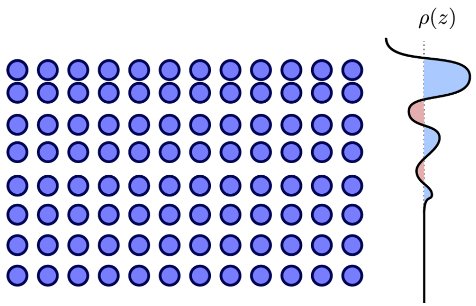
Side View



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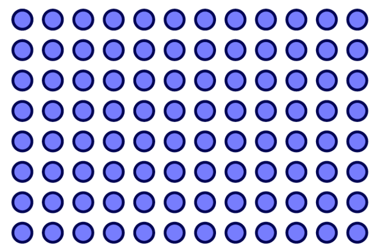

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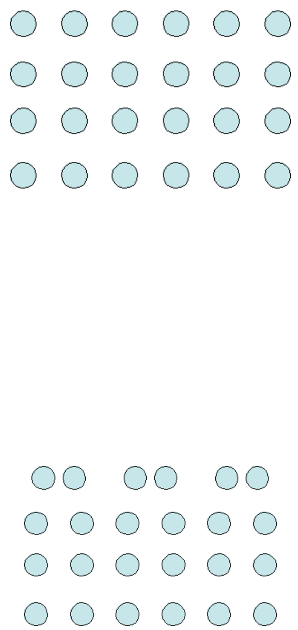

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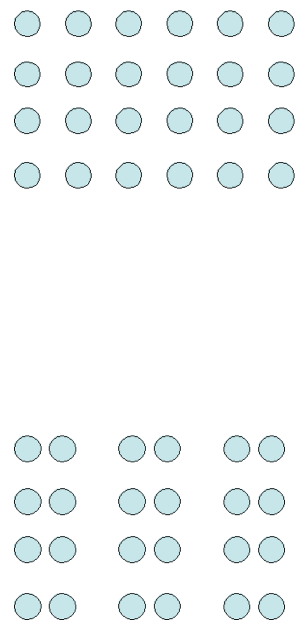

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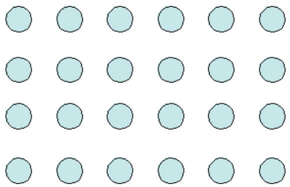
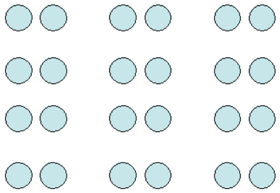
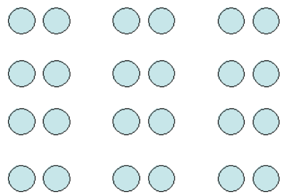


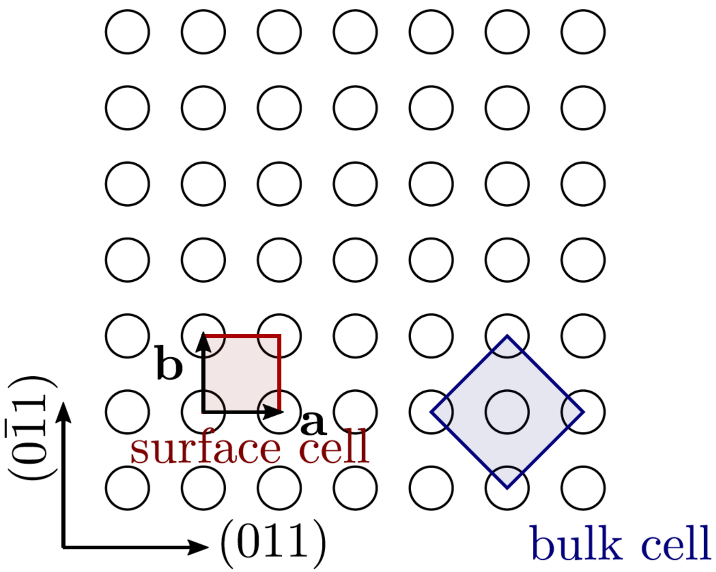


Reconstructions in Real Surfaces



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

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



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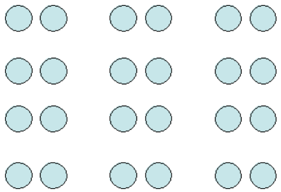

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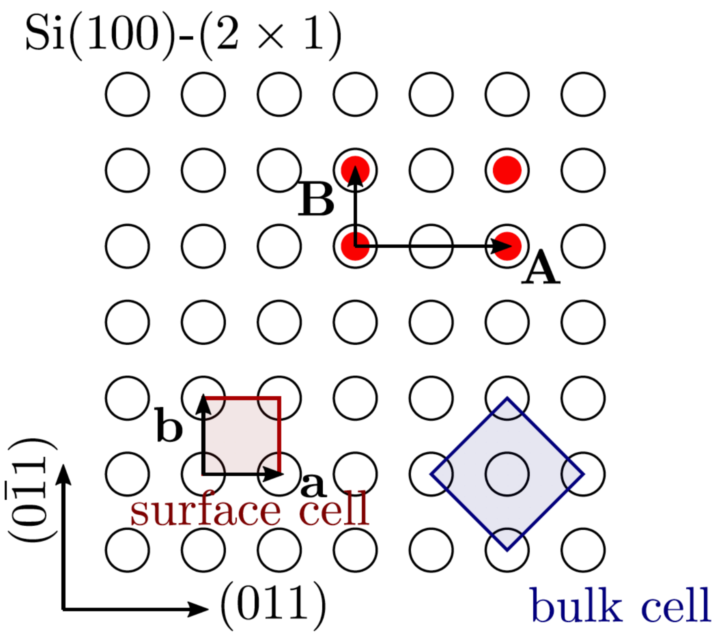

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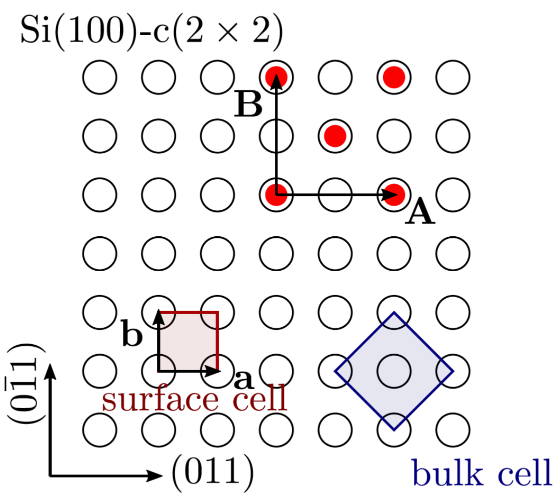
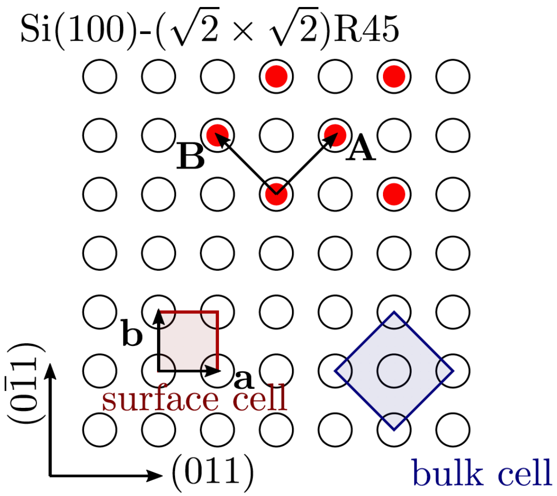
Reconstructions in Real Surfaces





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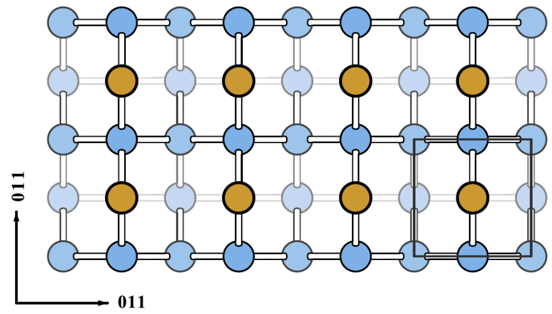

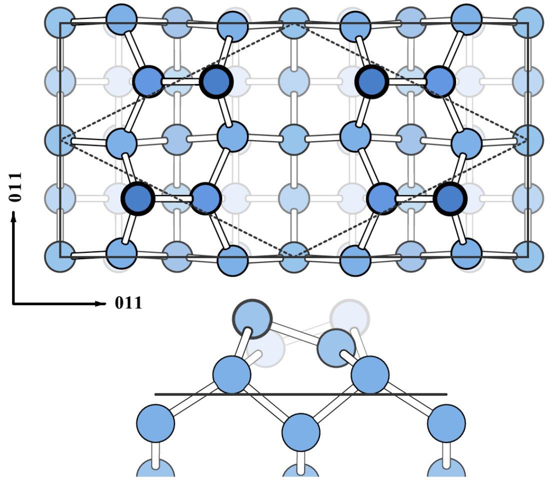

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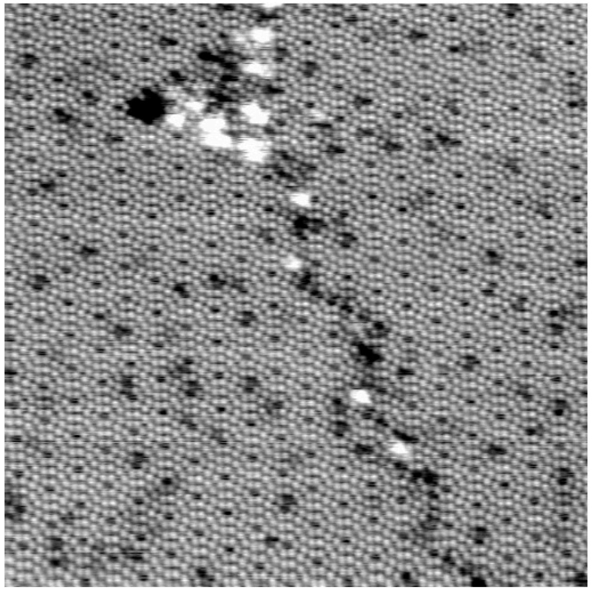
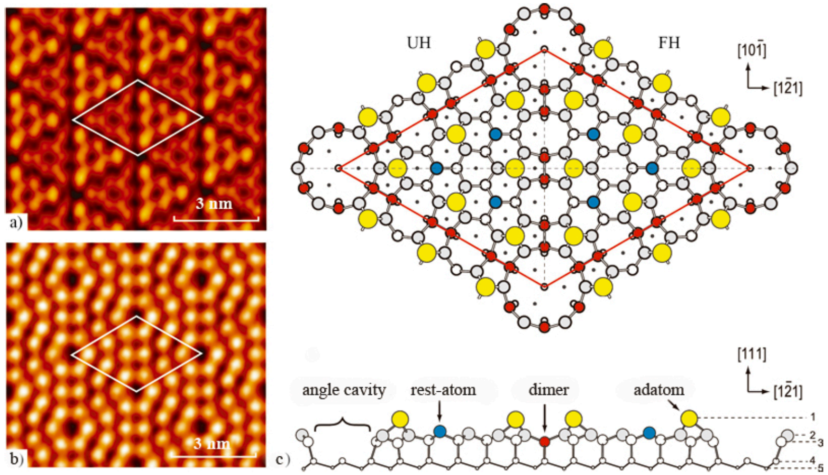


Si(111)-(7 × 7)



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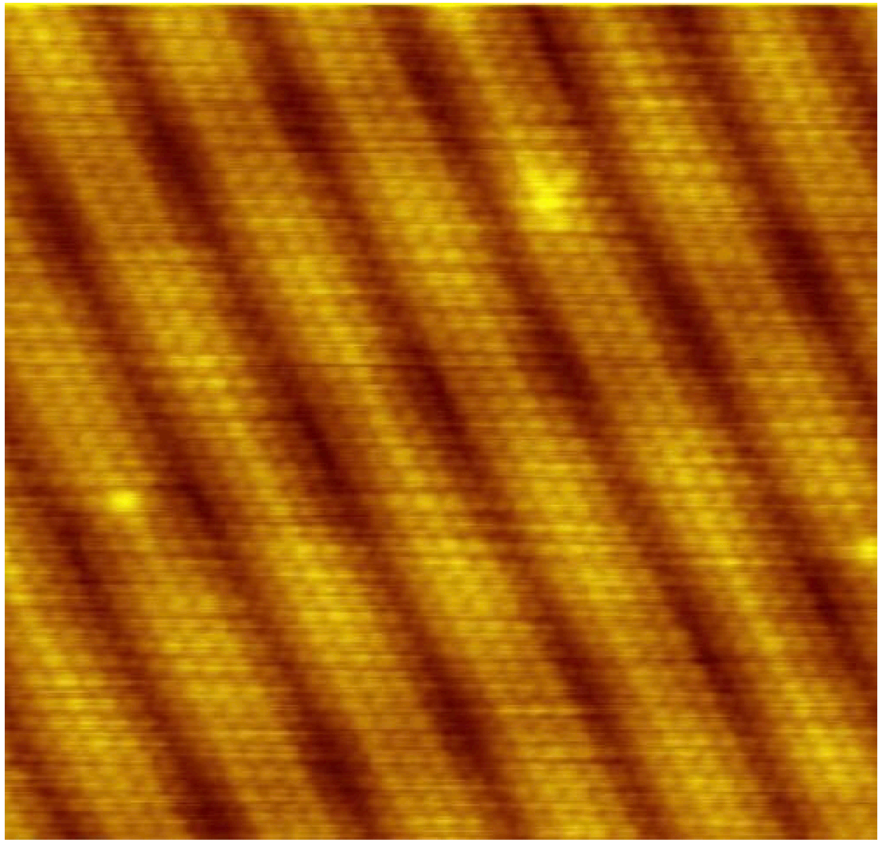
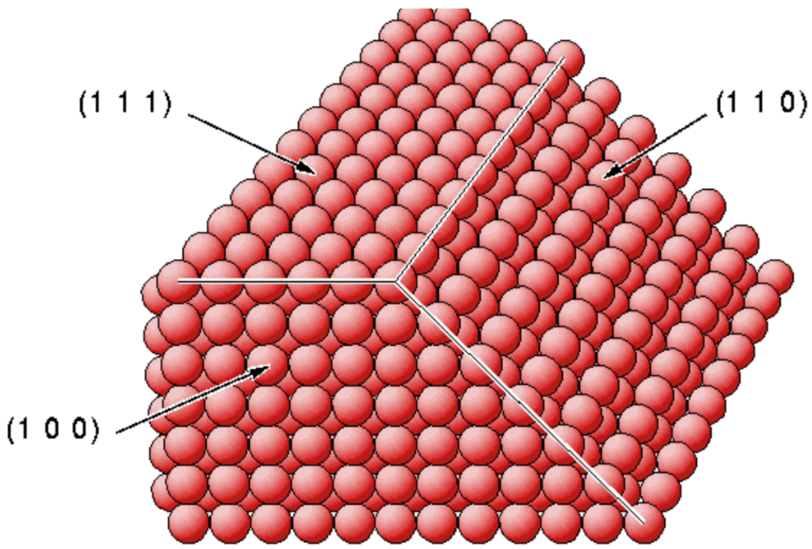


Au(100)-(28 × 5)

Conclusions



fcc lattice : different net planes

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