Real Surfaces

M. Ceriotti - MX304

EPFL

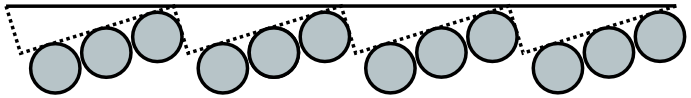
Outline

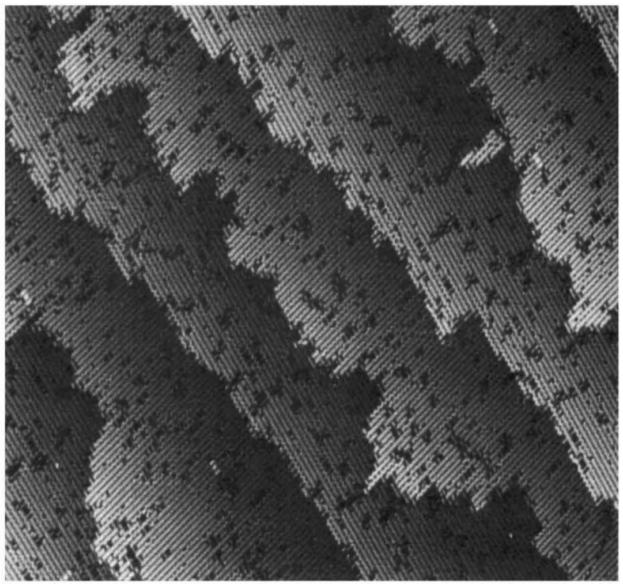
- Defects at surfaces
- Terraces, ledges, kinks
- Concentration of adatoms and vacancies, roughening
- Surface reconstructions and relaxation

Singular Surfaces and Faceting

- 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

$$\gamma_{sv}(\theta) = \gamma_0 \cos\theta + \frac{\eta E_l}{h_l} \sin\theta$$

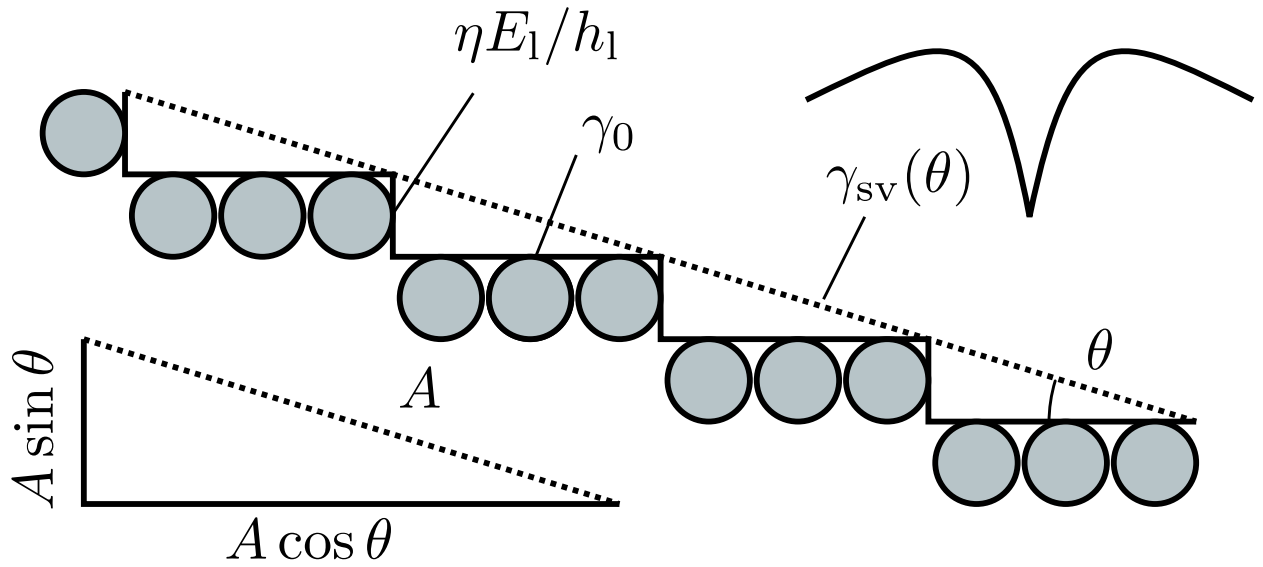




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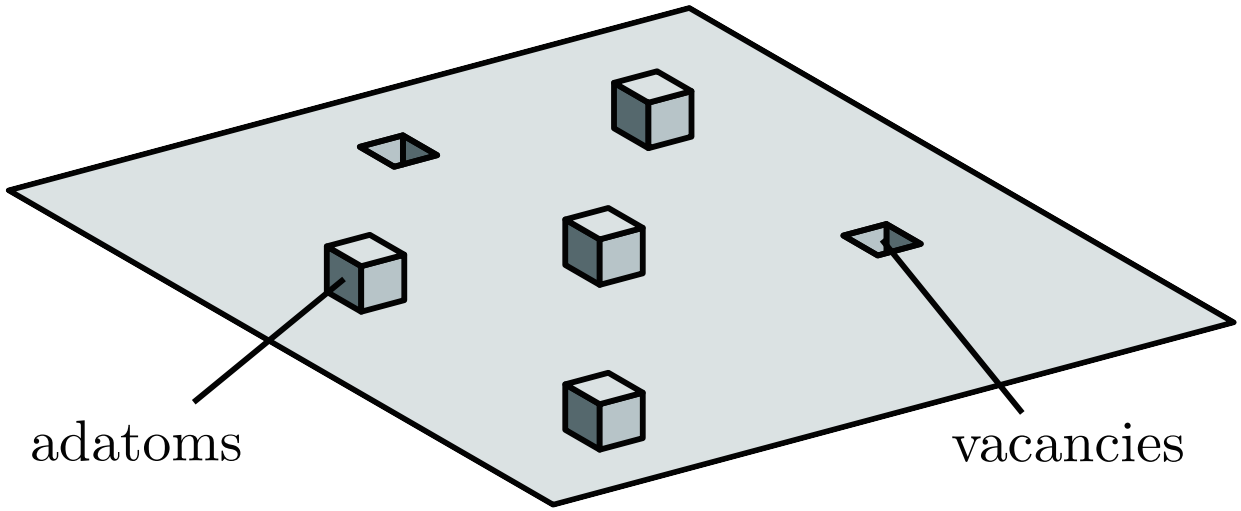
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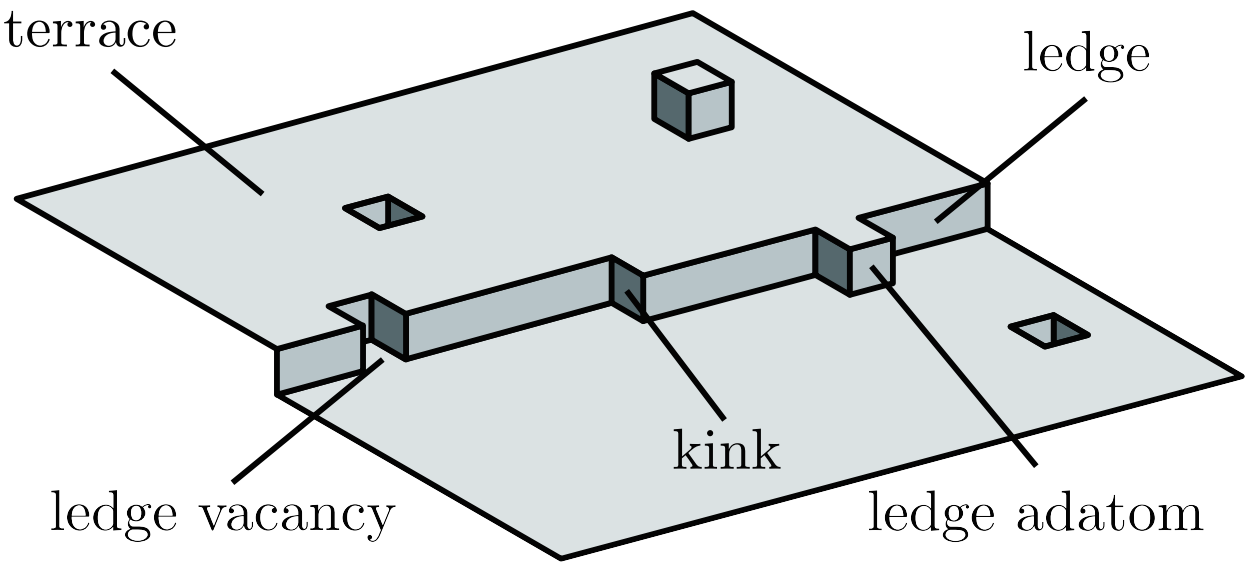
Surface Defects

- A surface can have point defects just as a solid crystal can (vacancies, adatoms)
- 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



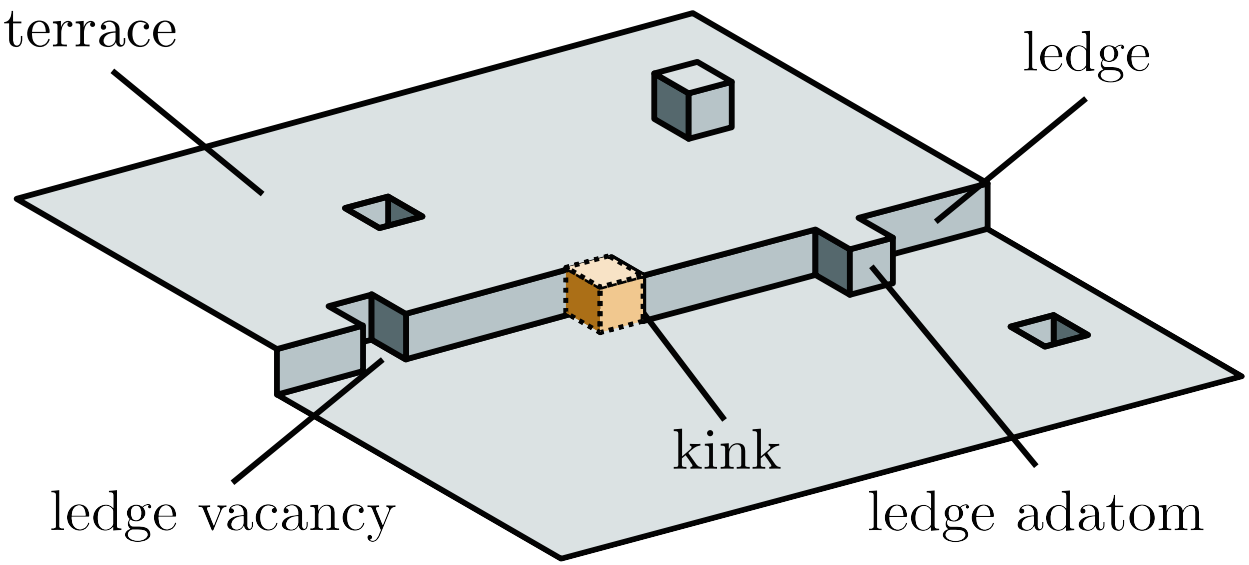
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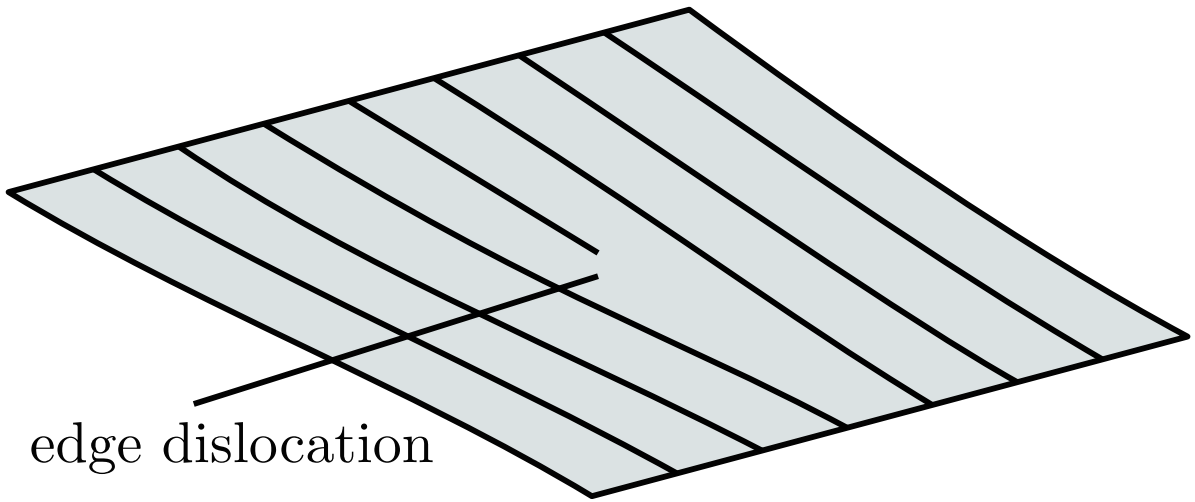
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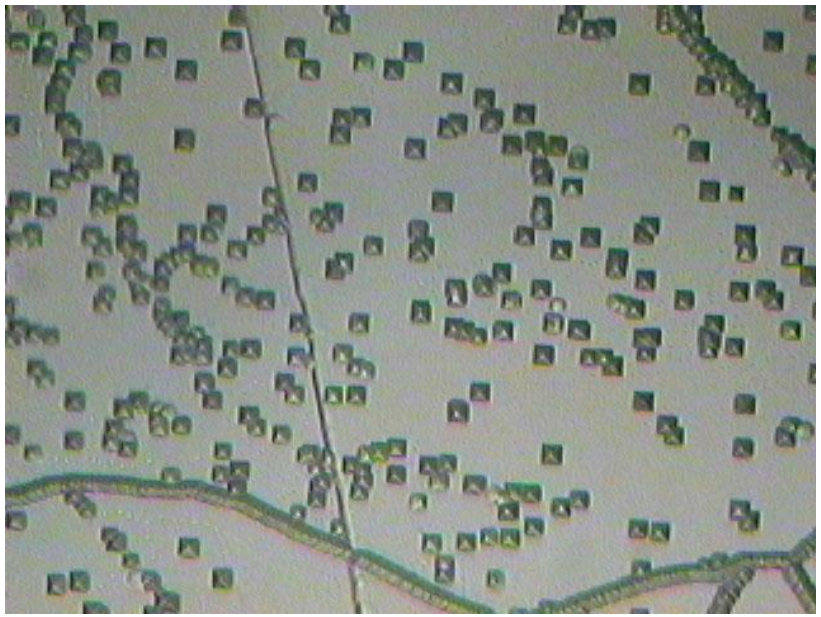
Bulk Defects at Surfaces

- 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



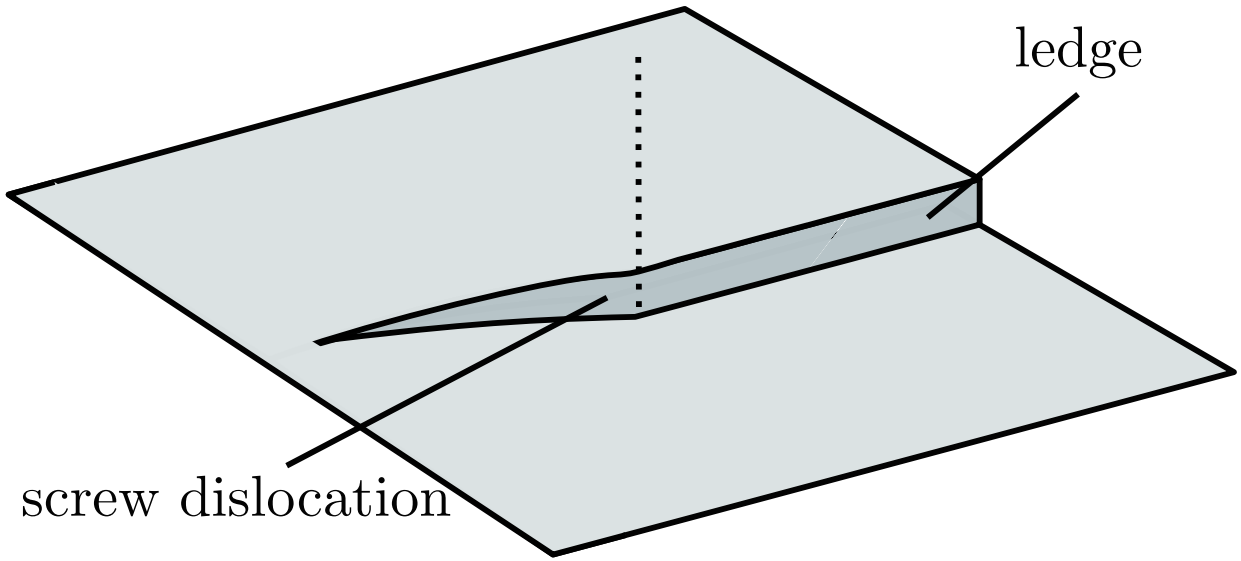
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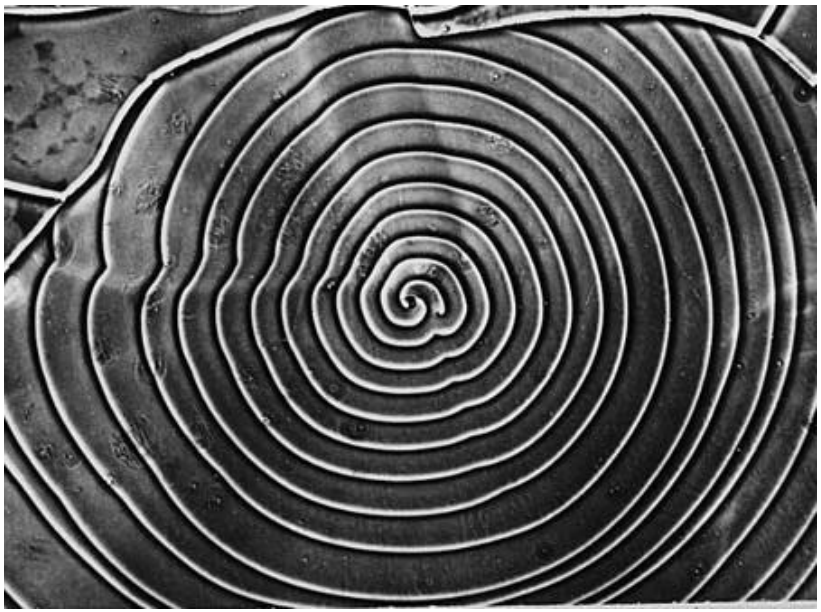
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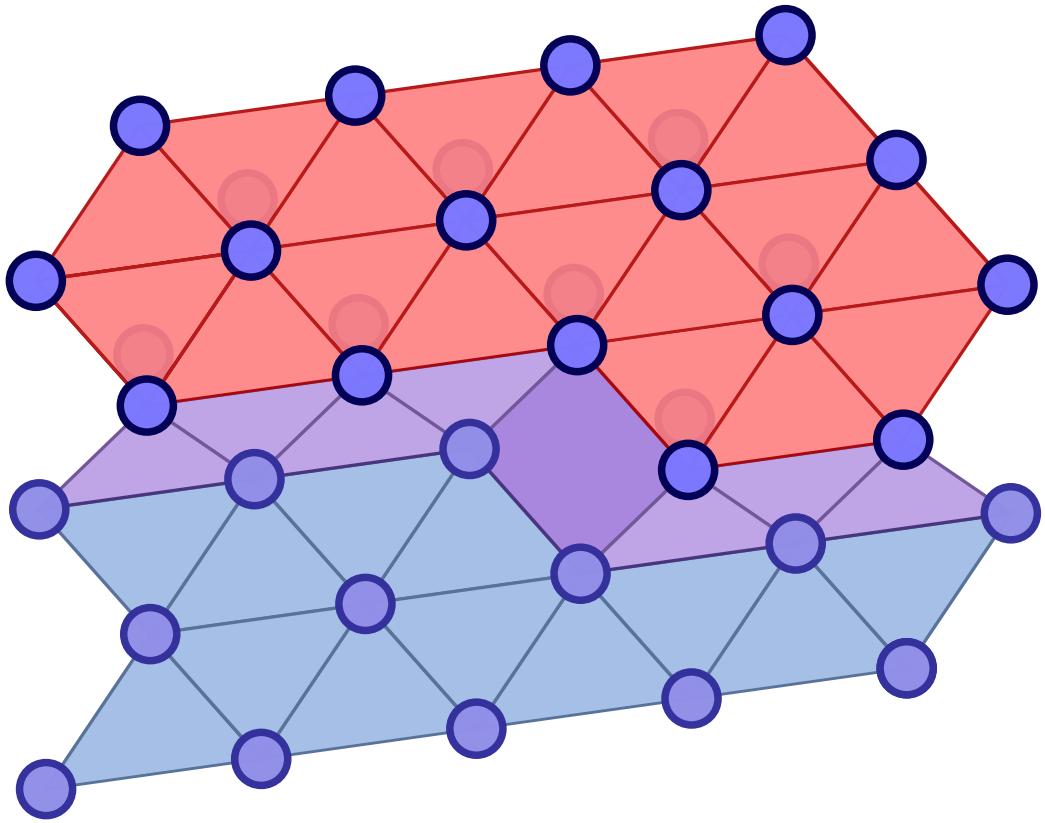
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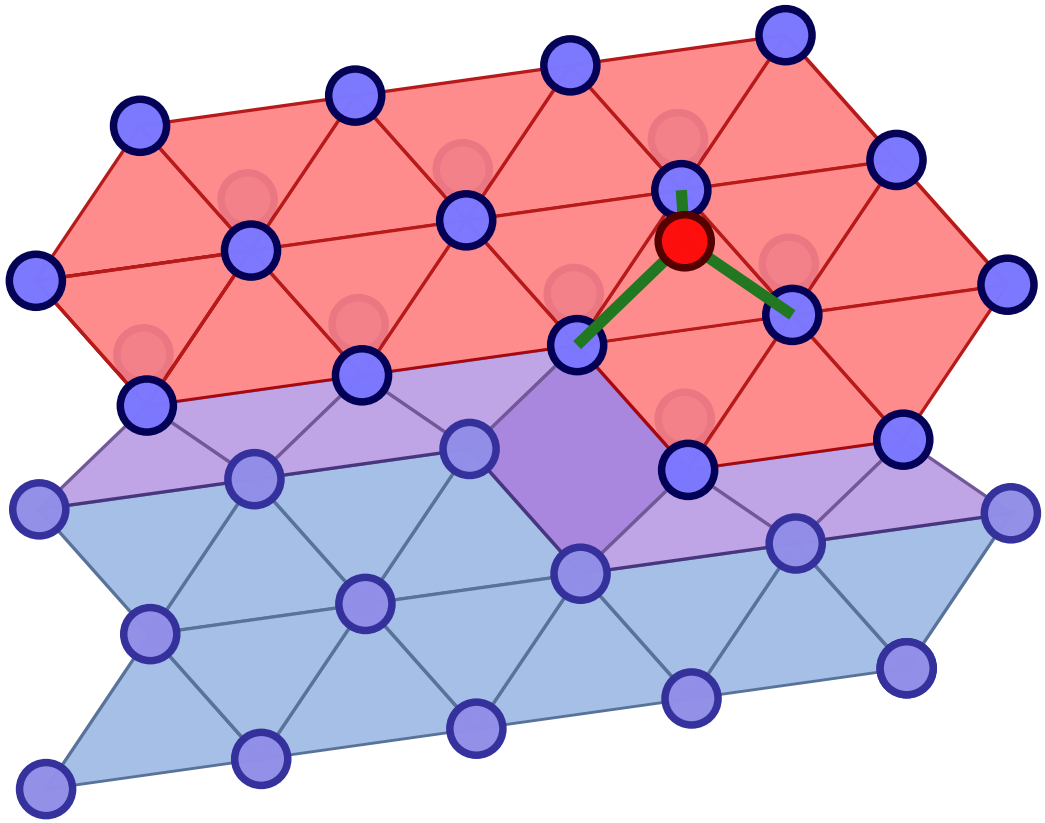
Energetics of Point Defects

- Let's count the number of intact bonds associated to each surface site on a (111) surface of an *fcc* crystal
- Adatom: 3; Terrace: 9; Ledge: 7; Kink: 6;



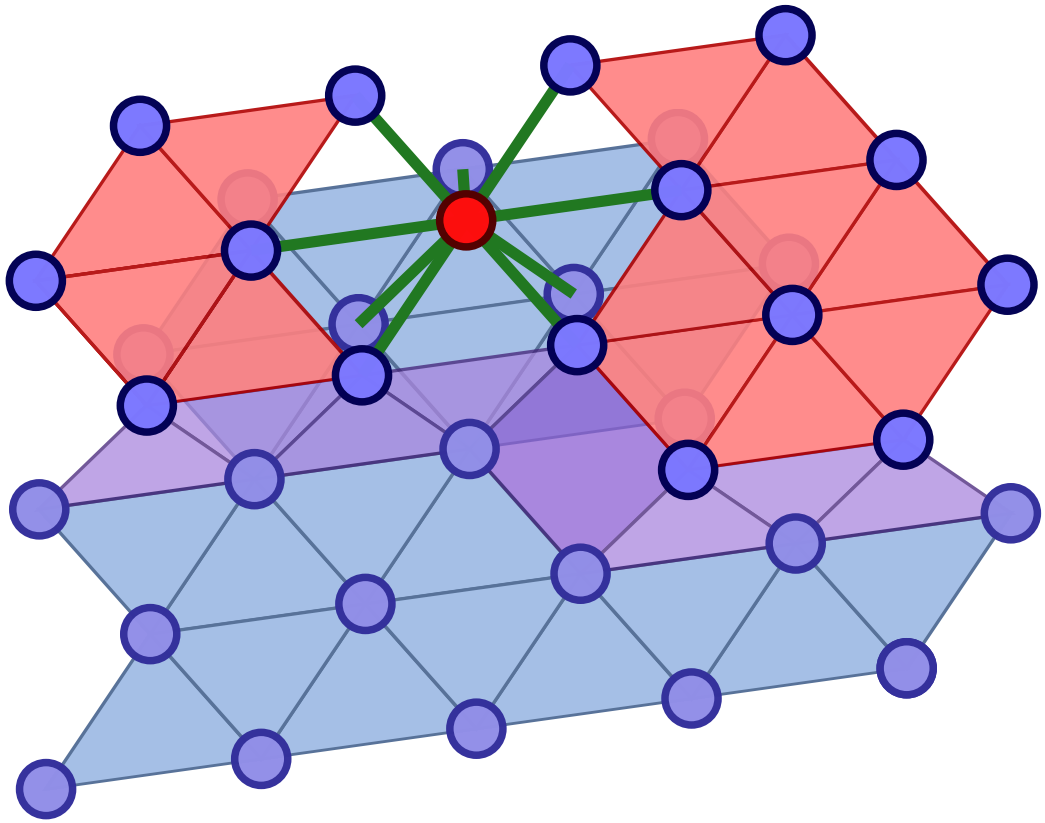
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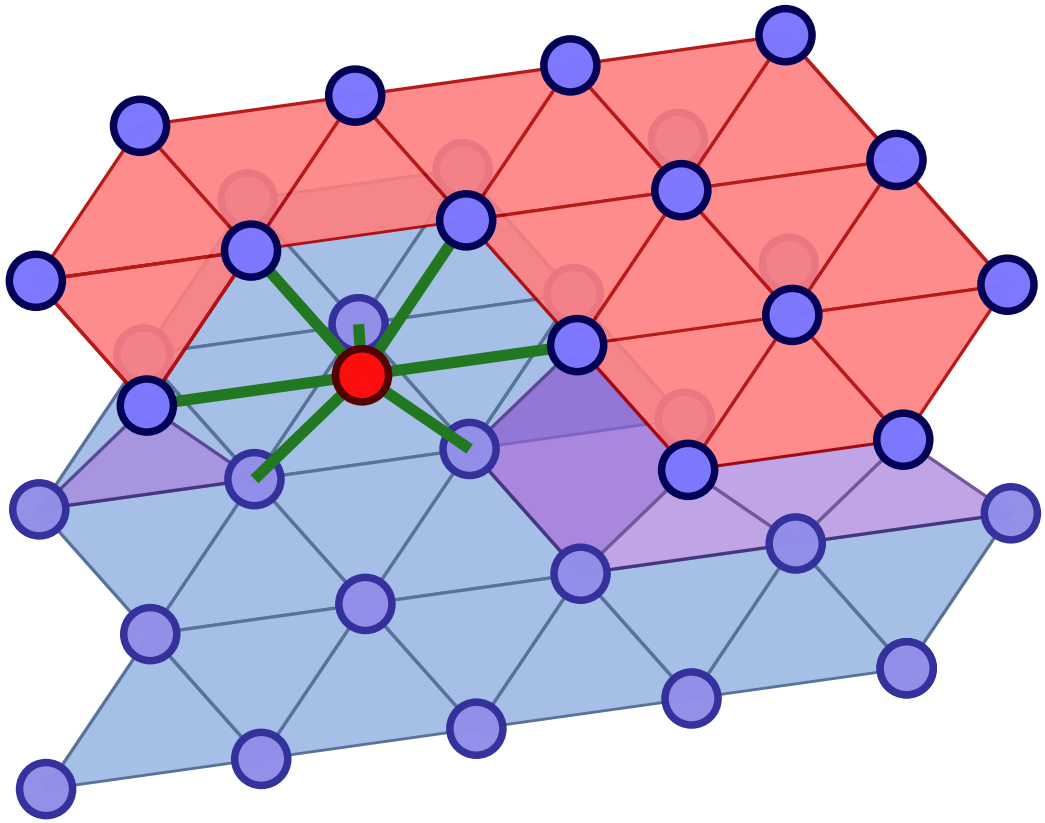
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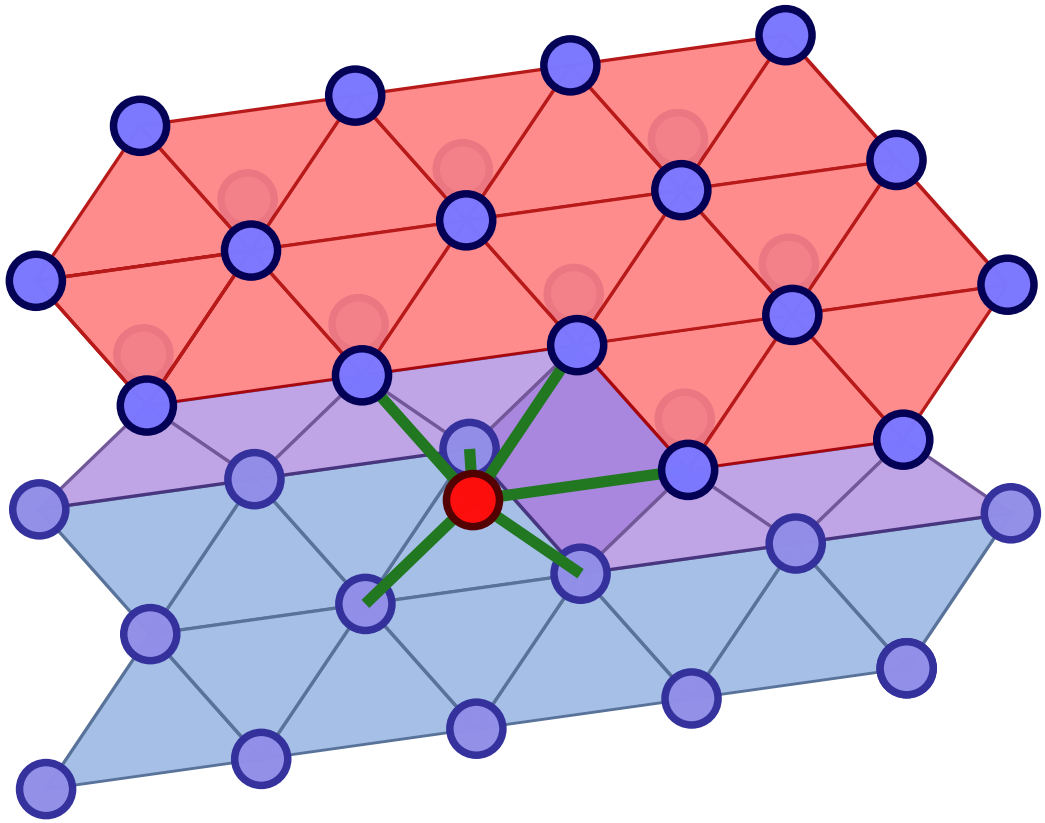
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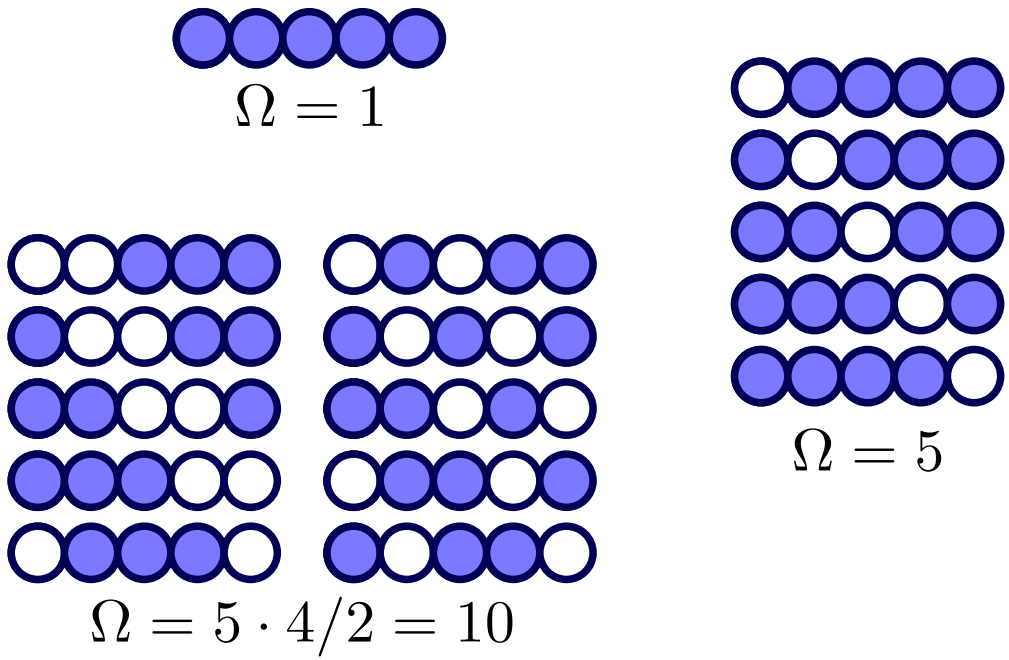
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Configurational Entropy for a Point Defect

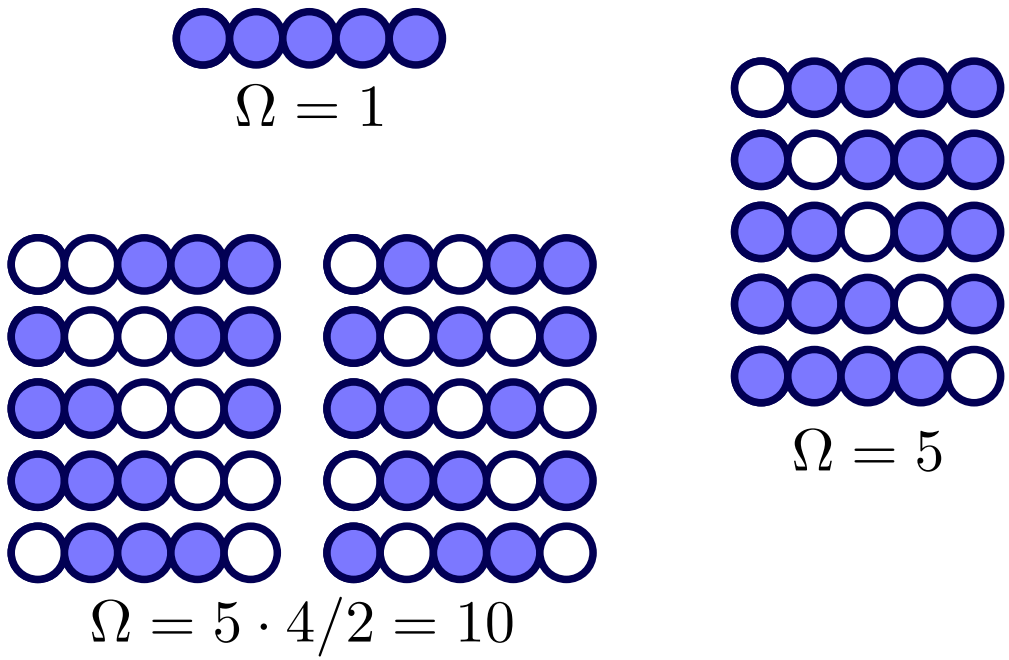
- Entropy is a counter of the number of ways you can realize a thermodynamic state: $S = k_B \ln \Omega$
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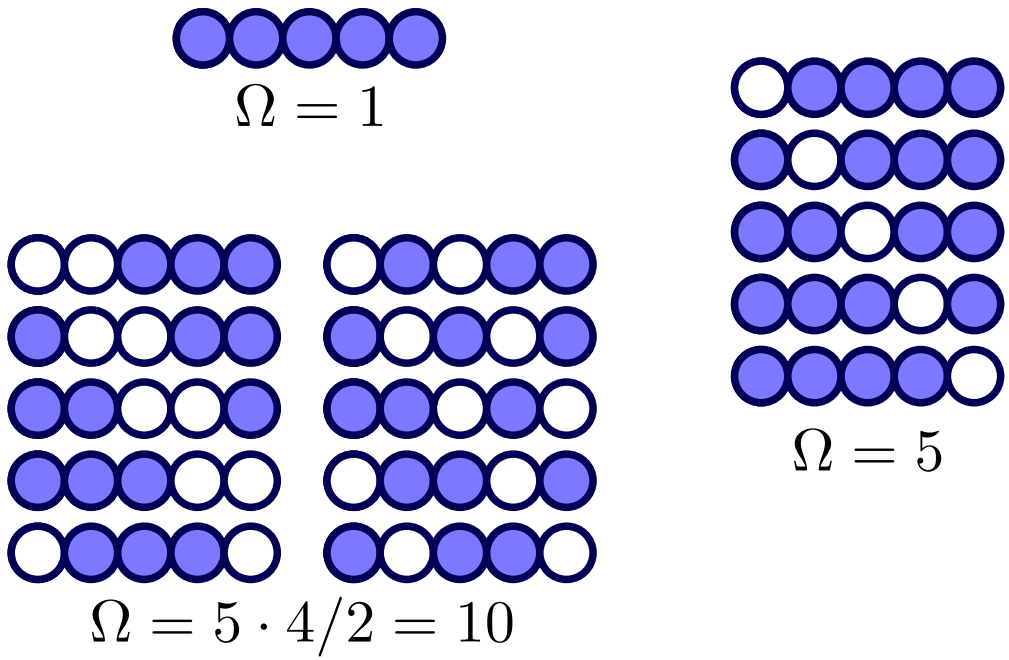
$$S(n_v) = k_B \ln \frac{N!}{(N - n_v)! n_v!}$$



Configurational Entropy for a Point Defect

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

$$S(n_v) = k_B \left[N \ln N - (N - n_v) \ln (N - n_v) - n_v \ln n_v \right]$$



Concentration of Defects in a Solid

- 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$\rightarrow$kink $\epsilon_v \approx (12\epsilon_b - 6\epsilon_b) = 6\epsilon_b$
- 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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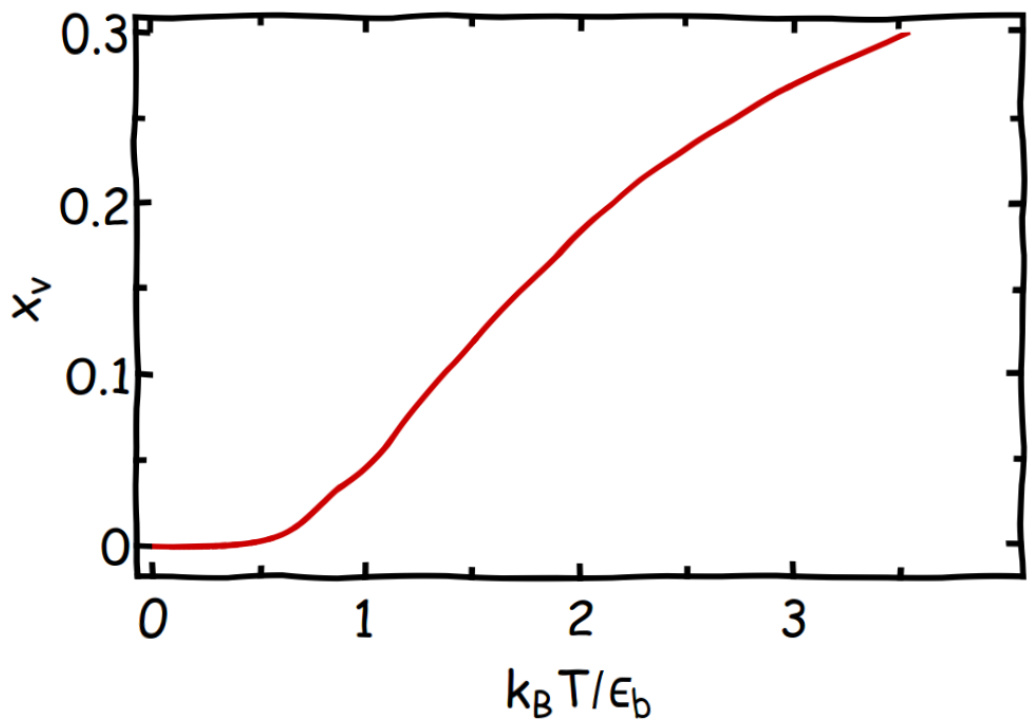
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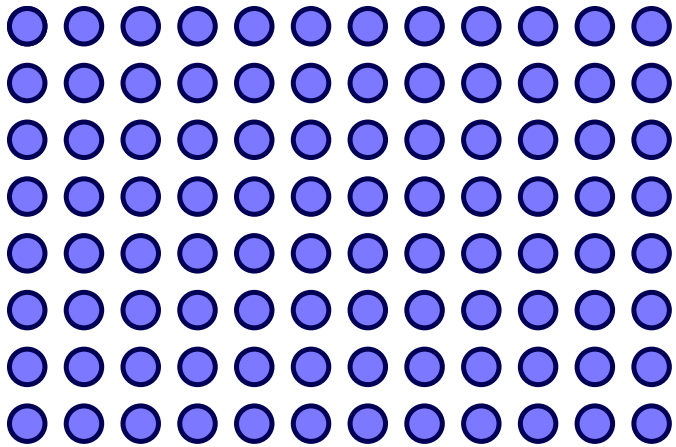
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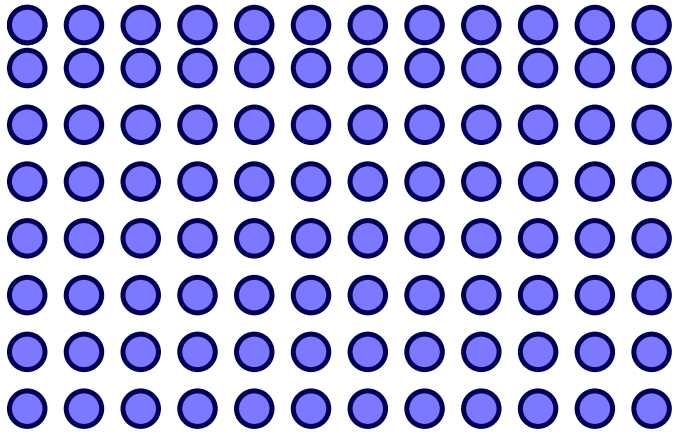
Surface relaxation

- Atoms at a freshly-cut surface do not stay fixed at bulk-like positions, but they relax to minimize their energy
- Charge-density effects can lead to oscillations of lattice parameters extending several layers below the surface



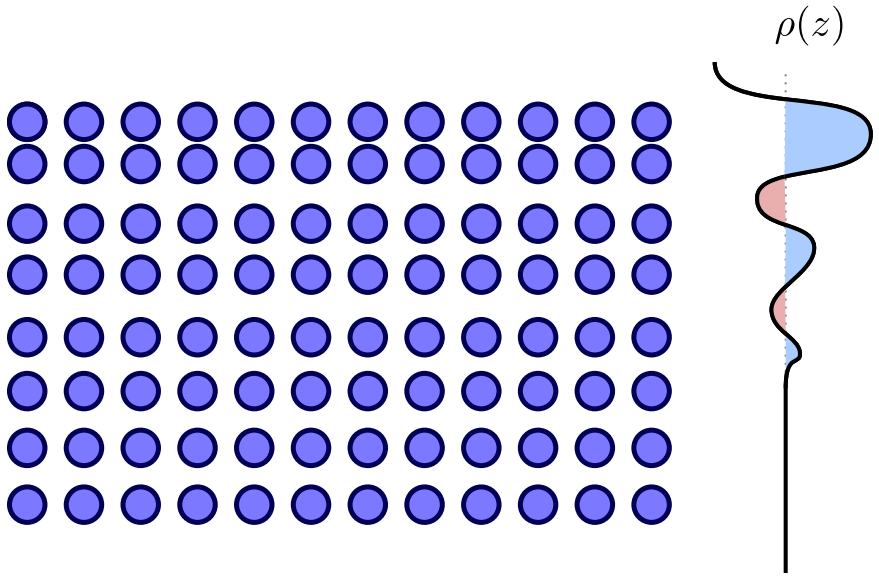
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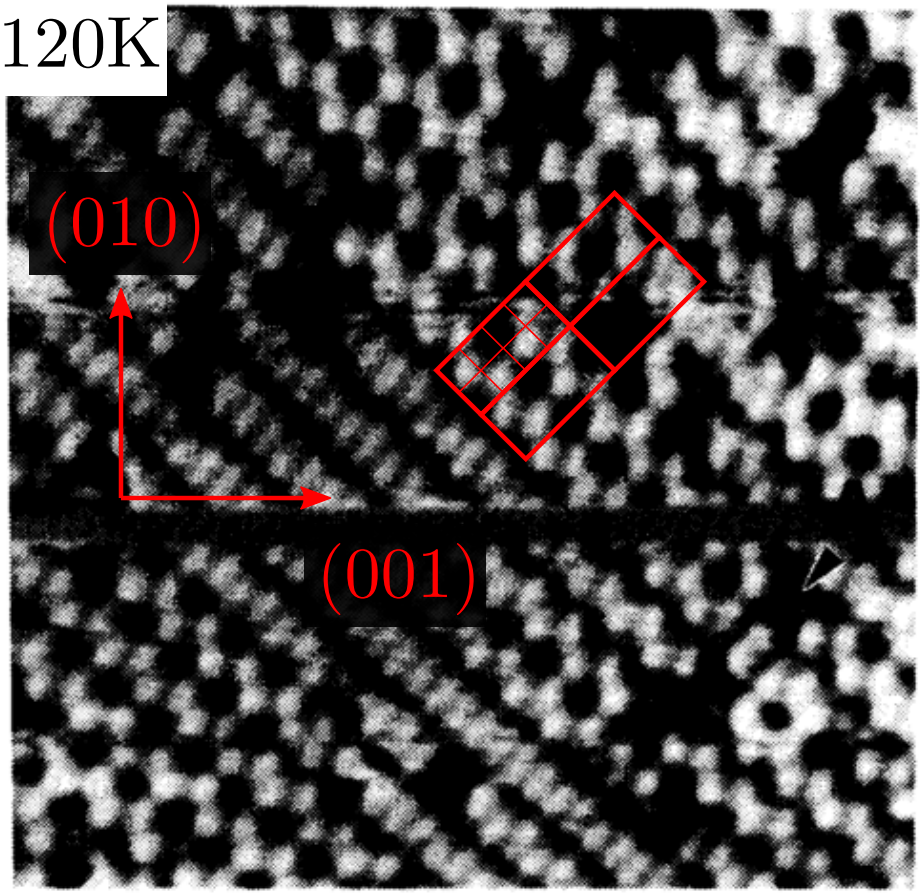
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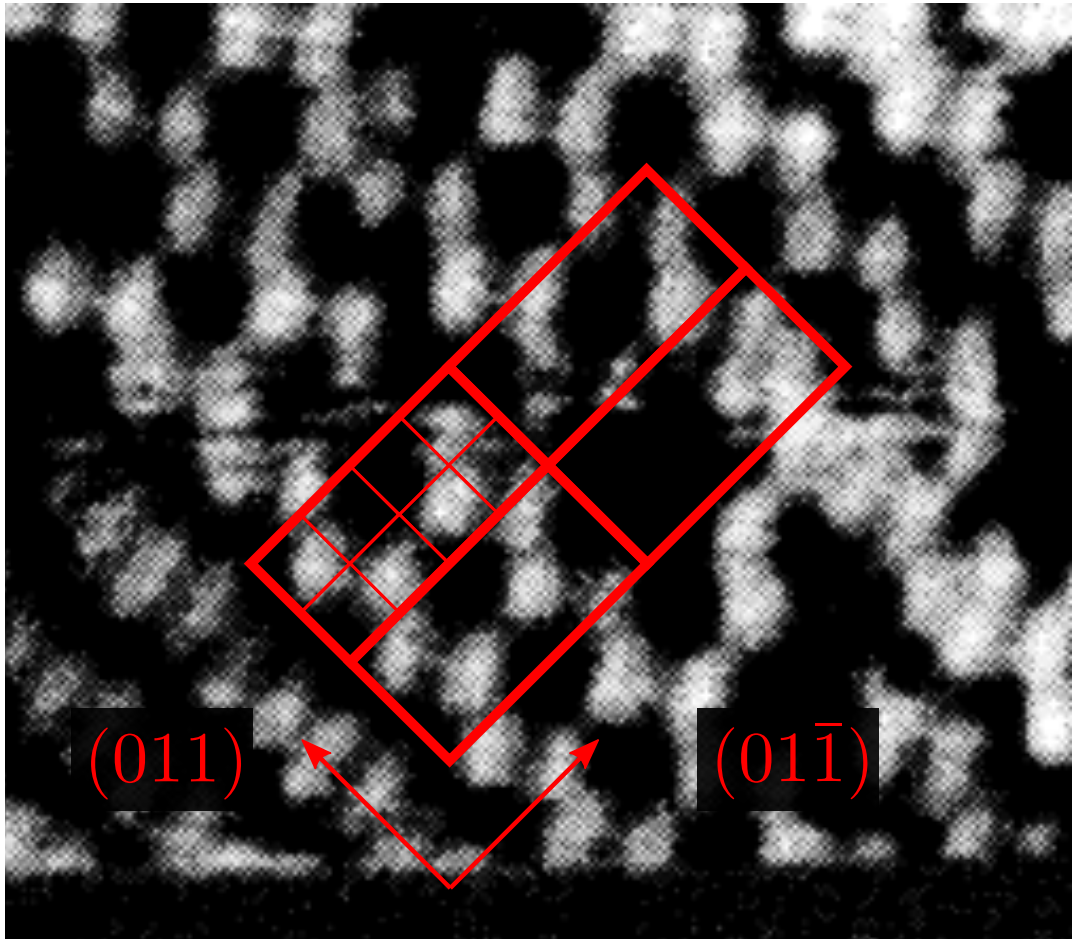
Surface Reconstructions

- Real surfaces can display different symmetry than a “truncated bulk” [e.g. Si(100)]
- **Reconstructions** lowers surface energy by forming new bonds



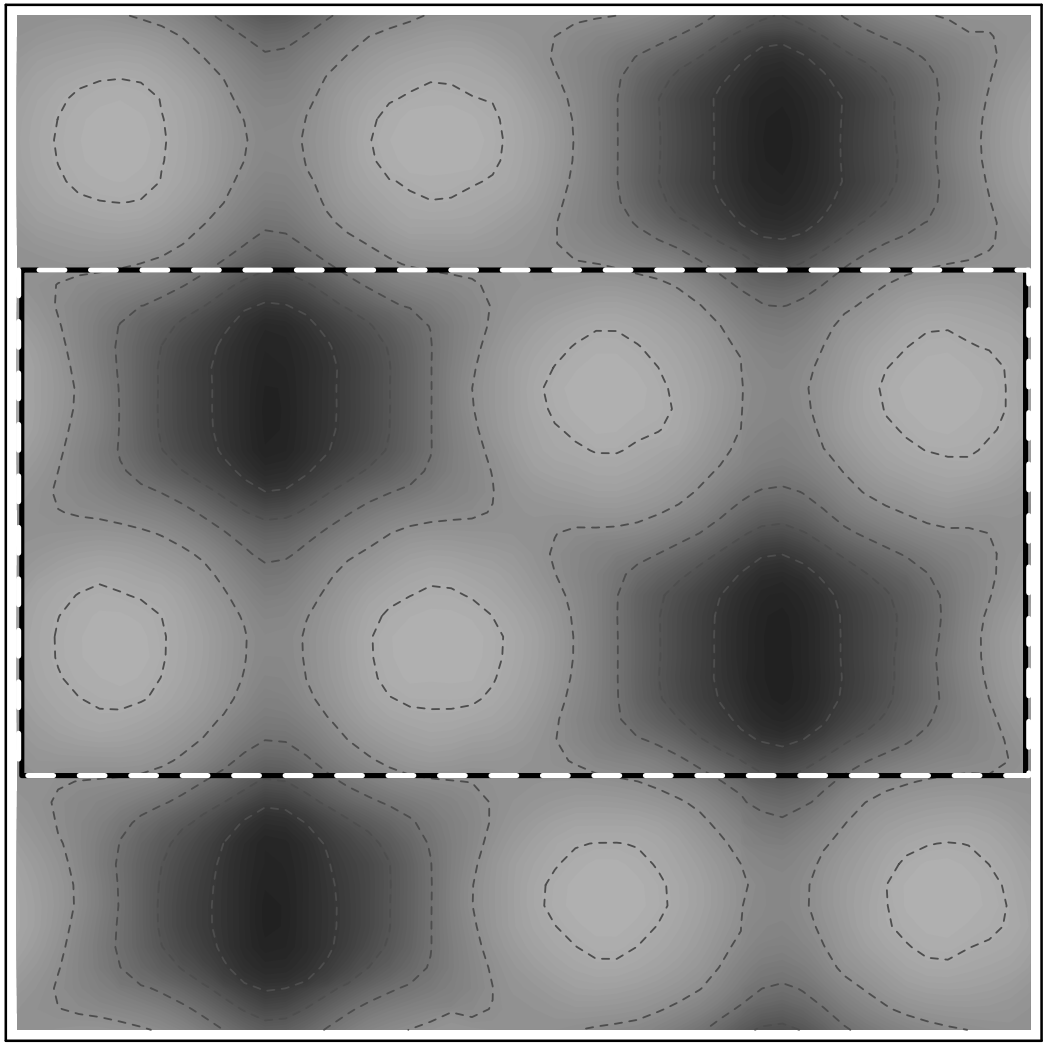
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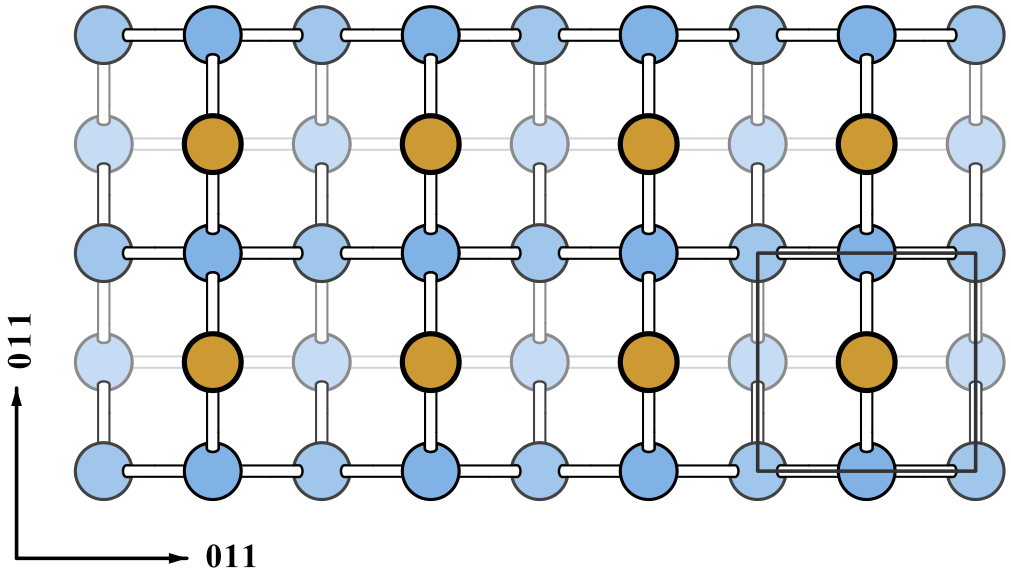
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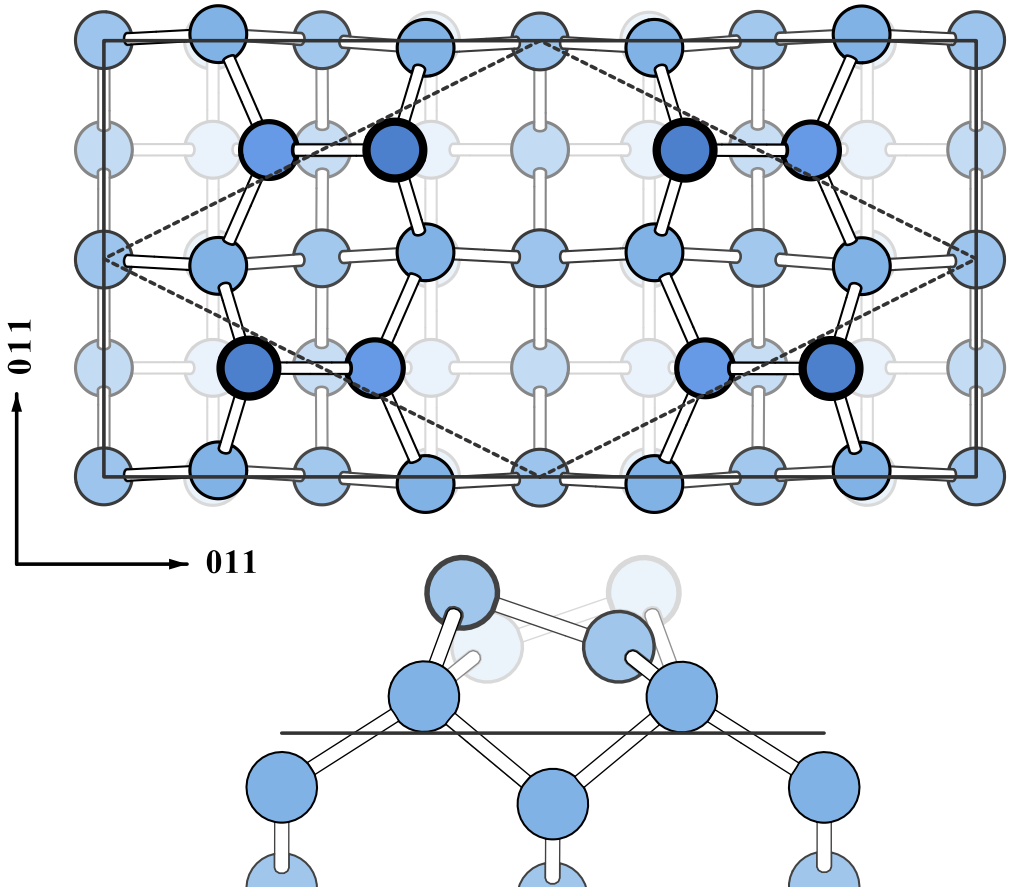
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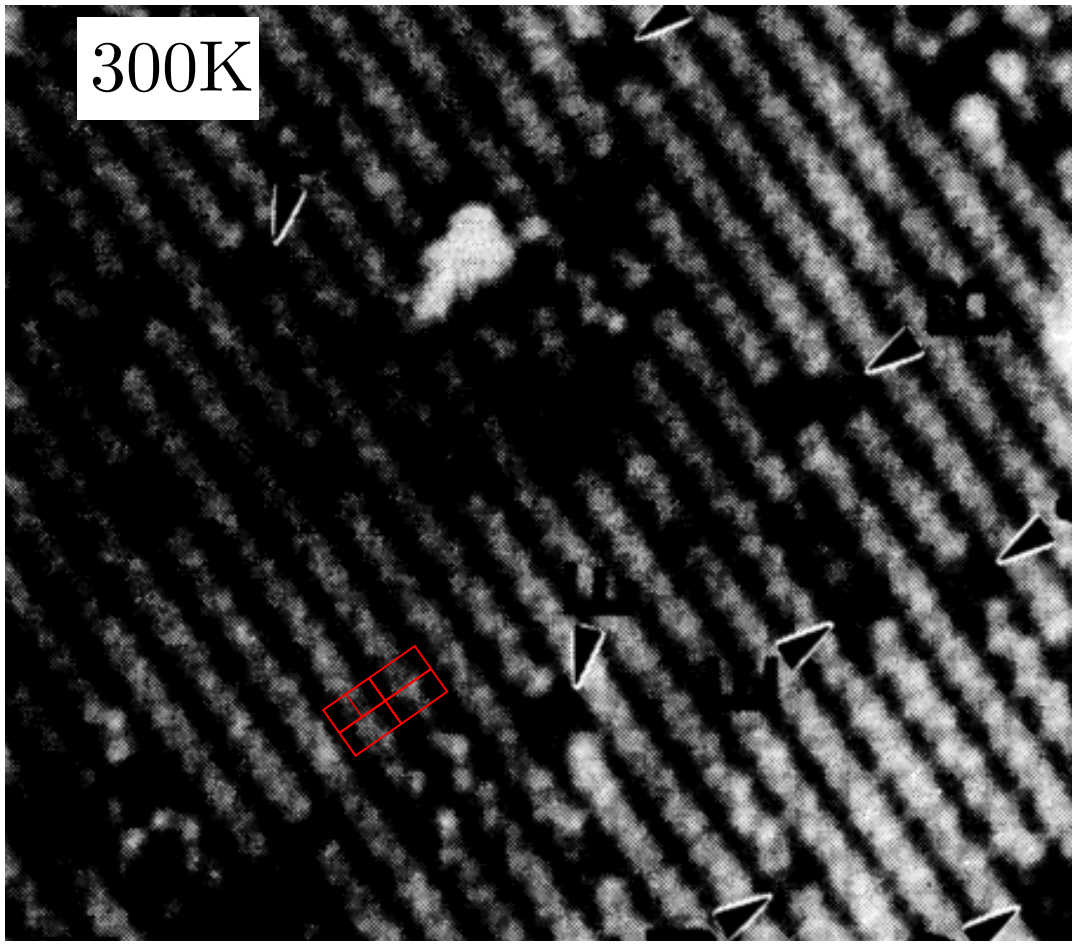
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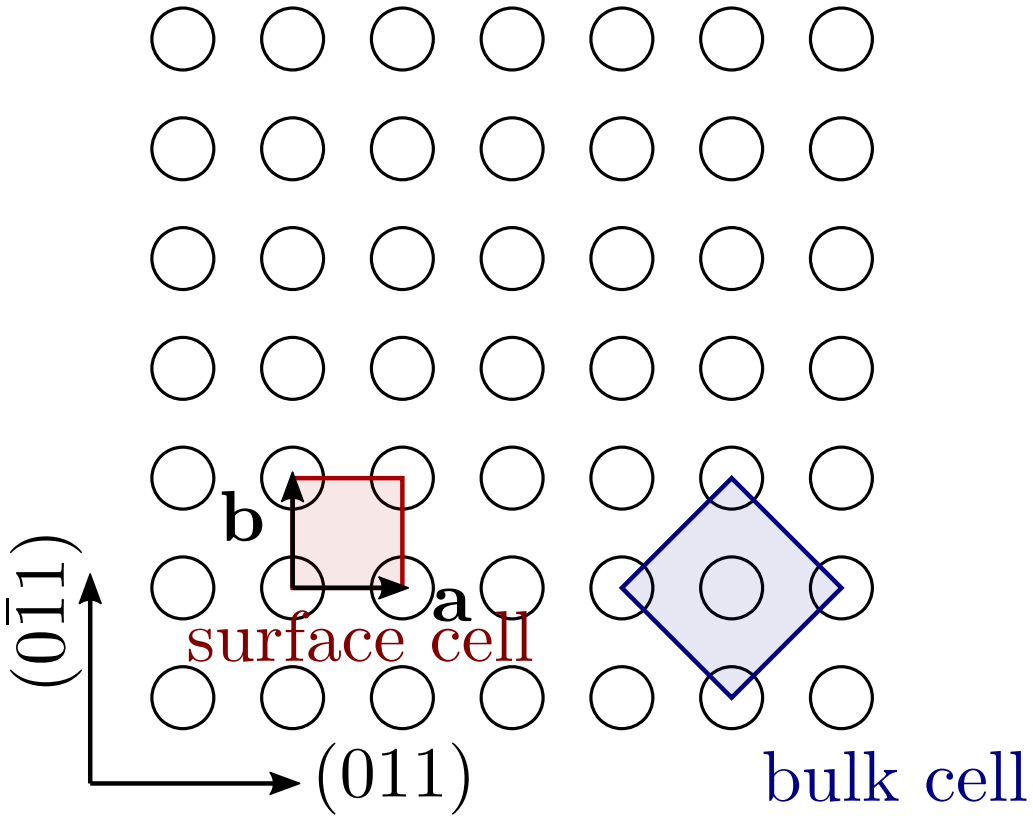


R. Wolkow, PRL 1992

Nomenclature For Surface Crystallography

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

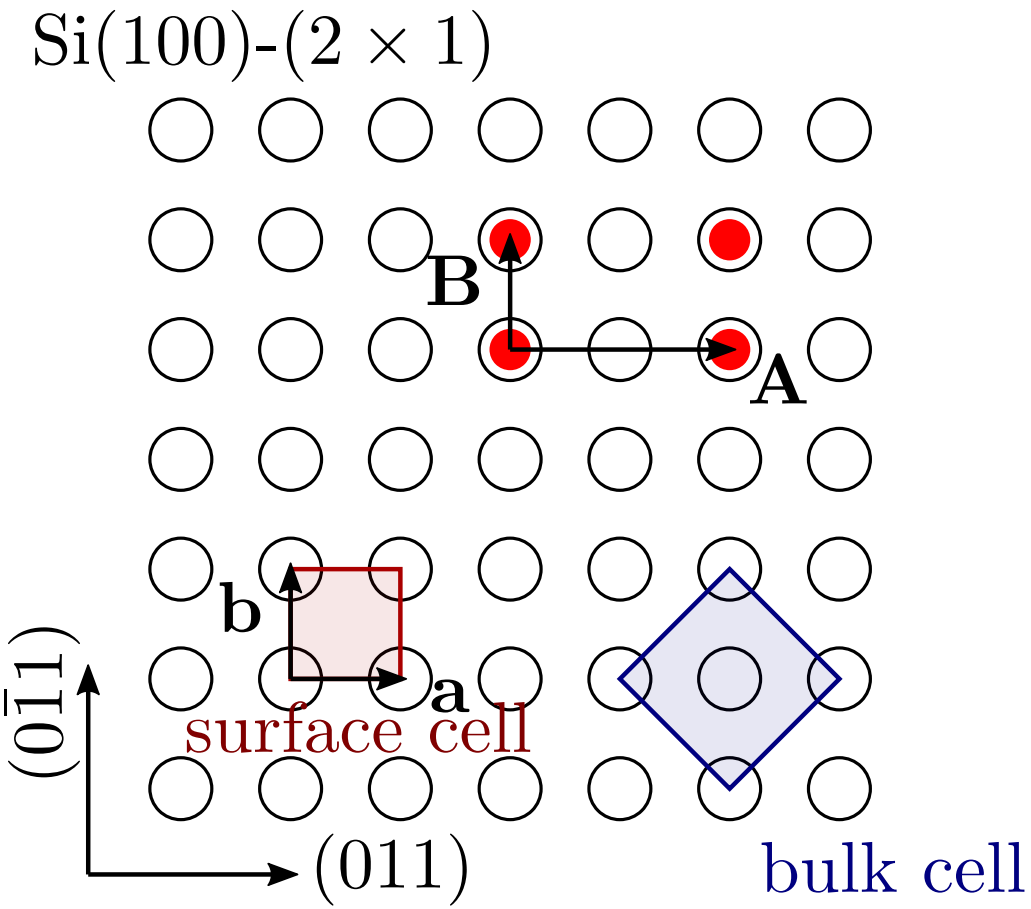
$$M\,(hkl) - [c|p]\,(m \times n)\,[R\alpha]$$



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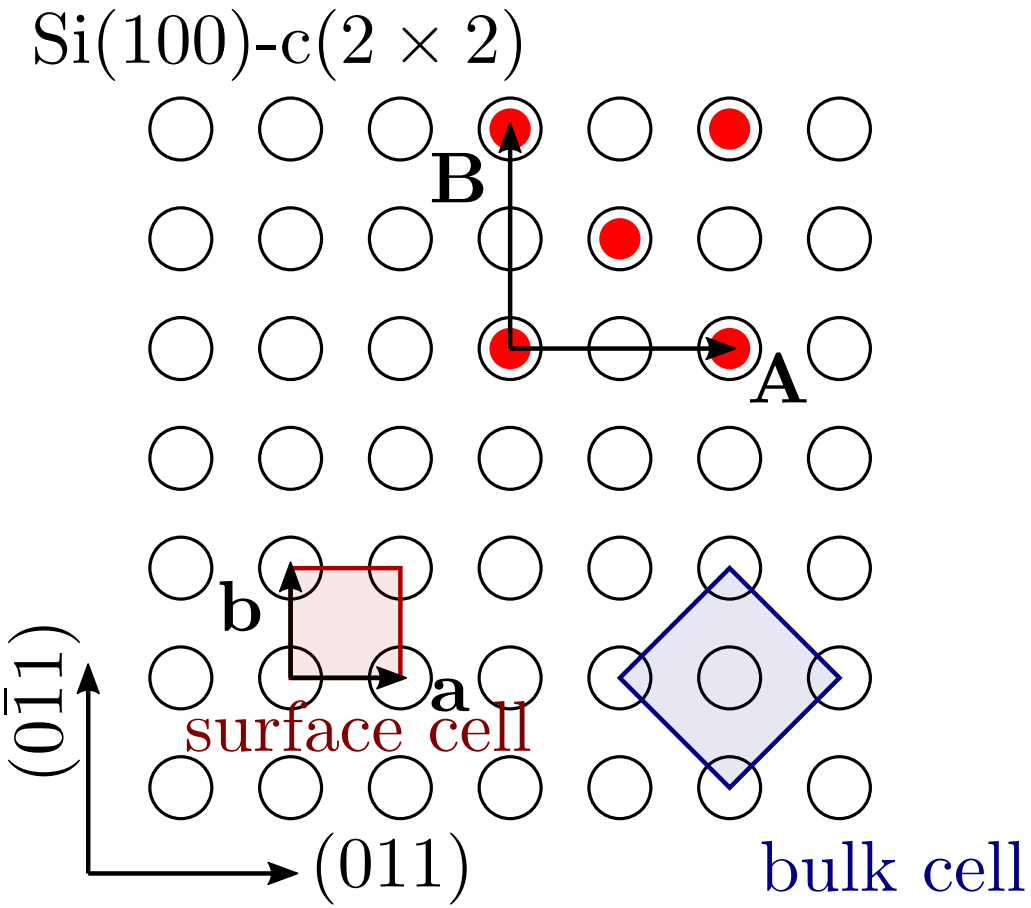
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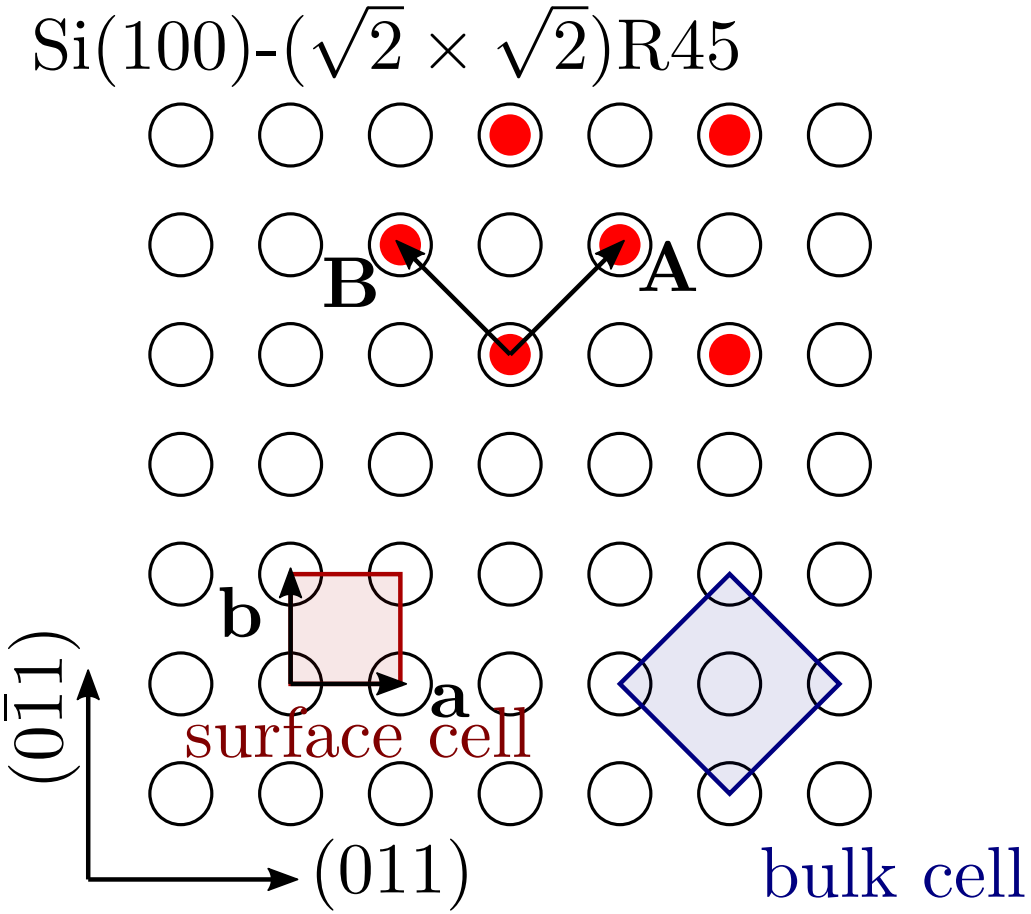
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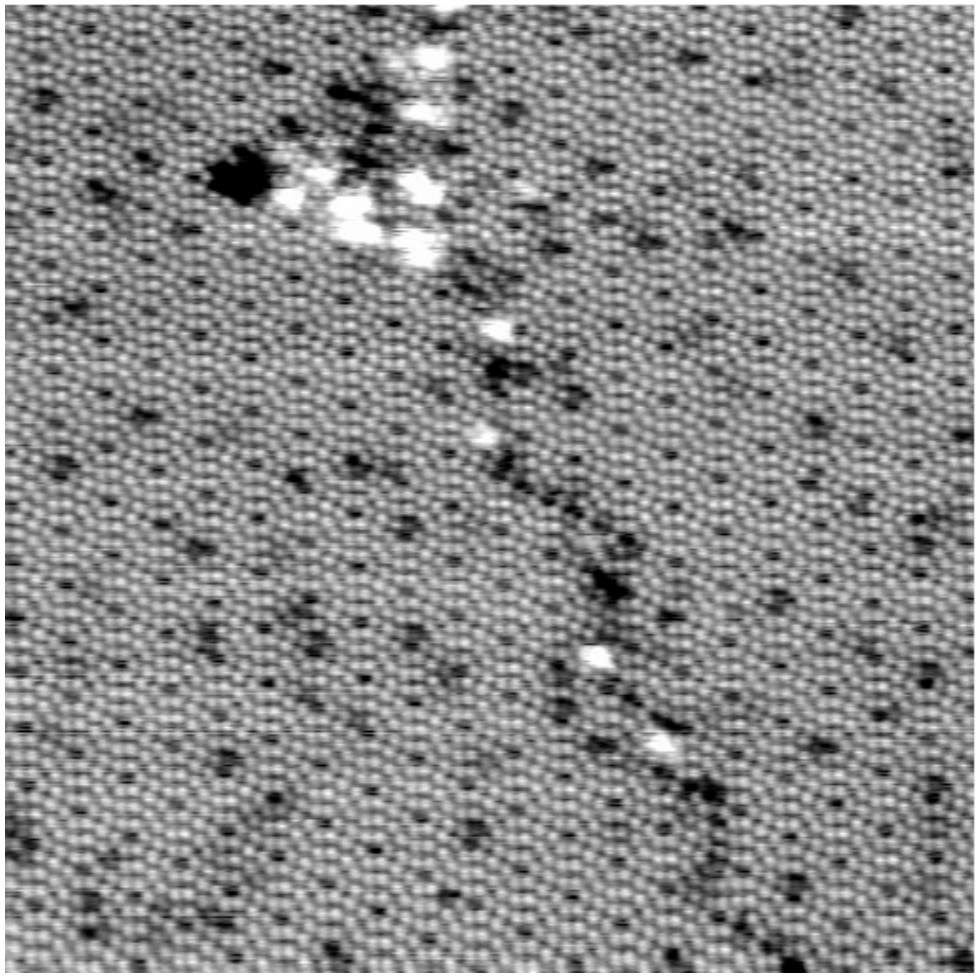
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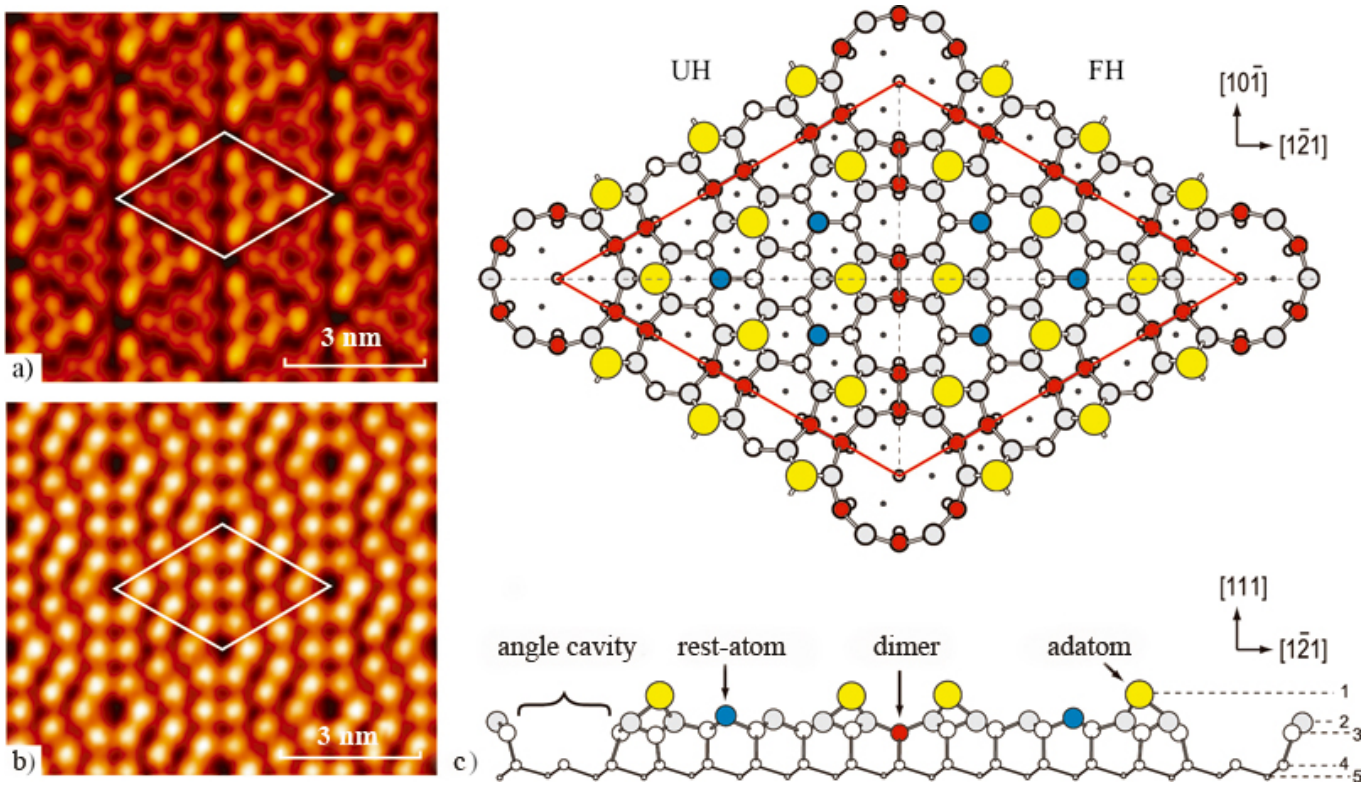


Si(111)-(7 × 7)

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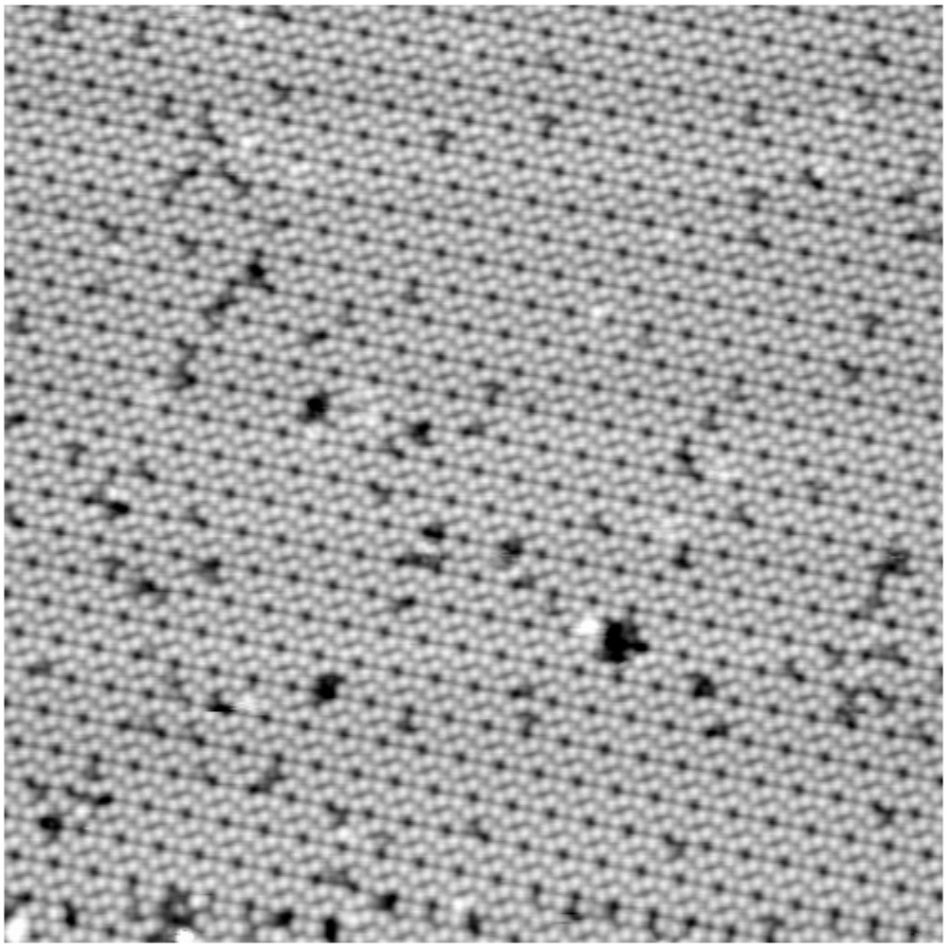
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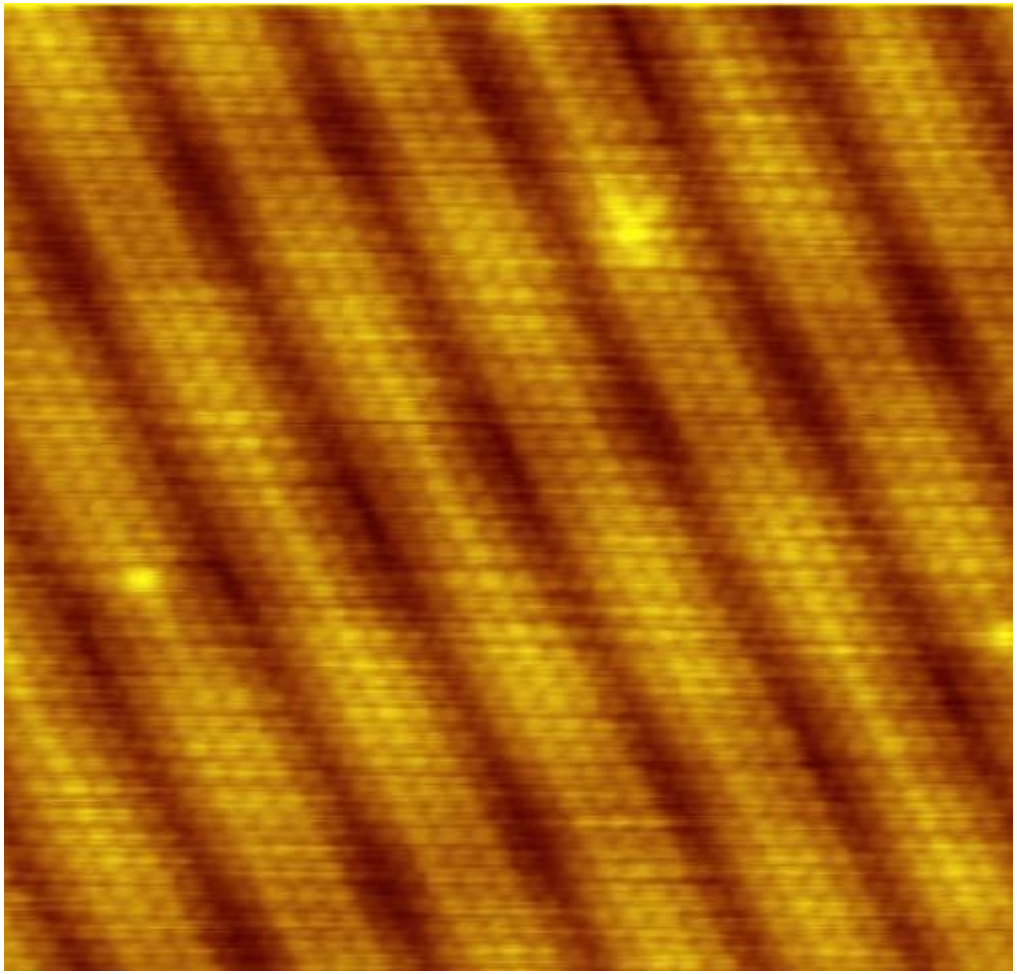


Si(111)-(5 × 5)

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Au(100)-(28×5)