

Crystal Growth: Physics, Technology and Modeling

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Lecture 2. Properties of crystal surfaces

<http://w3.unipress.waw.pl/~stach/cg-2024-25/>

Bonding in crystals

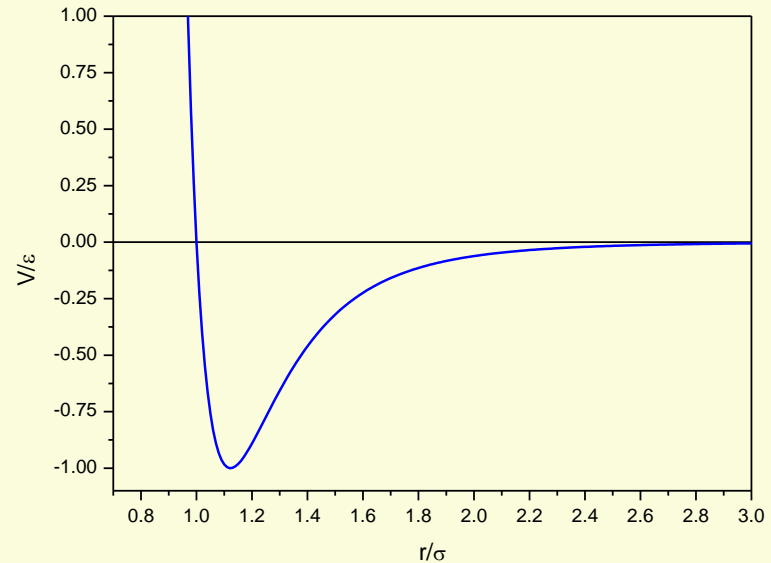
Condensed phases (solid, liquid) – enthalpy of the system is negative

Interaction potential – e.g. Lennard-Jones potential (noble gases)

$$V(r) = \epsilon \left[\left(\frac{r}{\sigma} \right)^{-12} - \left(\frac{r}{\sigma} \right)^{-6} \right]$$

ϵ – Interaction potential strength

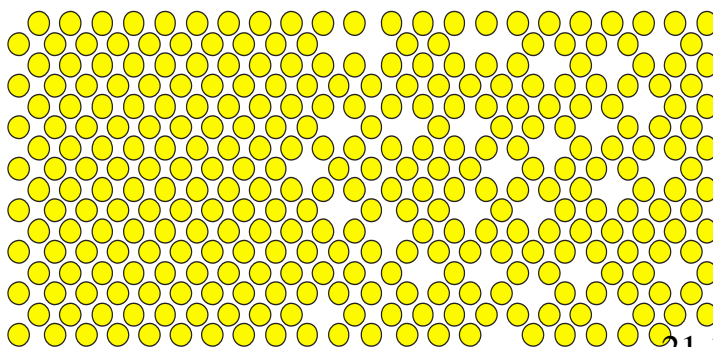
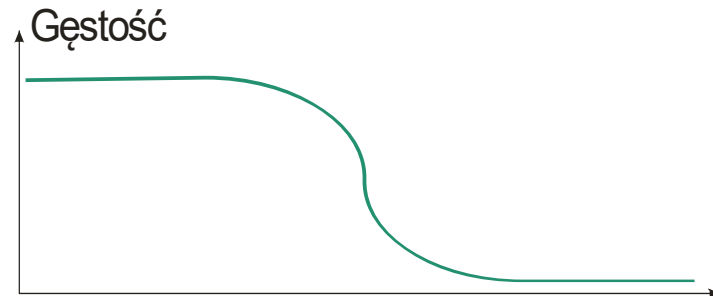
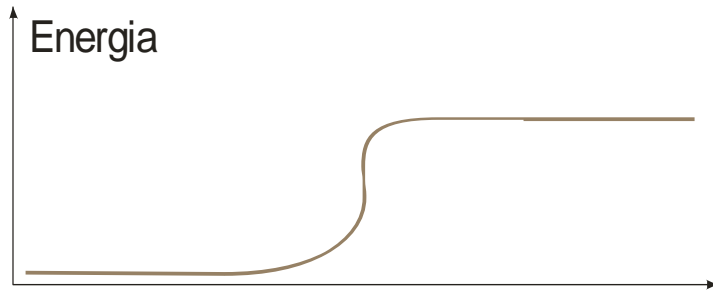
σ – Interaction potential range



Interactions – strength and range may be different.

In ionic crystal – range is essentially Infinite (Coulomb force)

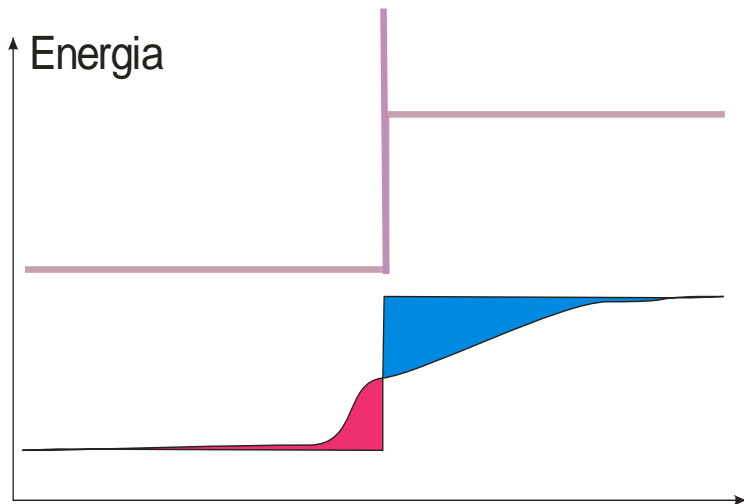
Surface layers – energetic properties



- **Large size crystals (above 20 nm in size)** – crystal body can be divided into interior and surface layer
- **Interior** – is uniform
- **Surface layer** – energy, density are changed, different from uniform properties
- **Gibbs description** – uniform bulk & additional surface contribution

Gibbs surface model

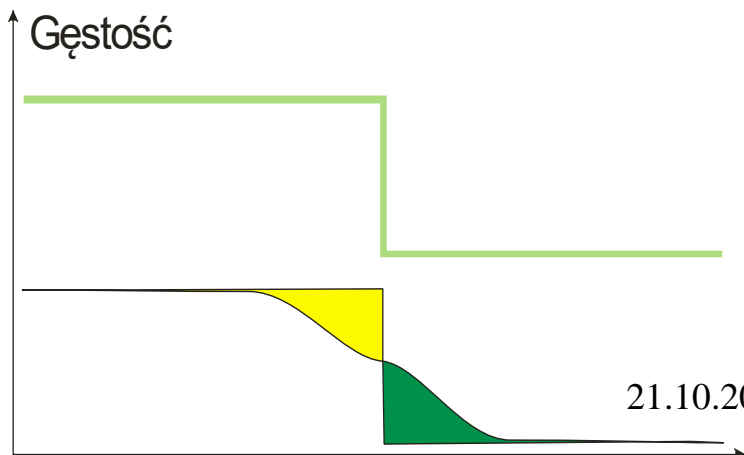
- **Gibbs model** – uniform properties of the bulk and additional surface density associated with the surface



Selection of the position of Gibbs surface :

- *Surface energy density disappears*

- *Surface mass density disappears*



Standard Gibbs selection of the surface – single component system

- Mass –contribution from the volume terms only

$$M = \int_{V_\alpha} \rho(r) d^3r + \int_{V_\beta} \rho(r) d^3r$$

No contribution from surface term.

- Free energy – contribution from the volume and the surface terms

$$F = \int_{V_\alpha} f_\alpha(r) d^3r + \int_{V_\beta} f_\alpha(r) d^3r + \int_S \gamma(r) d^2r$$

- Free energy – Gibbs model

$$F = f_\alpha V_\alpha + f_\beta V_\beta + \gamma A$$

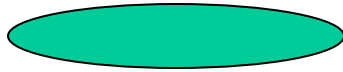
V_α, V_β - phase volume

A – interface area

For multi-component system the unique selection of the mass surface free position for all components is not possible.

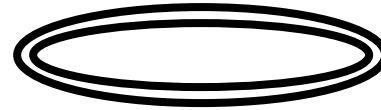
Surface tension and surface free energy density (liquids)

- Surface free energy density – energy for unit of the surface



$$F = \int_A \gamma(r) d^2r \approx \gamma A$$

- Surface tension – the force acting on the unit of circumference



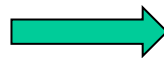
The work used by external force to increase surface area ($A \rightarrow A + \delta A$)

The surface energy change ($A \rightarrow A + \delta A$)

$$\Delta W = \oint_L \sigma \delta x dr = \sigma \delta A$$

$$\Delta F = \gamma \delta A$$

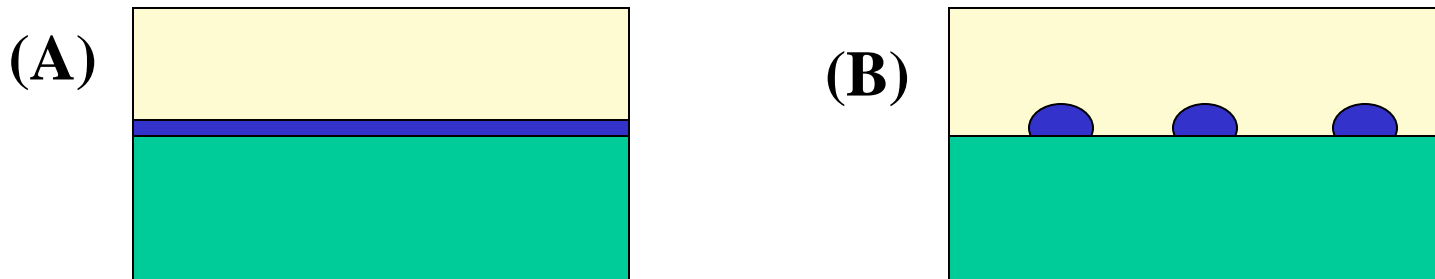
$$\Delta W = \Delta F$$



$$\sigma = \gamma$$

Surface wetting

- Consider three uniform, isotropic systems: **vapor(1)**, **solid(2)** and **liquid(3)**
- Interface energy is described by three parameters: γ_{12} , γ_{13} , γ_{23} .

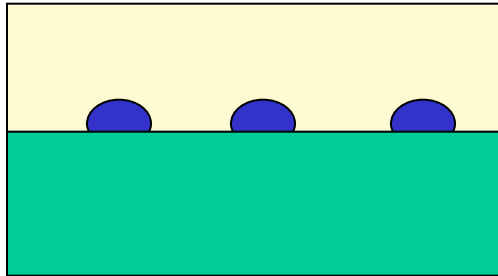


- The condition for full wetting of the surface by liquid is

$$\gamma_{13} > \gamma_{12} + \gamma_{23}$$

Partial surface wetting –wetting angle

- Partial surface (A) wetting occurs when

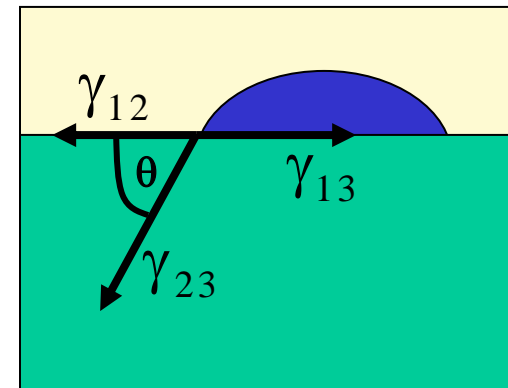


$$\gamma_{13} < \gamma_{12} + \gamma_{23}$$

$$\gamma_{23} > \gamma_{12} + \gamma_{13} \Rightarrow \gamma_{13} > \gamma_{12} - \gamma_{23}$$

- Wetting angle is defined as

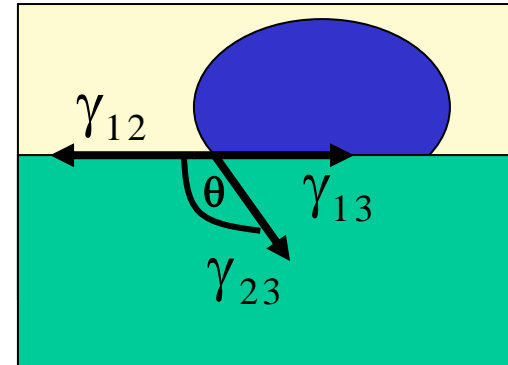
$$\gamma_{13} = \gamma_{12} + \gamma_{23} \cos(\theta)$$



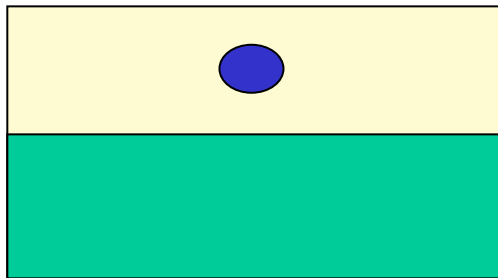
Absence of wetting

- Wetting angle is defined by the relation

$$\gamma_{13} = \gamma_{12} + \gamma_{23} \cos(\theta)$$



- Absence of wetting occurs when



$$\gamma_{12} < \gamma_{23} + \gamma_{13}$$

Isothermal, isochoric stability conditions

- Stability condition – minimal Helmholtz free energy F

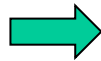
$$\delta F \geq 0 \quad \delta F = -p_\alpha \delta V_\alpha - p_\beta \delta V_\beta + \gamma \delta A + \mu_\alpha \delta N_\alpha + \mu_\beta \delta N_\beta$$

The constraints

$$N_\alpha + N_\beta = \text{const}$$

$$\delta N_\alpha = -\delta N_\beta$$

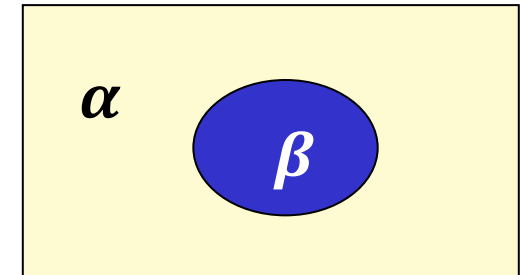
$$V_\alpha + V_\beta = \text{const}$$



$$\delta V_\alpha = -\delta V_\beta$$

$$T = \text{const}$$

$$\delta T = 0$$



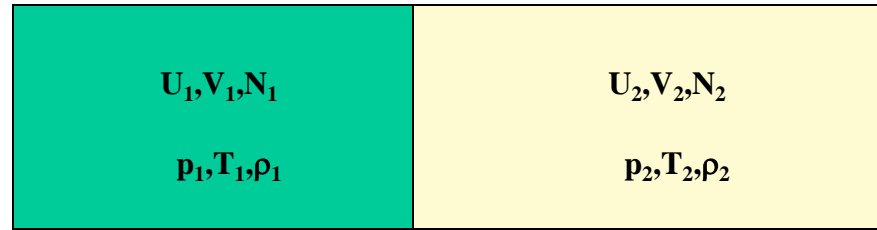
- Stability equations (equilibrium conditions)

$$p_\alpha = p_\beta + \gamma \frac{\delta A}{\delta V_\alpha}$$

$$\mu_\alpha(p_\alpha, T) = \mu_\beta(p_\beta, T)$$

Equilibrium state depends on the shape

Flat surface



- **Equilibrium conditions**

$$p_\alpha = p_\beta + \gamma \frac{\delta A}{\delta V_\alpha} \qquad \mu_\alpha(p_\alpha, T) = \mu_\beta(p_\beta, T)$$

- **Flat surface – its area could be kept constant under volume change of the phases**

$$\frac{\delta A}{\delta V_\alpha} = \frac{\delta A}{\delta V_\beta} = 0$$

The equilibrium conditions do not depend on the size – these conditions are tabulated in phase diagrams

$$p_\alpha = p_\beta = p$$

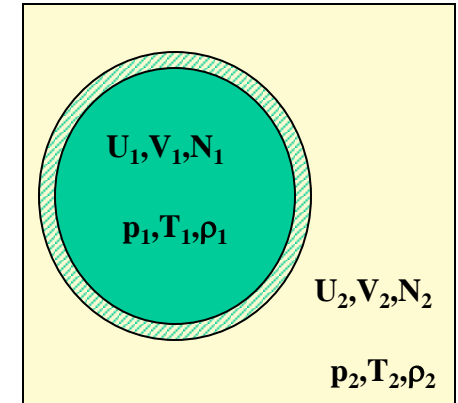
$$T_\alpha = T_\beta = T$$

Curved surface – isotropic case

- Equilibrium conditions

$$p_\alpha = p_\beta + \gamma \frac{\delta A}{\delta V_\alpha}$$

$$\mu_\alpha(p_\alpha, T) = \mu_\beta(p_\beta, T)$$



- Isotropic case - sphere

$$V = \frac{4\pi R^3}{3}$$

$$A = 4\pi R^2$$

$$\frac{\delta A}{\delta V} = \frac{2}{R} = \frac{1}{\kappa_\alpha} + \frac{1}{\kappa_\beta}$$

$\kappa_\alpha, \kappa_\beta$ - surface curvatures

The equilibrium conditions do depend on the size

$$p_\alpha = p_\beta + \frac{2\gamma}{R}$$

$$T_\alpha = T_\beta \neq T_{PT}$$

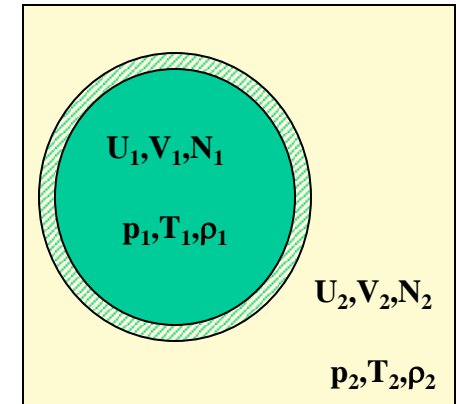
Curved surface – Gibbs-Thompson effect

- Equilibrium condition

$$p_{\alpha} = p_{\beta} + \frac{2\gamma}{R}$$

- Pressure change – chemical equilibrium condition is changed

$$\mu_{\alpha}(p + dp, T + dT) = \mu_{\beta}(p, T + dT)$$



Gibbs - Thompson effect – change of equilibrium temperature of the curved surface

Gibbs – Thompson effect

- Flat surface

$$\mu_{\alpha}(p, T) = \mu_{\beta}(p, T)$$

- Linear expansion

$$vdp - s_{\alpha}dT = -s_{\beta}dT \quad \Rightarrow$$

$$dp = \frac{2\gamma}{R} \quad \Rightarrow$$

- Curved surface

$$\mu_{\alpha}(p + dp, T + dT) = \mu_{\beta}(p, T + dT)$$

$$dT = \frac{vdp}{s_{\alpha} - s_{\beta}} = \frac{T_{PT}dp}{L}$$

$$dT = \frac{2T_{PT}\gamma}{LR} = \frac{2T_{PT}d_o}{R}$$

Gibbs – Thompson effect – curvature caused equilibrium temperature change

$$T(R) = T_{PT} \left(1 - \frac{2d_o}{R} \right)$$

$$d_o = \frac{\gamma}{L_{PT}} = \frac{\gamma}{T_{PT}(s_{\alpha} - s_{\beta})}$$

L – Latent heat of phase transition for volume unit

d_o - Capillary length

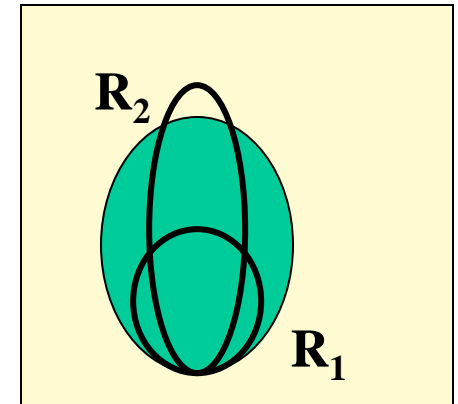
Curved surface – anisotropic case

- Equilibrium condition

$$p_\alpha = p_\beta + \gamma(\theta, \varphi) \left[\frac{1}{R_1} + \frac{1}{R_2} \right] = p_\beta + \gamma(\theta, \varphi) [\kappa_1 + \kappa_2]$$

- Two curvatures causes the chemical potential difference

$$\mu_\alpha(p + dp, T + dT) = \mu_\beta(p, T + dT)$$



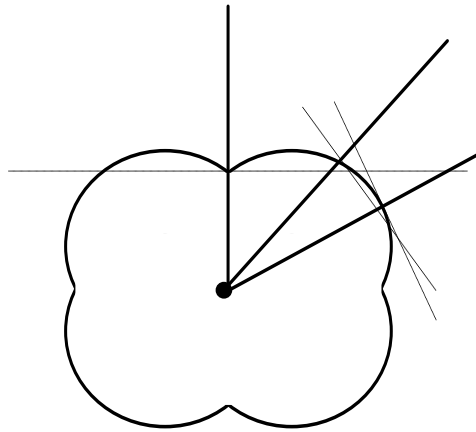
Gibbs – Thompson effect – curvature caused equilibrium temperature change

$$T(R) = T_{PT} \left(1 - \left[\frac{d_1(\theta, \varphi)}{R_1} + \frac{d_2(\theta, \varphi)}{R_2} \right] \right)$$

$$d_{1,2}(\theta, \varphi) = \frac{\gamma(\theta, \varphi)}{L_{PT}} = \frac{\gamma(\theta, \varphi)}{T_{PT}(s_\alpha - s_\beta)}$$

Anisotropic surfaces – the surfaces of real crystals

- **Crystal surfaces have orientation dependent surface energy density**
- **The angular diagram of this dependence is known as γ - plot.**



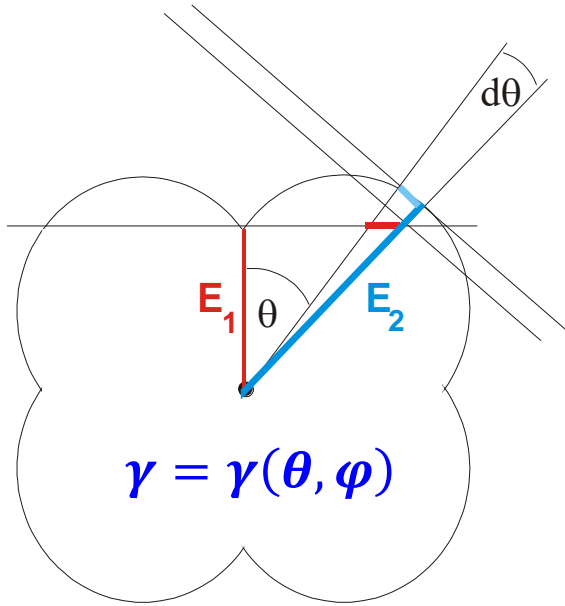
$$\gamma = \gamma(\theta, \varphi)$$

γ - plot and Wulff construction

Wulff construction

Crystal equilibrium shape is equal to the minimal volume contained within the surfaces, perpendicular to the lines from the γ - plot origin, drawn at their intersections with the γ - plot .

Wulff construction



- The angular diagram of this dependence is given as γ - plot.
- Calculate the energy ΔE contained with the minimal angle interval $d\theta$

• Case 1

$$\Delta E_1 = E_1 dl_1 = \frac{E_1 dl_{\perp}}{\cos(\theta)} = \frac{E_1}{\cos(\theta)} dl_{\perp}$$

$$\Delta E_2 > \Delta E_1$$

$$\Delta E_2 < \Delta E_1$$



• Case 1

• Case 2

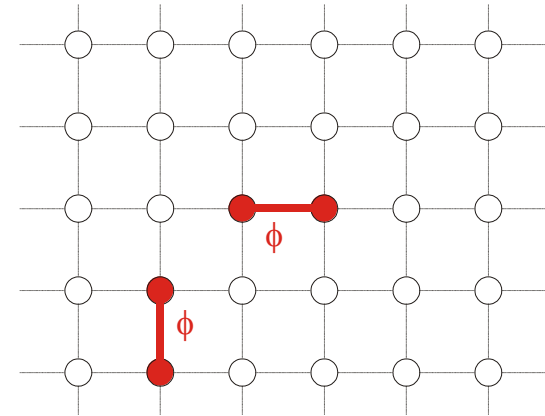
• Case 1

$$\Delta E_2 = E_2 dl_{\perp}$$

Wulff construction

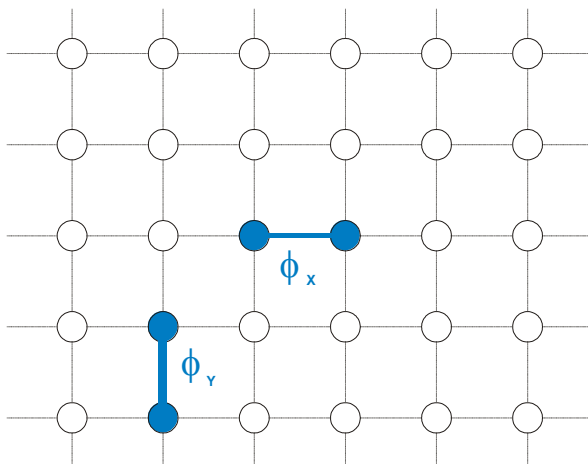
Kossel crystal – the simplest case

- **Square lattice**
- **Nearest neighbor (nn) interaction**
- **Interaction energy is isotropic (ϕ - nn interaction energy (bond energy))**
- **Z – number of nn (d =2 Z = 4, d=3 Z = 6)**

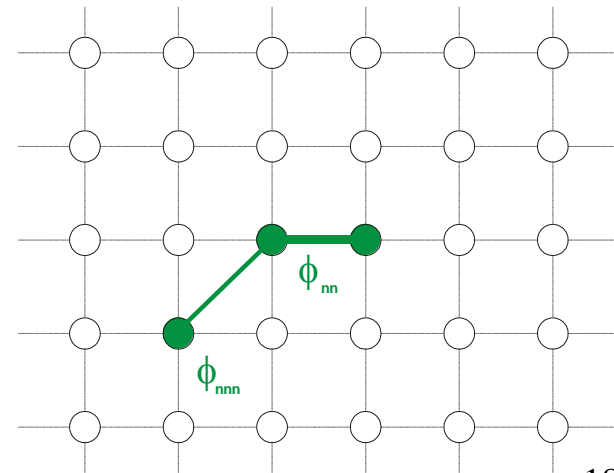


- **Extensions**

- **Anisotropic interactions**



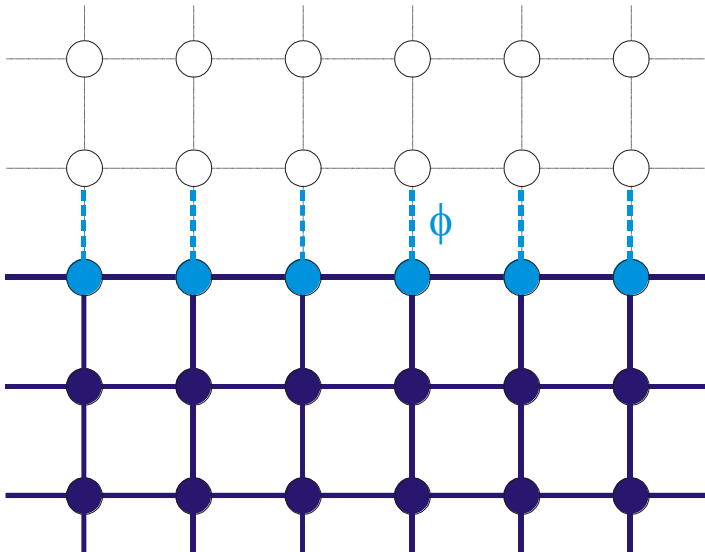
- **Next nearest neighbors (nnn) interaction**



Kossel crystal surfaces

- Surface – layer of atoms with broken (not saturated) bonds

$$E_s = -\frac{ZN_s\phi}{2} = -N_{\text{bond-S}}\phi$$



- Bulk crystal energy

$$E_{cr} = -\frac{ZN\phi}{2}$$

- Surface energy

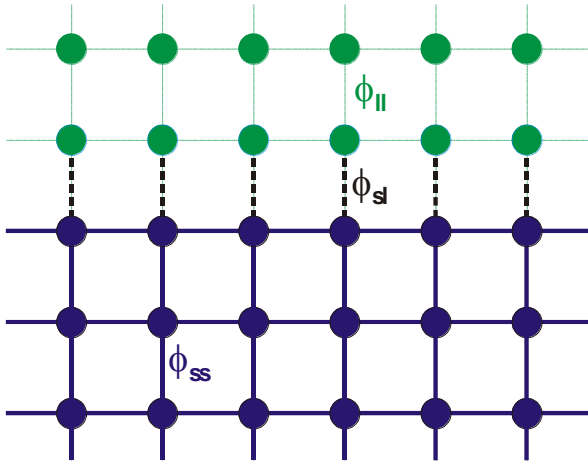
$$E_{sur} = N_{sur}\phi$$

- Total energy

$$E_{tot} = E_{cr} + E_{sur} = -\frac{ZN\phi}{2} + N_{sur}\phi$$

The simplest coherent model of the bulk and the surface.

Liquid-crystal interfaces in Kossel model



- Bond energy in crystal- ϕ_{cr} , in liquid - ϕ_{li} and crystal-liquid interface - ϕ_{cl}
- Number of atoms in crystal N_{cr} , liquid N_l
- Number of bonds in crystal N_{cr}^{bond} , liquid N_l^{bond} , in crystal-liquid interface N_{cr-l}^{bond}

- Crystal energy

$$E_{cr} = -N_{cr}^{bond} \phi_{cr} = -\frac{N_{cr} Z \phi_{cr}}{2}$$

- Liquid energy

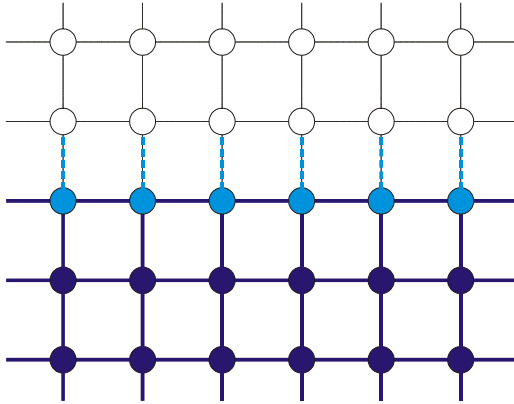
$$E_l = -N_l^{bond} \phi_{li} = -\frac{N_l Z \phi_{li}}{2}$$

- Crystal-liquid interface energy

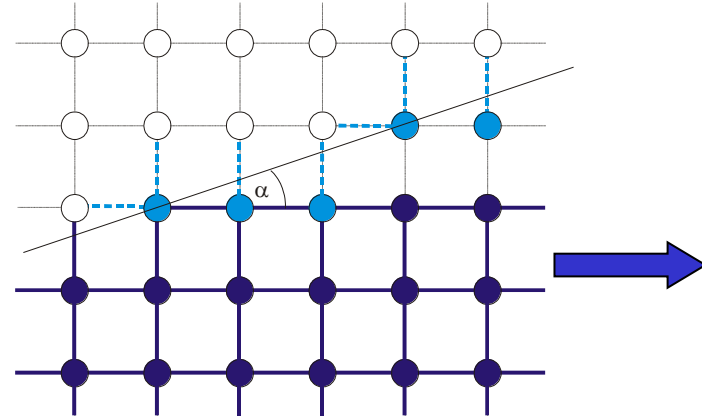
$$E_{cr-l} = -N_{cr-l}^{bond} \left[\phi_{cr-l} - \frac{\phi_{cr} + \phi_{li}}{2} \right]$$

Example in 2d – crystallographic (01) and vicinal surfaces

- Crystallographic flat surface (01)



- Vicinal surface

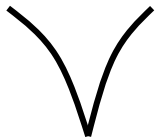


- n - step width
- α - step angle

$$|\tan(\alpha)| = \frac{1}{n}$$

- Vicinal surface energy

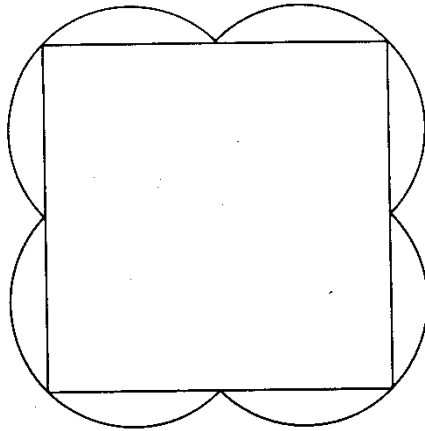
$$\gamma(\alpha) = \frac{1 + n}{n |\cos(\alpha)|} = \gamma(|\cos(\alpha)| + |\sin(\alpha)|)$$



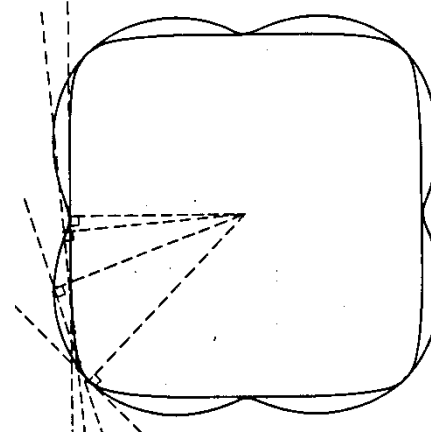
γ - plot – cusp for low Miller index surfaces

2-d Kossel crystal – equilibrium shape at $T > 0$

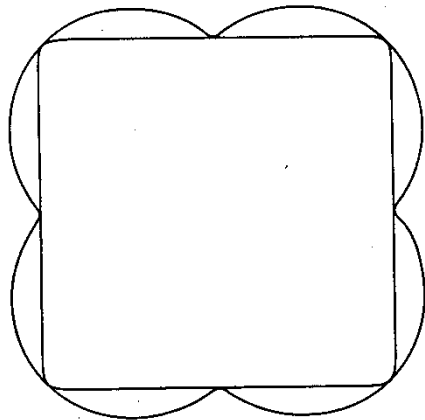
$kT/\varphi = 0$



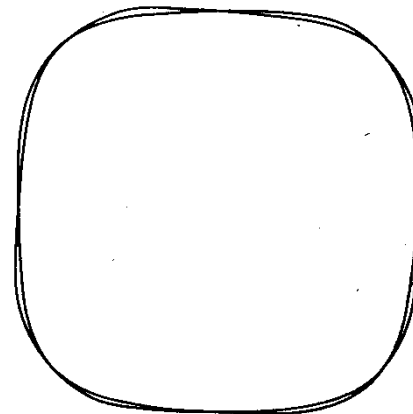
$kT/\varphi = 0.3$



$kT/\varphi = 0.1$



$kT/\varphi = 0.6$



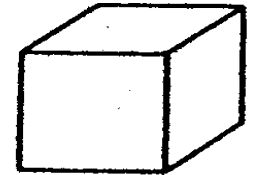
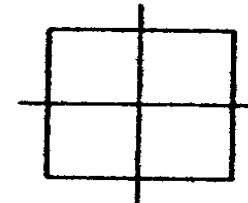
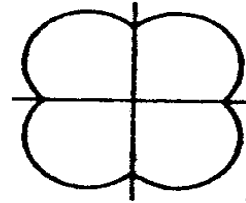
C. Rottman & M. Wortis Phys. Rev. B 24 (1981) 6274

3-d Kossel crystal – equilibrium shapes

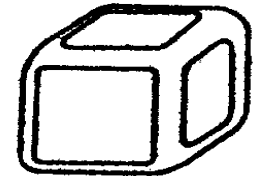
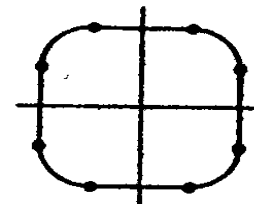
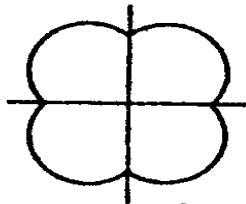
Wulff Plot

Crystal Shape
(equatorial plane) (perspective)

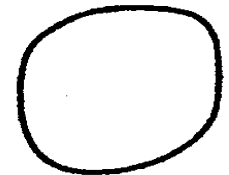
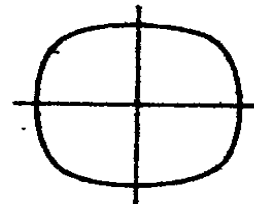
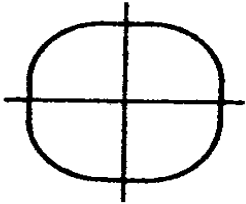
$T = 0$



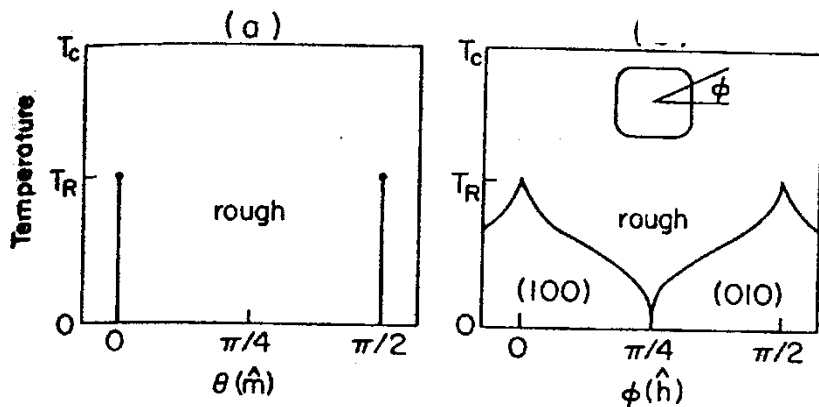
$0 < T < T_R$



$T_R < T < T_c$



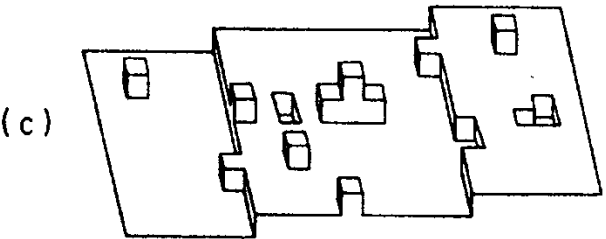
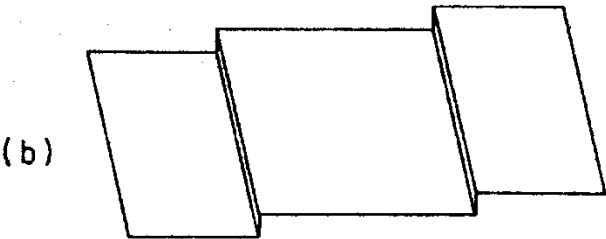
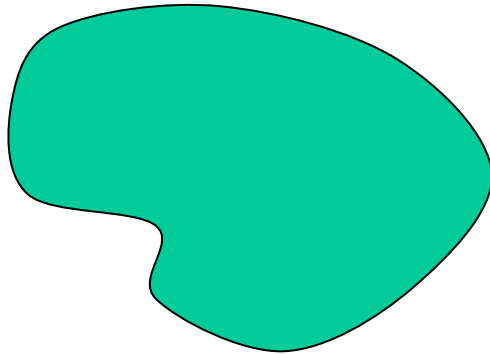
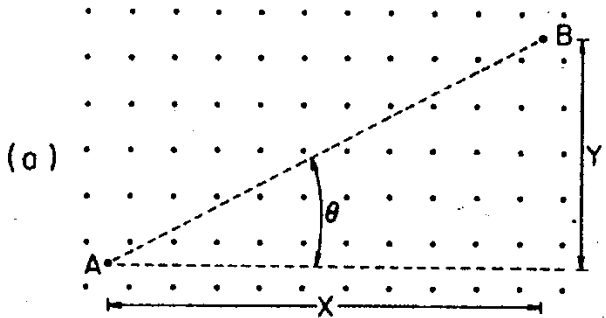
Phase diagram



Dark dots – transition from flat to vicinal surface

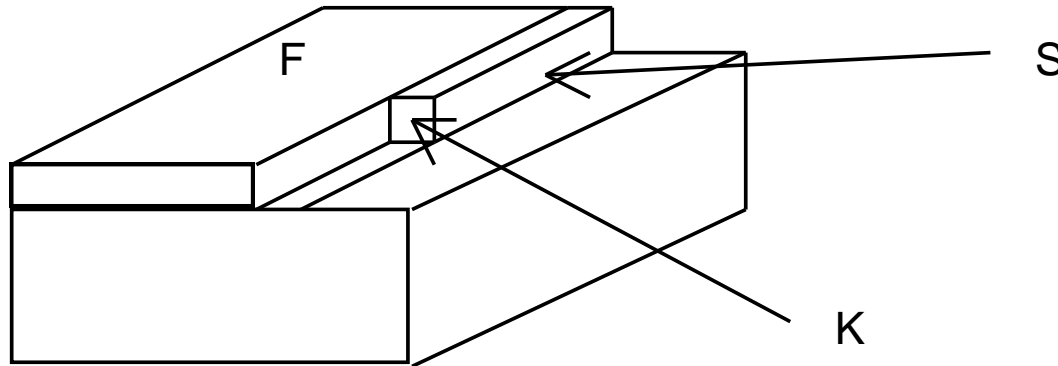
C. Rottman & M. Wortis Phys. Rep. 103 (1984) 59

2-d oraz 3-d surfaces



• step is one-dimensional object (line)

Atomic structure of three-dimensional surfaces

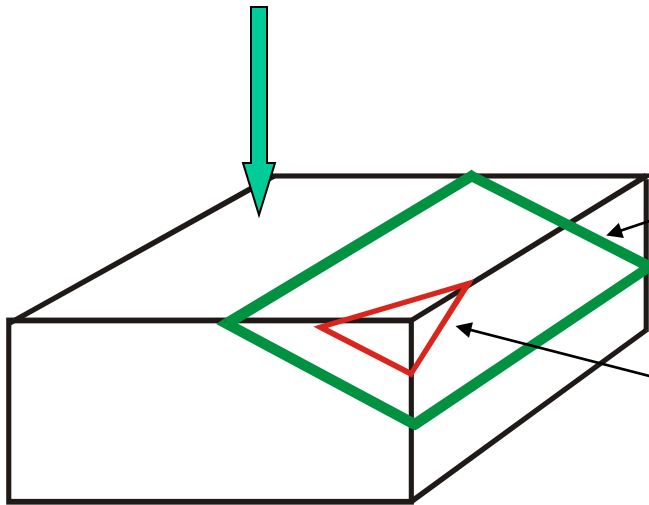


- **Low Miller index surfaces are denoted as F surfaces (F – flat)**
- **Atomic layers are terminated by edge. Atomic layer edges are called steps (S).**
- **Termination of the atoms row at the edge is called kink (K)**

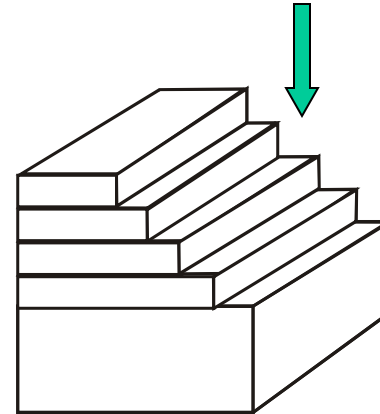
Traditionally the model is called TLK – terrace – ledge – kink model.

3-d surface types

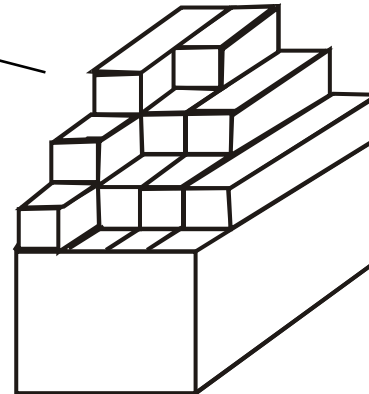
Flat surface (F surface)



Stepped surface (S surface)



Kinked surface (K surface)



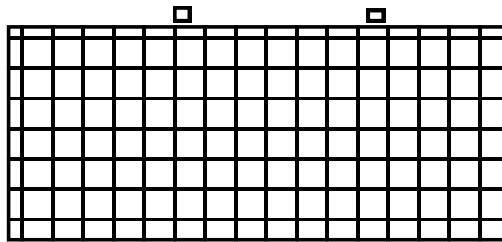
Flat and rough surfaces

- Surface roughness R is defined as:

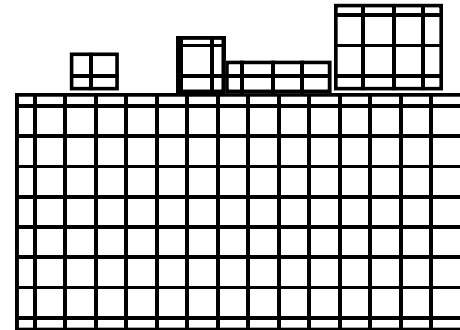
$$R \equiv \frac{N - N_o}{N_o}$$

N – number of broken bonds

N_o – minimal number of broken bonds



gladka



szorstka

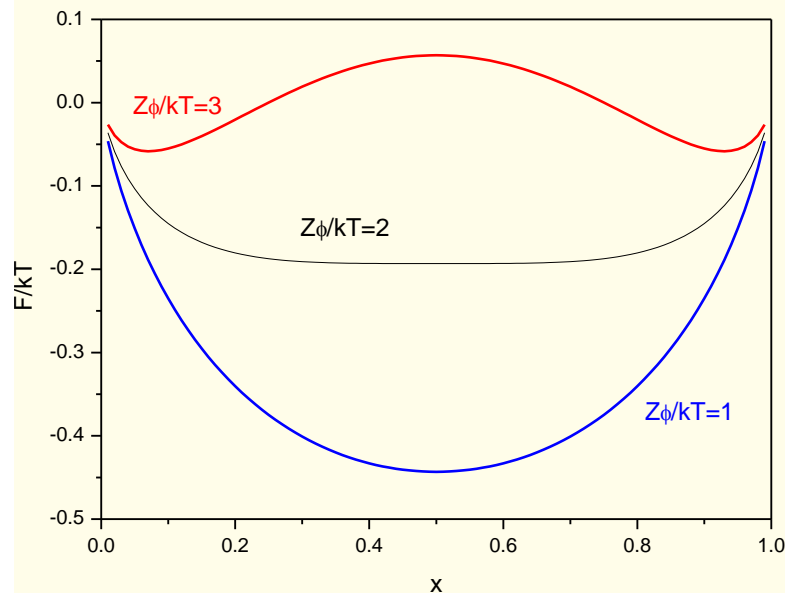
Mathematical roughness is different from Atomic Force Microscope roughness.

Surface phase transition rough-flat

- **Single layer model:**
- **Mean field theory (Bragg – Williams approximation)**

Surface free energy

$$F = kT[x\ln(x) + (1 - x)\ln(1 - x)] + Z\phi x(1 - x)$$



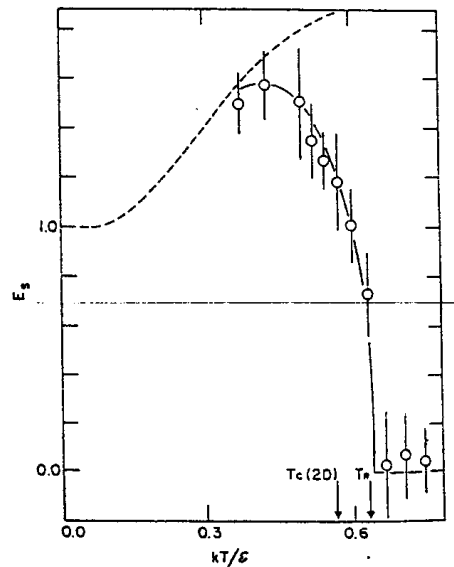
$$x = \frac{N_{at}}{N_o}$$

Phase transition at $Z\phi=2kT$

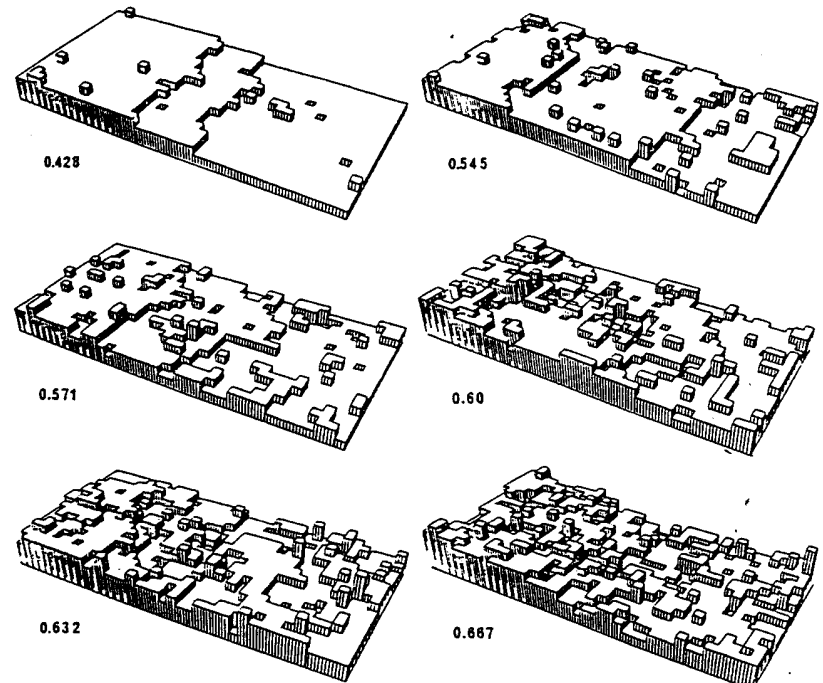
Surface phase transition rough-flat: numerical simulations

- Stepped surface with quasi-periodic boundary conditions
- Solid-on-Solid (SOS) approximation
- Stepped and step-free surfaces energy difference

$$\alpha = \frac{kT}{\phi} = \frac{kT}{\varepsilon}$$



- Microscopic configurations at different temperatures



Phase transition at $kT = 0.61\phi$

H.J. Leamy & G.H. Gilmer J. Cryst. Growth 24 (1974) 499

Equilibrium step properties

- **Step – 1-d object (line)**
- **No phase transitions**
- **Step – rough object**
- **Step – solid – surface exchange of atoms**

$$T_R = 0$$

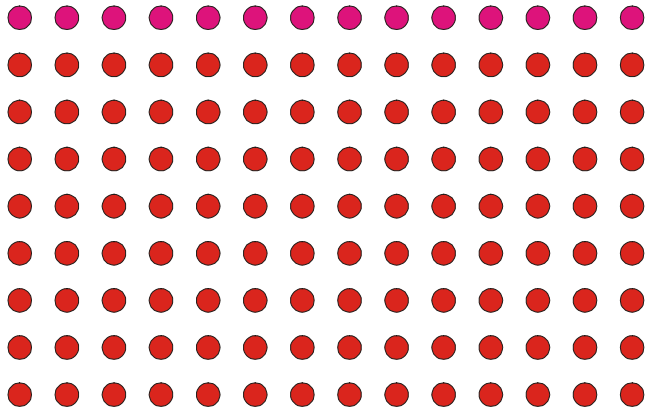
Surfaces of real crystals – clean (no foreign atoms)

- **Jahn-Teller effect – lattice symmetry breaking to lower system energy**
- **Two basic effects: relaxation and reconstruction**
- **Surface relaxation: modification of atom positions preserving translational lattice symmetry (parallel to the surface)**
- **Surface reconstruction: modification of atom positions breaking translational lattice symmetry**

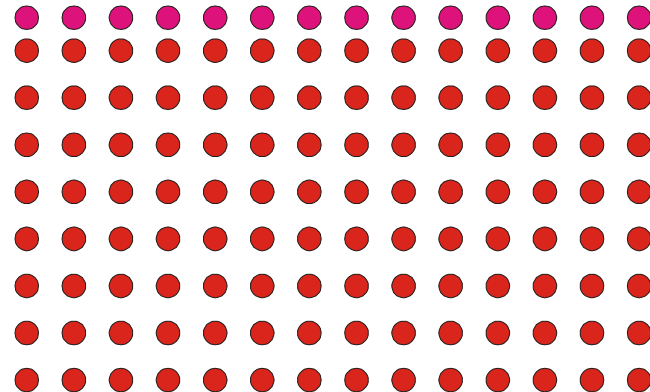
Surface relaxation

- **Observed at metal surfaces**
- **Electric properties of the surface are not changed**

Termination surface

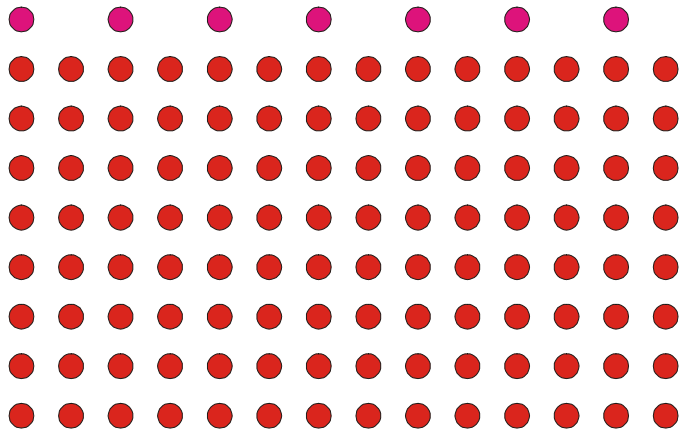


Relaxed surface

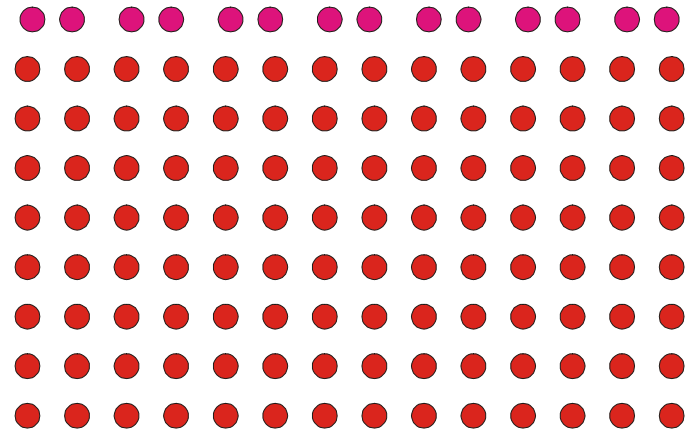


Reconstructed surfaces - examples

2x1 – missing row reconstruction



2x1 – pairing reconstruction

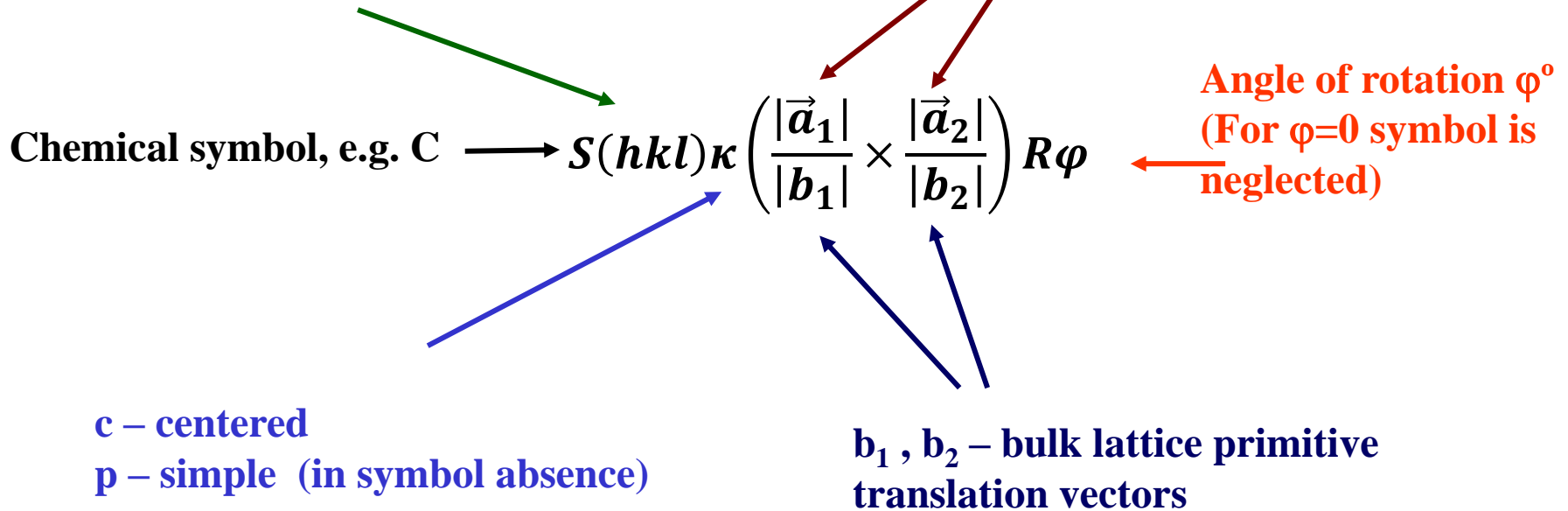


Wood notation – description of reconstructed surfaces

Wood notation (Wood Symbol)

Surface Miller index (hkl)

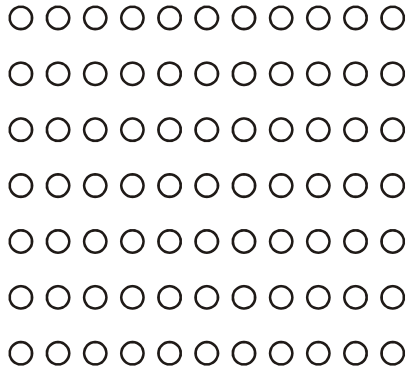
a_1, a_2 - surface primitive translation vectors



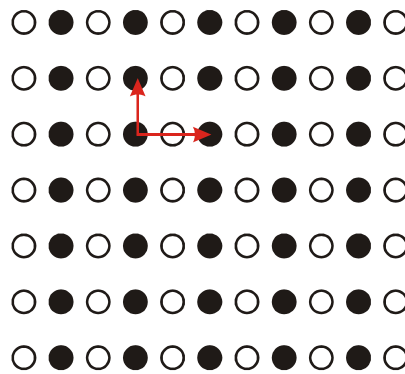
Wood notation is not unique (the same structure may be denoted by different symbols)

Wood symbols - examples

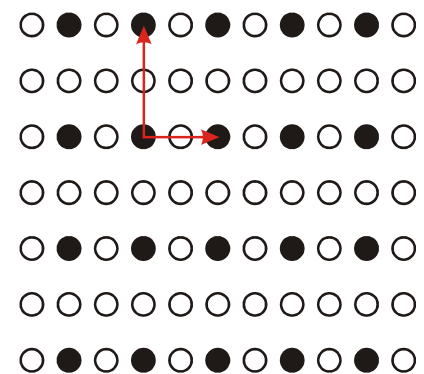
(1x1)



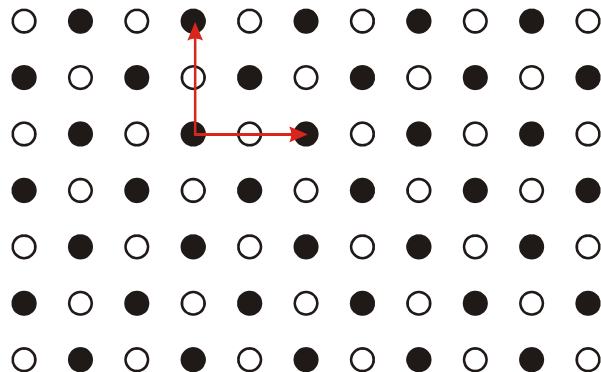
(2x1)



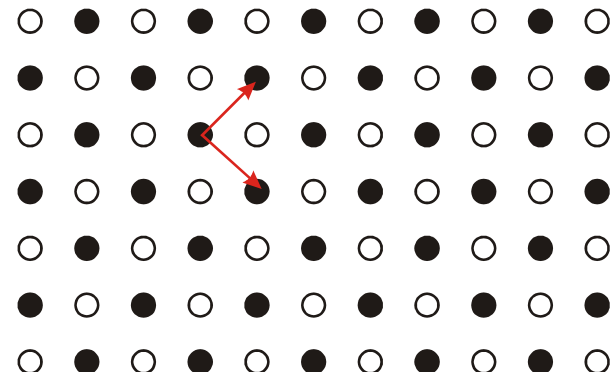
(2x2)



(2x2)



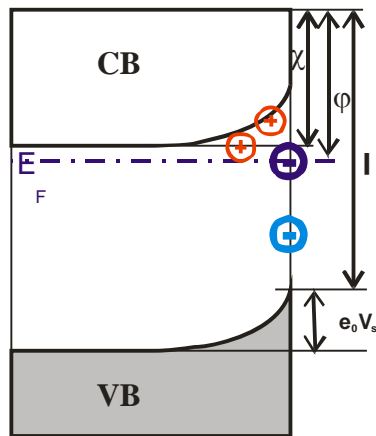
$(\sqrt{2} \times \sqrt{2})$



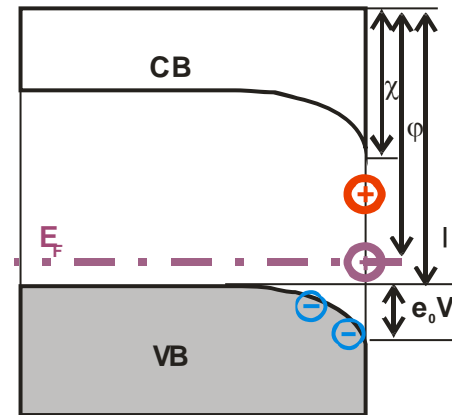
Semiconductor surfaces – reconstruction, charges and fields

- Strong, directional bonds, saturation by creation of new bonds
- Strong tendency to saturation by attachment of foreign atoms
- Reconstruction – may include several atomic layers
- Charged surface states induce fields that penetrate into deep interior

- **Surface acceptor**



- **Surface donor**



I – ionization energy

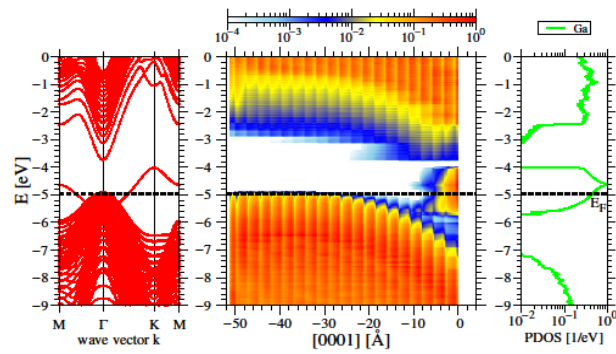
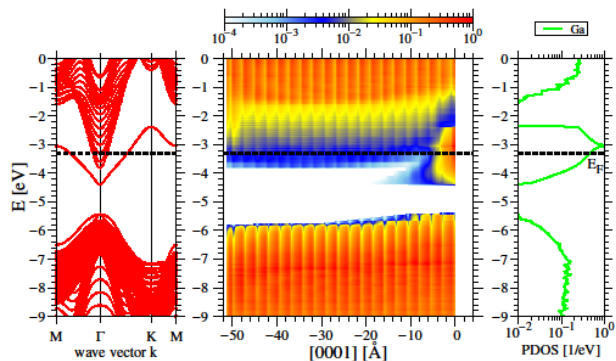
ϕ – work function

χ – electron affinity

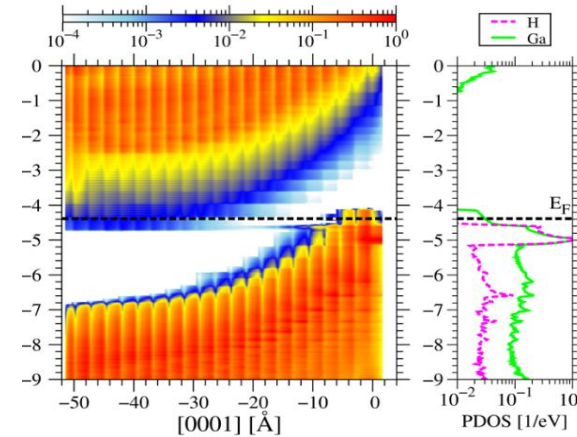
In metal all values are identical

Electronic properties of semiconductor surfaces – GaN(0001) surface

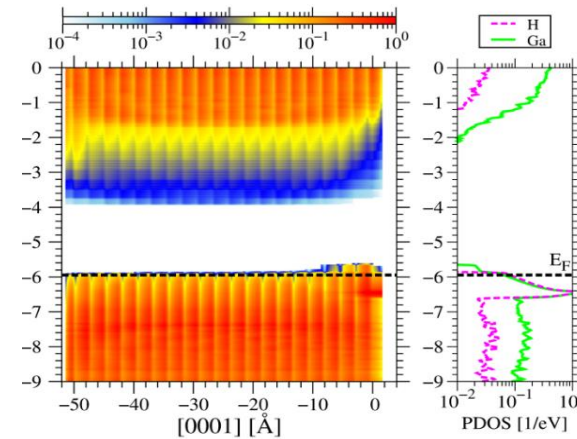
Clean surface



1 ML coverage



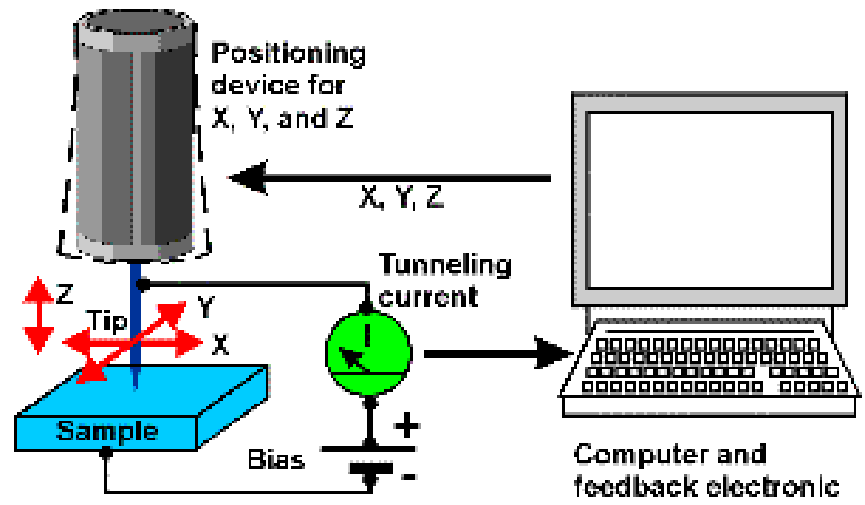
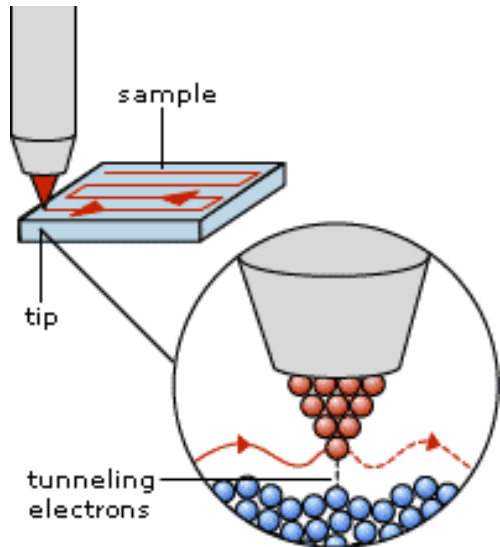
n type



p type

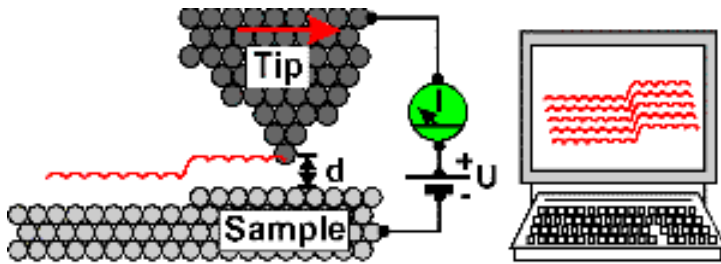
P. Kempisty et al.
AIP Adv. 4 (2014) 117109-1-24.

Scanning Tunneling Microscope – STM

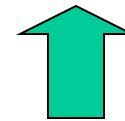
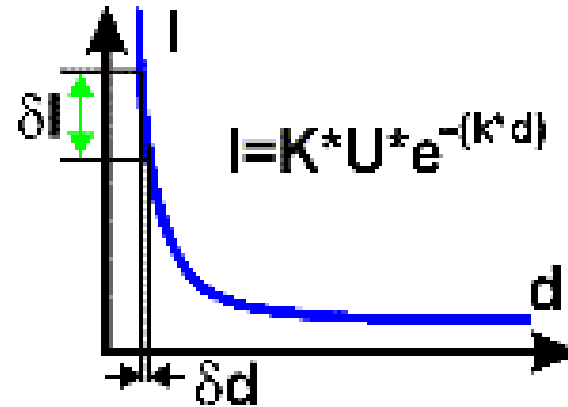


**Nobel Laureates:
Heinrich Rohrer and Gerd Binnig 1986**

STM work mode



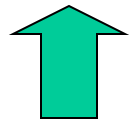
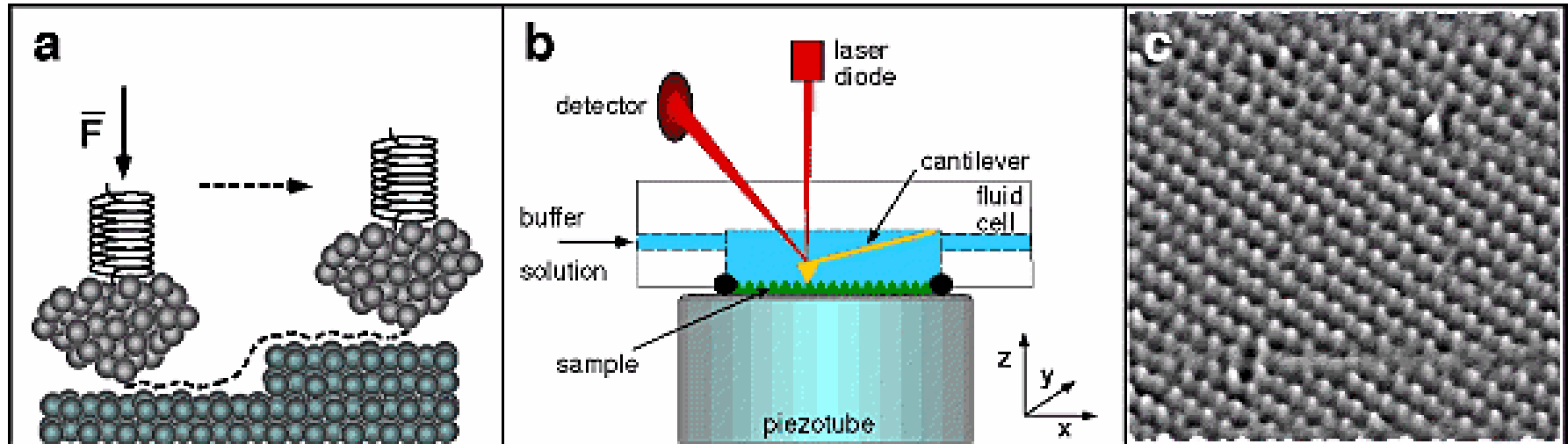
The tip interacts with the surface



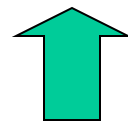
Tunneling current vs distance
 K and k – constants

STM can achieve atomic resolution!

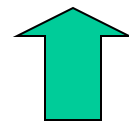
AFM – measurement technique



AFM tip – surface interaction



Laser detection of tip motion



Atomic resolution – mica surface ($d = 5.4 \text{ \AA}$).

AFM – Atomic Force Microscope

Atomic Force Microscope - NovaScan

ESPM II



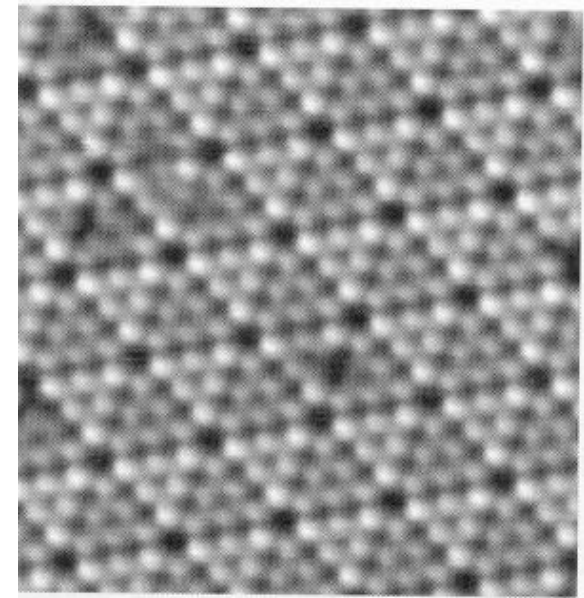
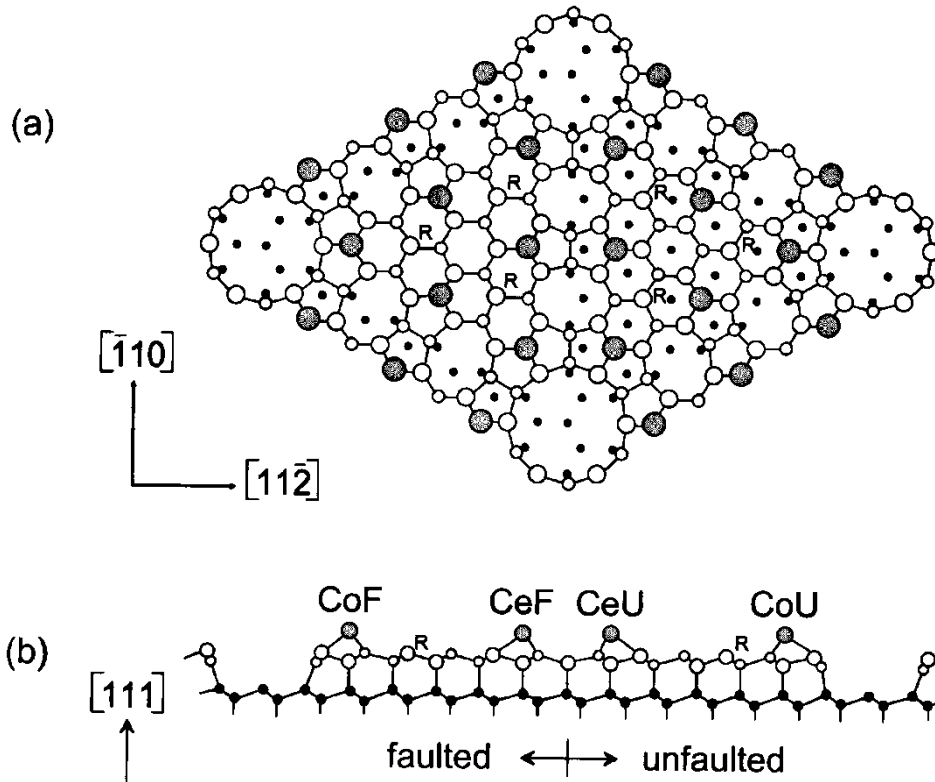
OSPM II



Si (111) 7x7 surface (dimer – adatom – stacking fault)

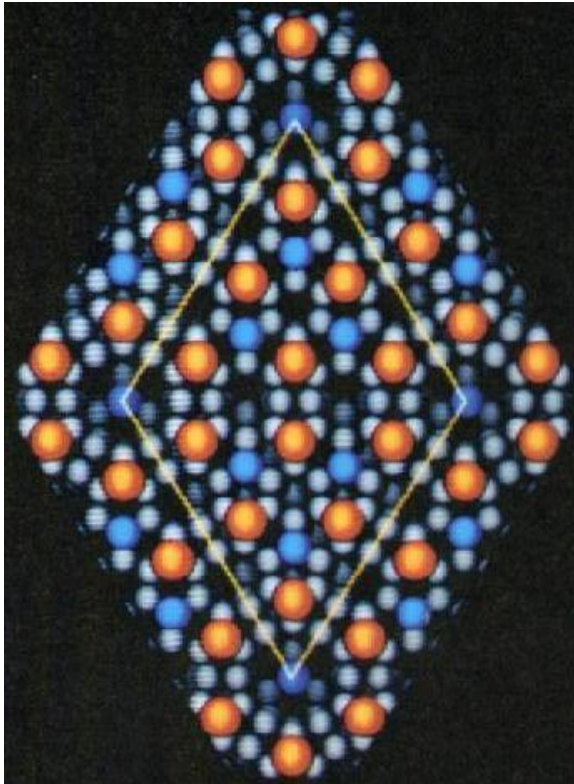
Si (111) (7 x 7) surface - model

STM picture

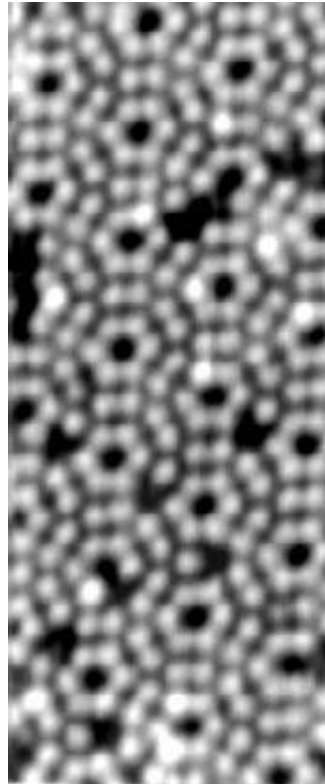


K. Takanayagi et al. Surf. Sci. 164 (1985) 367

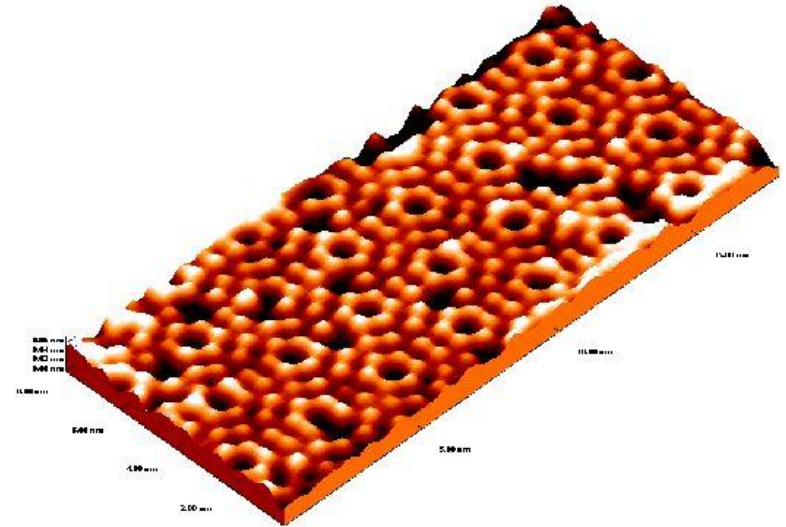
Si(111) (7x7) reconstruction – STM picture



**Model -
R.M. Tromp (IBM)**



STM picture



3-d model

Literature

- Springer series in Surface Science
- W. Monch, *Semiconductor Surfaces and Interfaces*. Springer 2001
- W. Schommers, P. Von Blanckenhagen, *Structure and Dynamics of Surfaces II*, Ch. 3.2, Springer 1987.
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- H. Luth, *Solid Surfaces, Interfaces and Thin Films*, Springer 2010
- A. Zangwill, *Physics at Surfaces*, Cambridge Univ. Press. 1996