Crystal Growth: Physics, Technology and Modeling

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Lecture 4. Properties of crystal surfaces

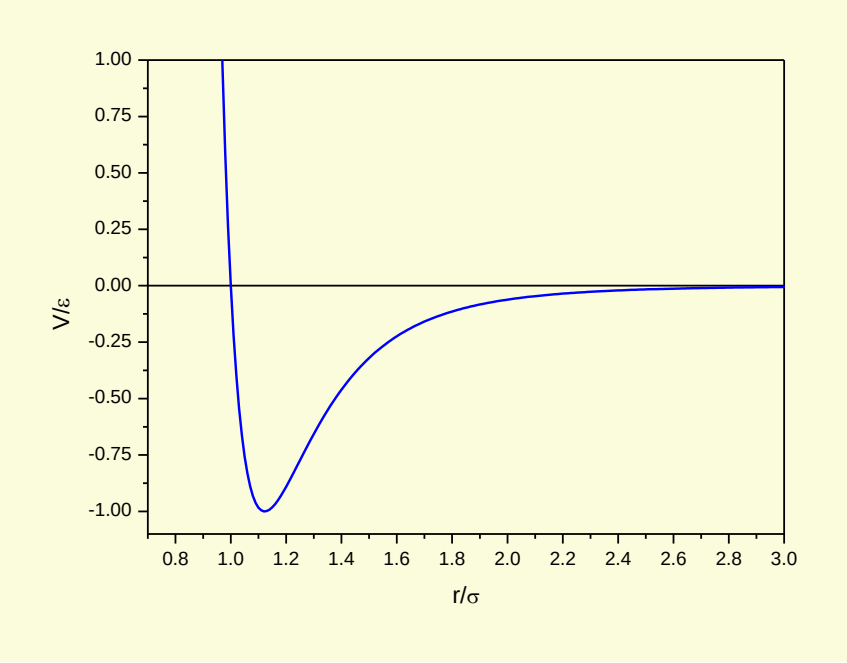
http://w3.unipress.waw.pl/~stach/cg-2022-23/

Bonding in crystals

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

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

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



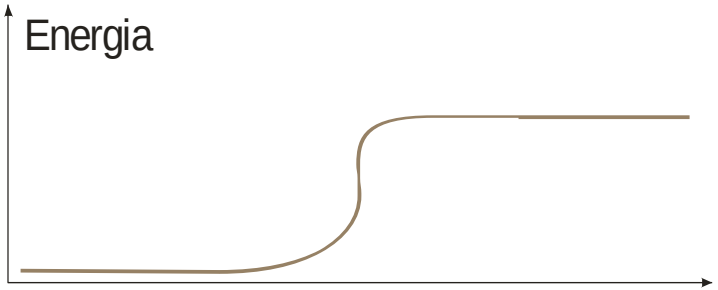
ε – Interaction potential strength

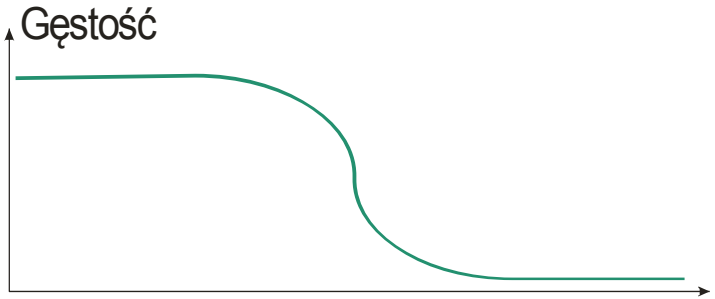
σ – Interaction potential range

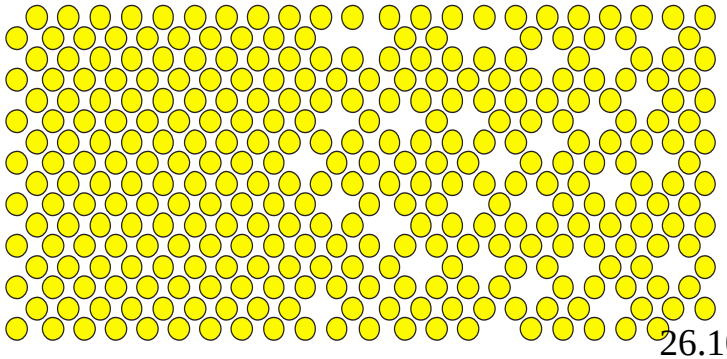
Interactions – strength and range may be different.

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

Surface layers – energetic properties



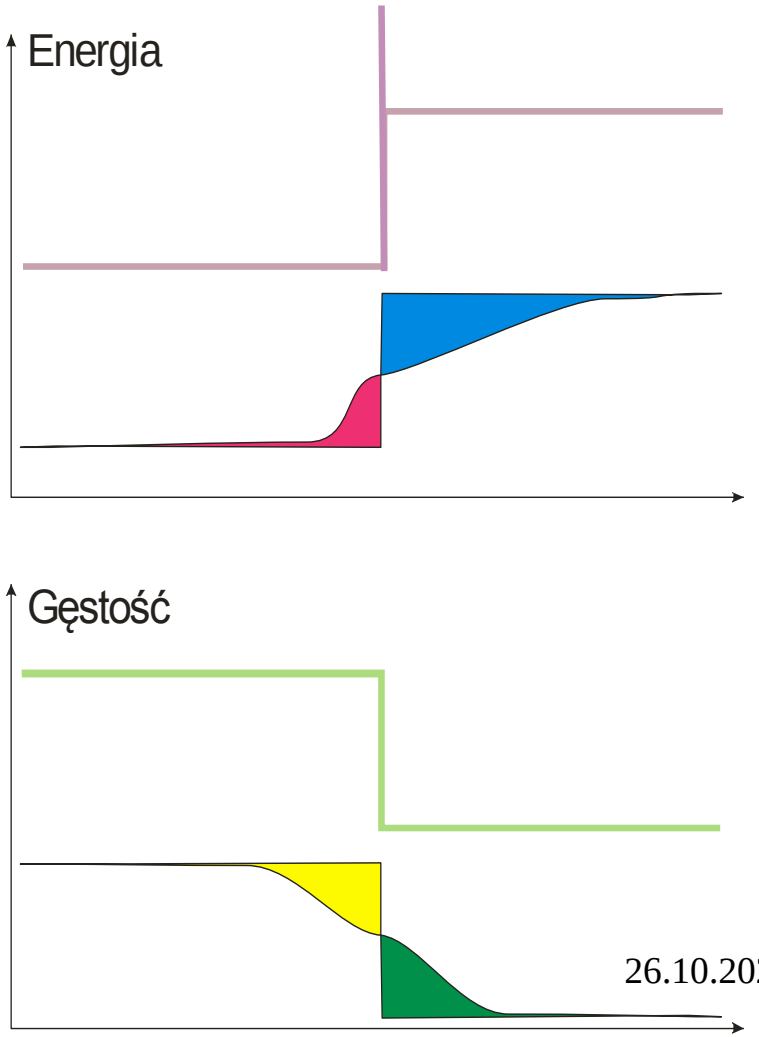




- **Large size crystals (above 20 nm in size) – crystal body can eb divided into interior and surface layer**
- **Interior – is uniform**
- **Surface layer – energy, density are changed, different from uniform properties**
- **Gibbs description – uniform bulk & additional surface contribution**

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**

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

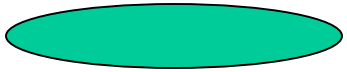
V_α, V_β **- phase volume**

A **– interface area**

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

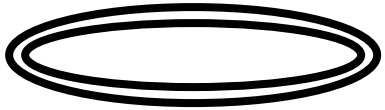
Surface tension and surface free energy density (liquids)

- **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 ($A \longrightarrow A + \delta A$)

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

$$\Delta W = \oint_L \sigma\ \delta x\, dr = \sigma \delta A \qquad \Delta F = \gamma\, \delta A$$

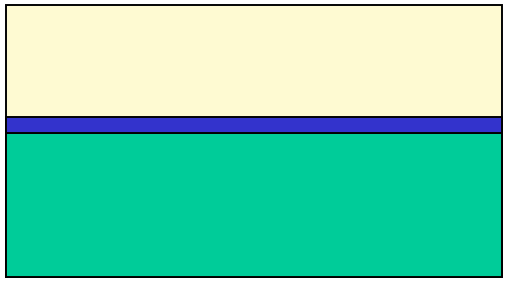
$$\Delta W = \Delta F \quad \Longrightarrow \quad \sigma = \gamma$$

Surface wetting

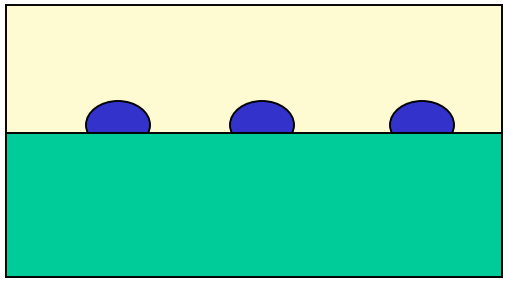
- **Consider three uniform, isotropic systems: gas(1), solid(2) and liquid(3)**

- **Interface energy is described by three parameters: γ_{12}, γ_{13}, γ_{23}.**

(A)



(B)

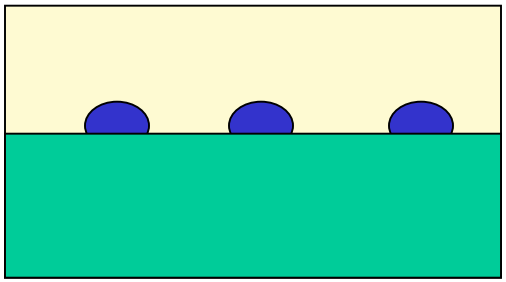


- **The condition for full wetting of the surface by liquid is**

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

Partial surface wetting –wetting angle

- **Partial surface (A) wetting occurs when**

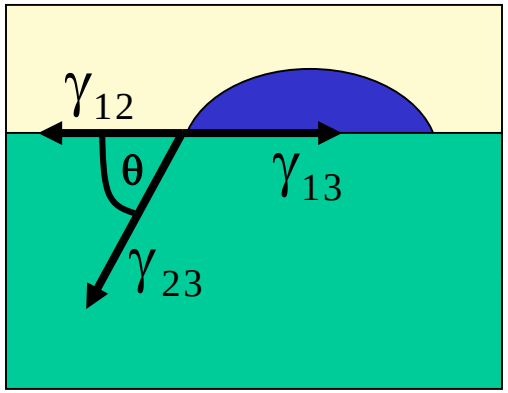


$$\gamma_{13} < \gamma_{12} + \gamma_{23}$$

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

- **Wetting angle is defined as**

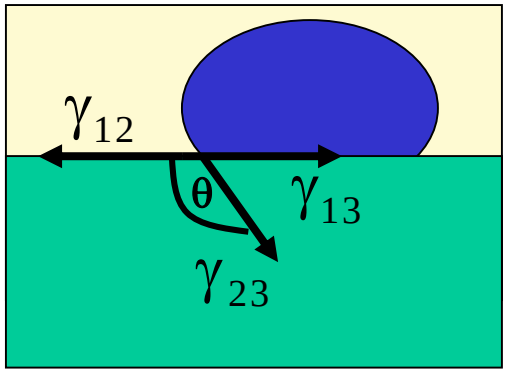
$$\gamma_{13} = \gamma_{12} + \gamma_{23}cos(\theta)$$



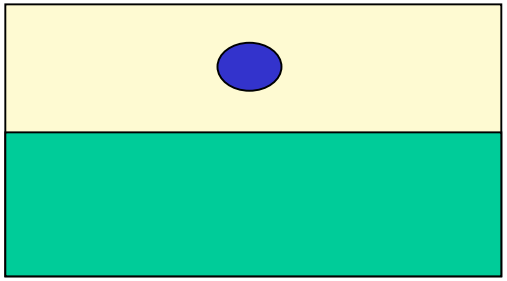
Absence of wetting

- **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**

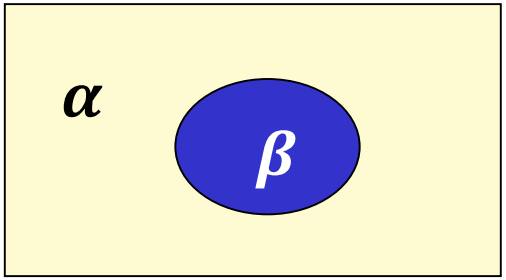
$$\delta F \geq 0 \qquad \delta F = -p_\alpha \delta V_\alpha - p_\beta \delta V_\beta + \gamma \delta A + \mu_\alpha \delta N_\alpha + \mu_\beta \delta N_\beta$$

The constraints

$$N_\alpha + N_\beta = const \qquad \delta N_\alpha = -\delta N_\beta$$

$$V_\alpha + V_\beta = const \qquad \delta V_\alpha = -\delta V_\beta$$

$$T = const \qquad \delta T = 0$$

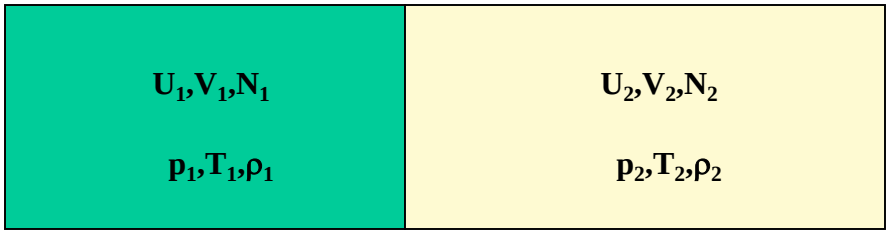


- **Stability equations (equilibrium conditions)**

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

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**

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

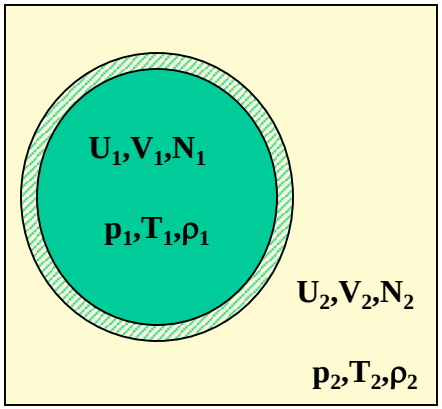
The equilibrium conditions do not depend on the size – these conditions are tabulated in phase diagrams

$$p_\alpha = p_\beta = p \qquad T_\alpha = T_\beta = T$$

Curved surface – isotropic case

- **Equilibrium conditions**

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



- **Isotropic case - sphere**

$$V = \frac{4\pi R^3}{3} \qquad A = 4\pi R^2 \qquad \frac{\delta A}{\delta V} = \frac{2}{R} = \frac{1}{\kappa_\alpha} + \frac{1}{\kappa_\beta}$$

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

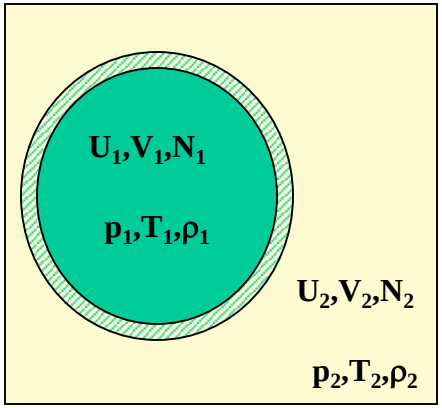
The equilibrium conditions do depend on the size

$$p_\alpha = p_\beta + \frac{2\gamma}{R} \qquad T_\alpha = T_\beta \neq T_{PT}$$

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**

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

- **Curved surface**

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

- **Linear expansion**

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

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

Gibbs – Thompson effect – curvature caused equilibrium temperature change

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

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

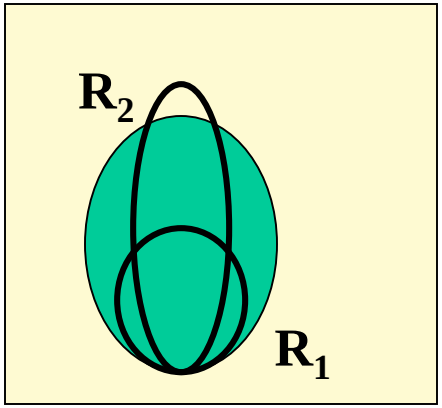
L – Latent heat of phase transition for volume unit

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**

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

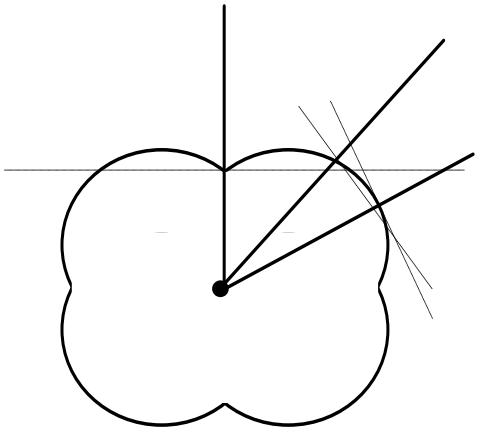
Gibbs – Thompson effect – curvature caused equilibrium temperature change

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

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

Anisotropic surfaces – the surfaces of real crystals

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

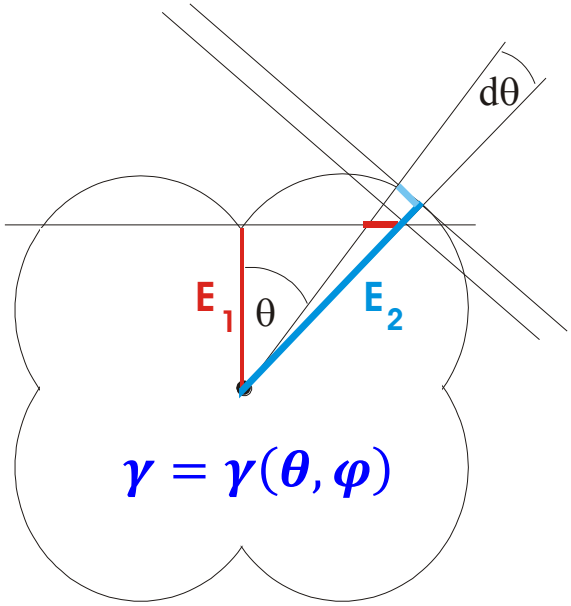


$$\gamma = \gamma(\theta, \varphi)$$

γ- plot and Wulf construction

Wulf 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 .



Wulf construction

- **The angular diagram of this dependence in given as γ - plot.**
- **Calculate the energy ΔE contained with the minimal angle interval dθ**

- **Case 1**

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

- **Case 1**

$$\Delta E_2 = E_2 dl_\perp$$

$$\Delta E_2 > \Delta E_1$$

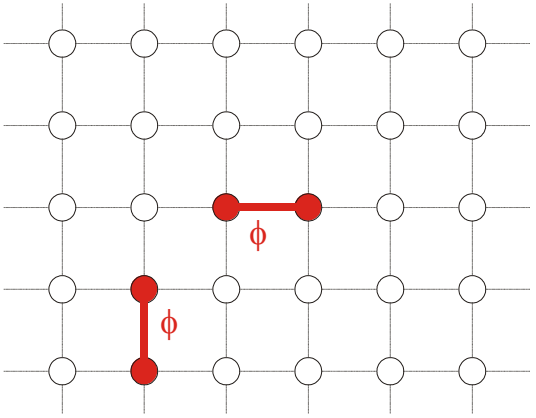
$$\Delta E_2 < \Delta E_1$$

- **Case 1**
- **Case 2**

Wulf construction

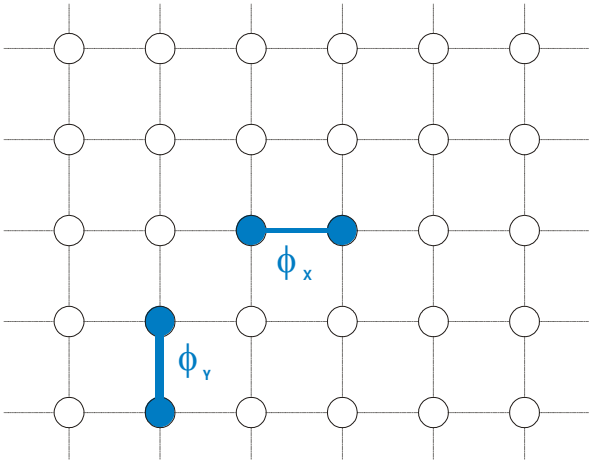
Kossel crystal – the simplest case

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

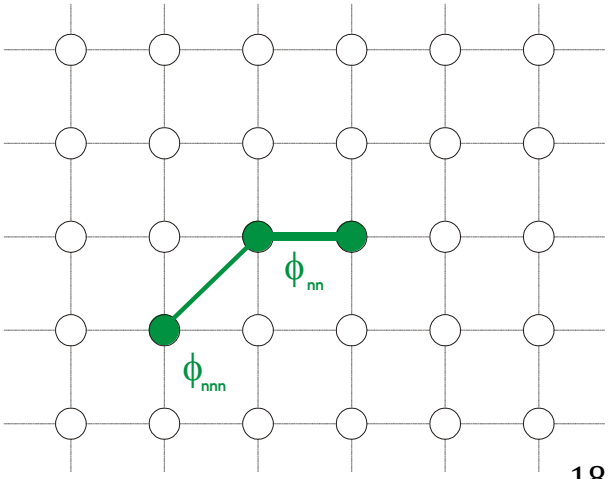


- **Extensions**

- **Anisotropic interactions**



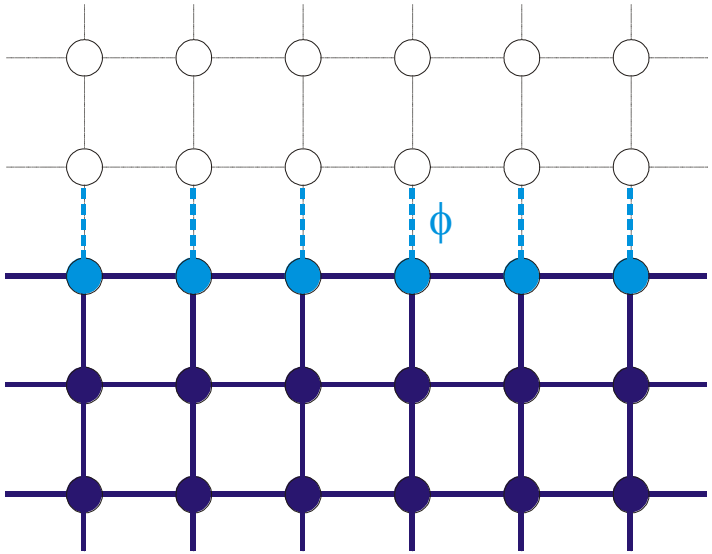
- **Next nearest neighbors (nnn) interaction**



Kossel crystal surfaces

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

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



- **Bulk crystal energy**

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

- **Surface energy**

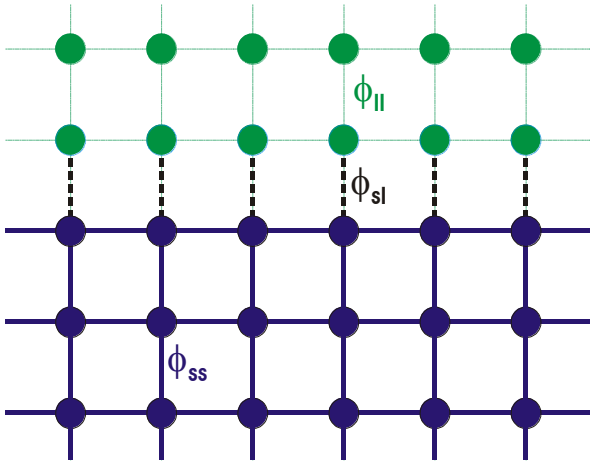
$$E_{sur} = N_{sur}\phi$$

- **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- $\phi_{cr,}$ in liquid - ϕ_{ll} 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 , in crystal-liquid interface**

- **Crystal energy**

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

- **Liquid energy**

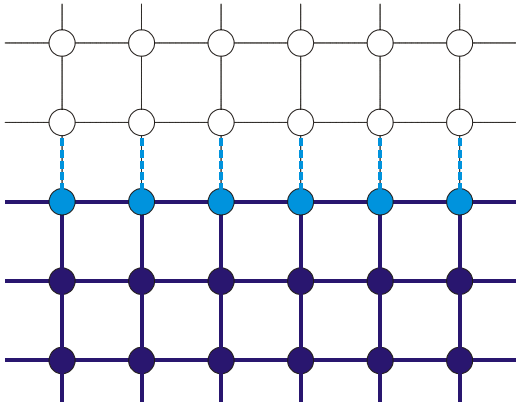
$$E_{cr} = -N_{l}^{bond}\phi_{cr} = -\frac{N_{l}Z\phi_{ll}}{2}$$

- **Crystal-liquid interface energy**

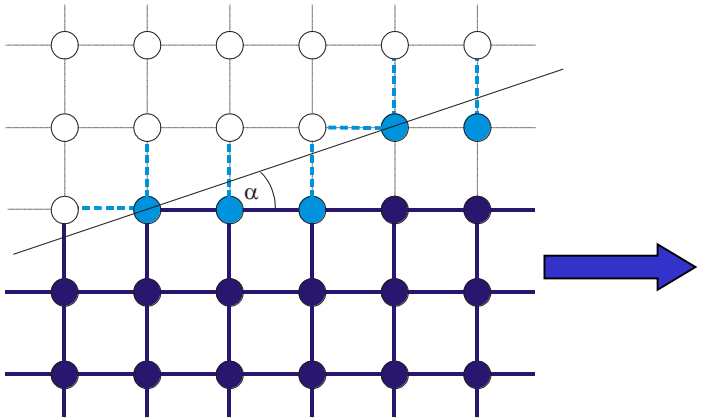
$$E_{cr-l} = -N_{cr-l}^{bond}\left[\phi_{cr-l} - \frac{\phi_{cr}+\phi_{ll}}{2}\right]$$

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

- **Crystallographic flat surface (01)**



- **Vicinal surface**

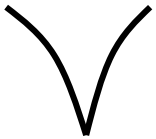


- **n - step width**
- **α - step angle**

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

- **Vicinal surface energy**

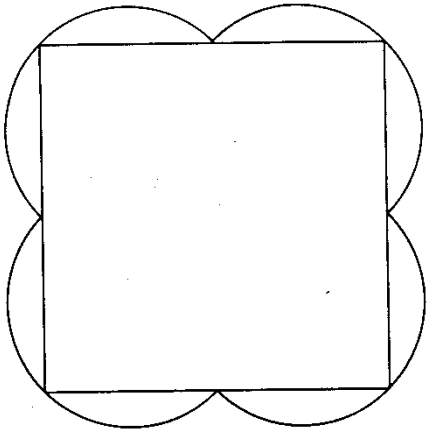
$$\gamma(\alpha) = \frac{1+n}{n\,|cos(\alpha)|} = \gamma(|cos(\alpha)| + |sin(\alpha)|)$$

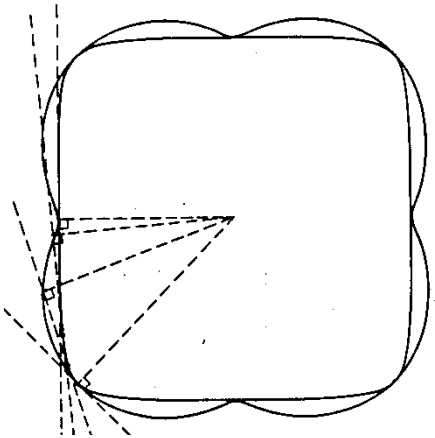


γ - plot – cusp for low Miller index surfaces

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

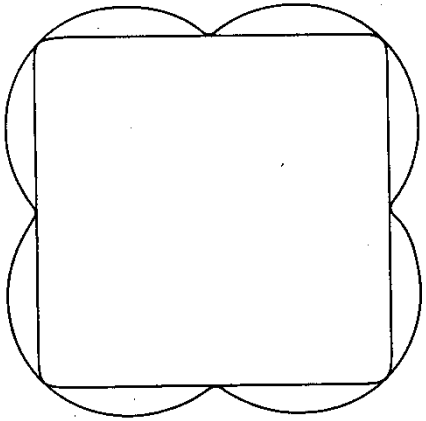
kT/φ = 0

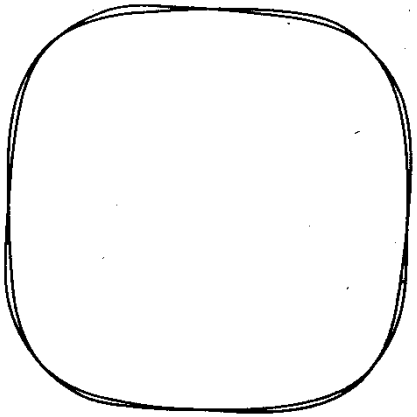




kT/φ = 0.3

kT/φ = 0.1

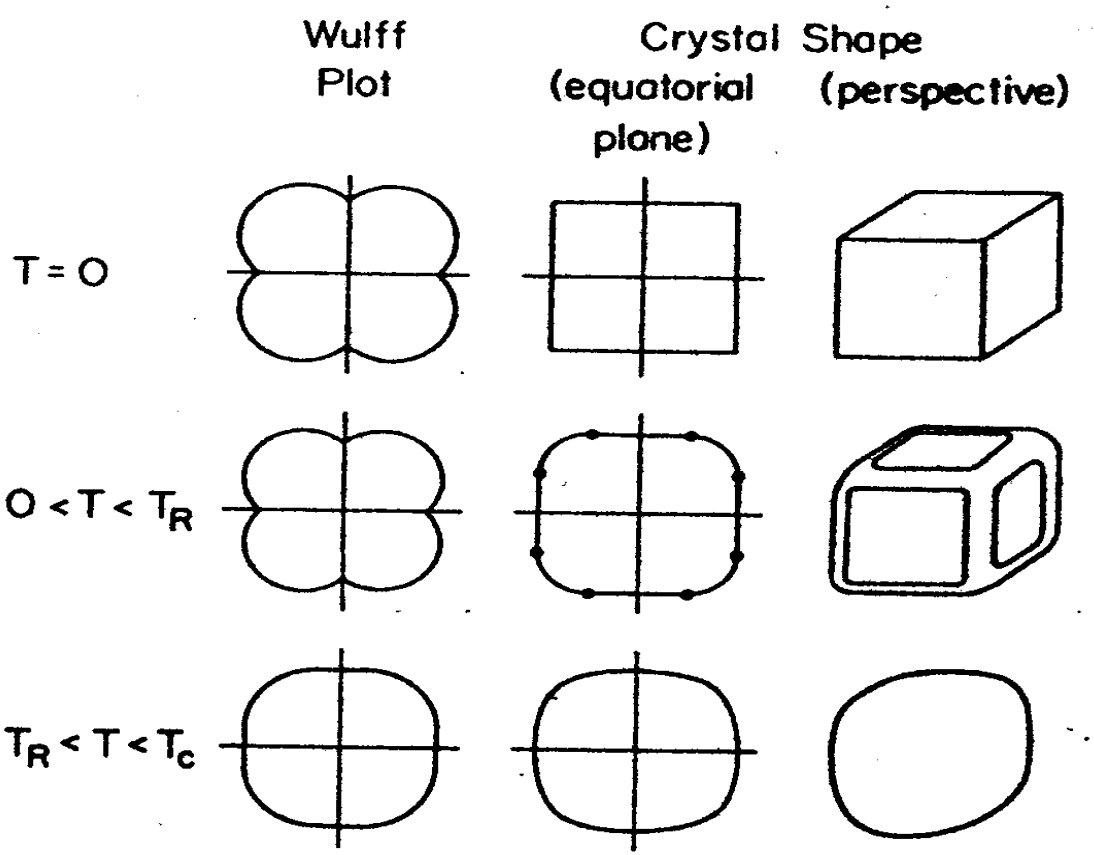




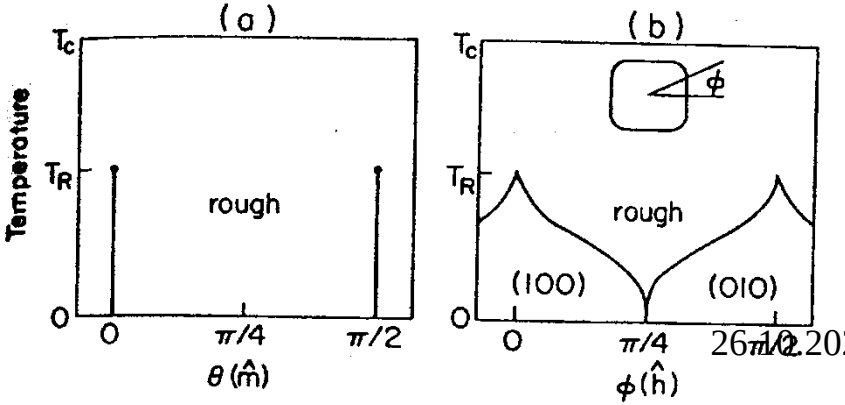
kT/φ = 0.6

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

3-d Kossel crystal – equilibrium shapes



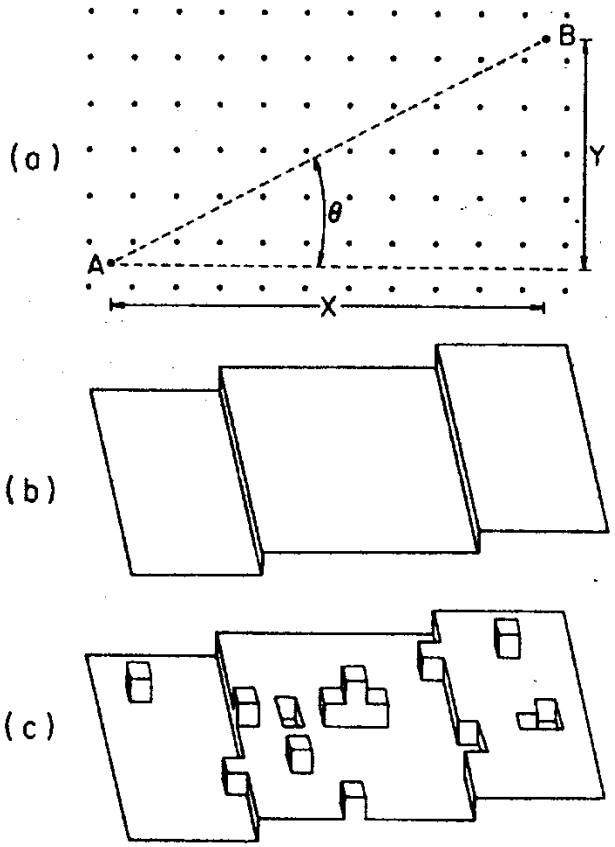
Phase diagram

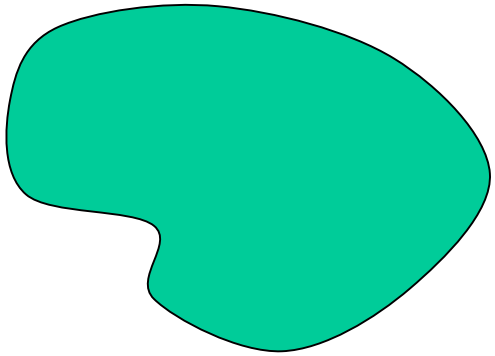


Dark dots – transition from flat to vicinal surface

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

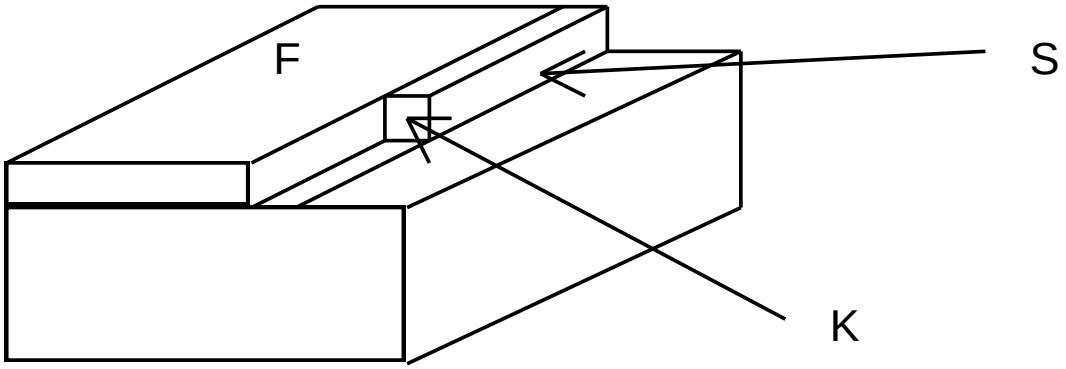
2-d oraz 3-d surfaces





- **step is one-dimensional object (line)**

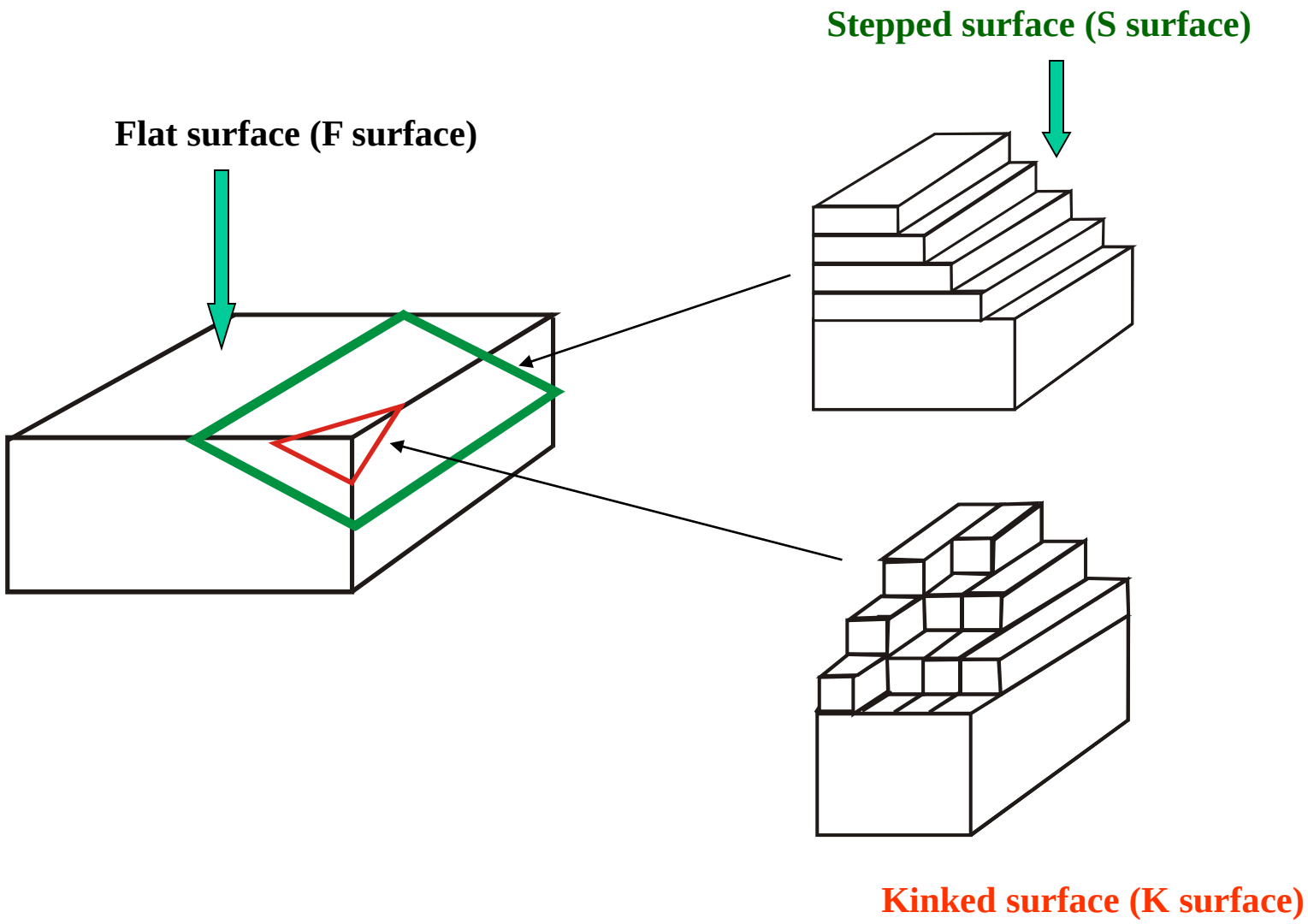
Atomic structure of three-dimensional surfaces



- **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



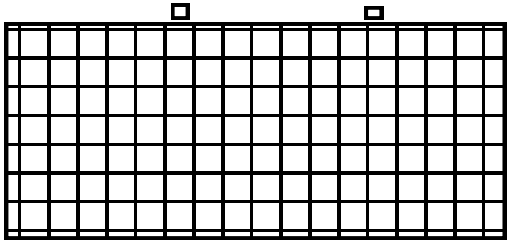
Flat and rough surfaces

- **Surface roughness R is defined as:**

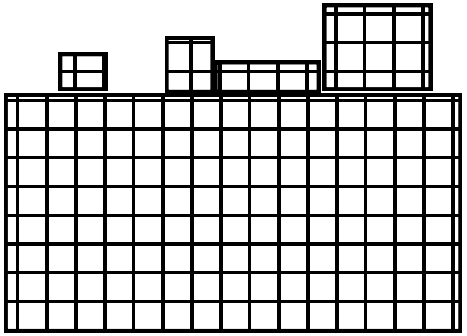
$$R \equiv \frac{N - N_o}{N_o}$$

N – number of broken bonds

N_o – minimal number of broken bonds



gladka



szorstka

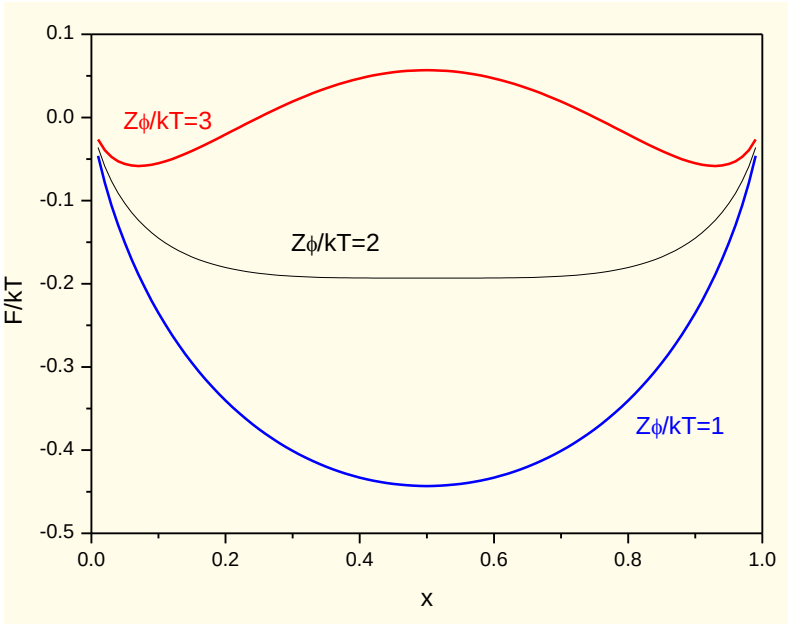
Mathematical roughness is different from Atomic Force Microscope roughness.

Surface phase transition rough-flat

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

Surface free energy

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



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

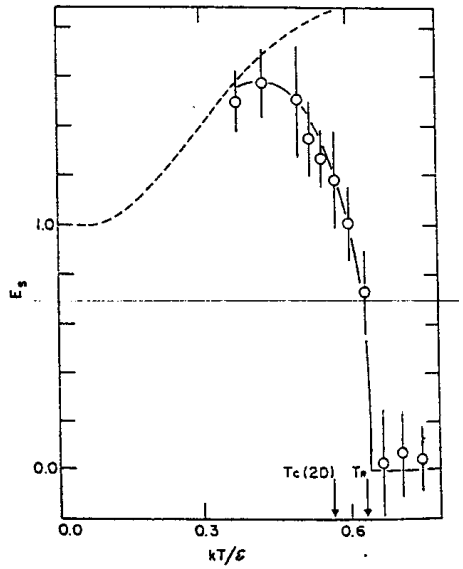
Phase transition at $Z\phi$=2kT

Surface phase transition rough-flat: numerical simulations

- **Stepped surface with quasi-periodic boundary conditions**
- **Solid-on-Solid (SOS) approximation**

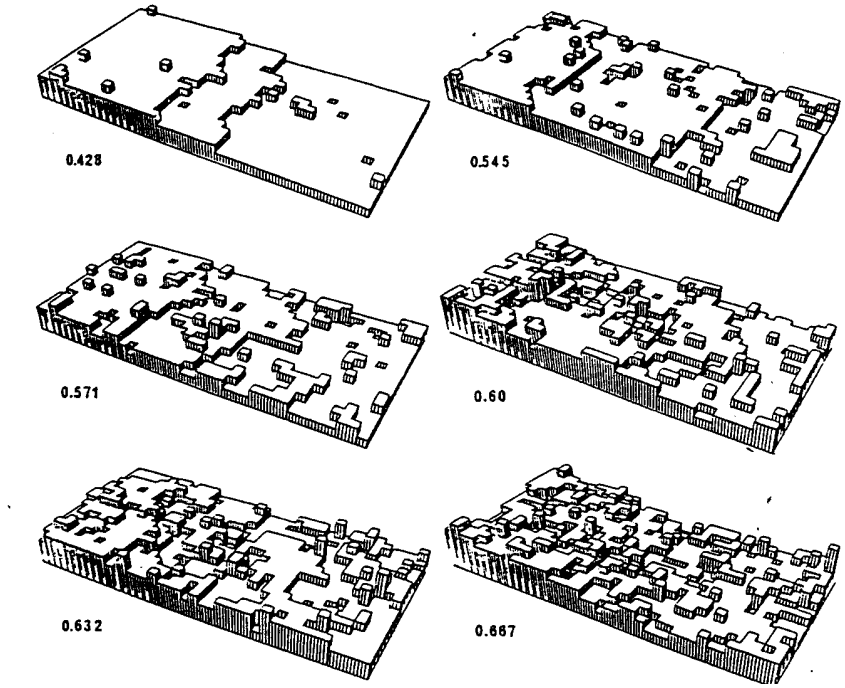
$$\alpha = \frac{kT}{\phi} = \frac{kT}{\varepsilon}$$

- **Stepped and step-free surfaces energy difference**



Phase transition at kT = 0.61ϕ

- **Microscopic configurations at different temperatures**



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**

$$T_R = 0$$

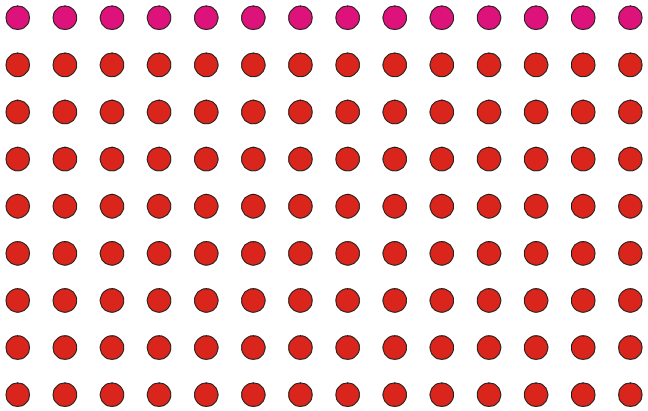
Surfaces of real crystals – clean (no foreign atoms)

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

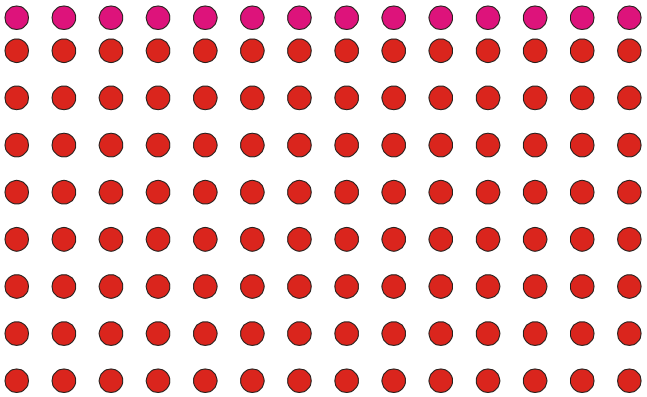
Surface relaxation

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

Termination surface

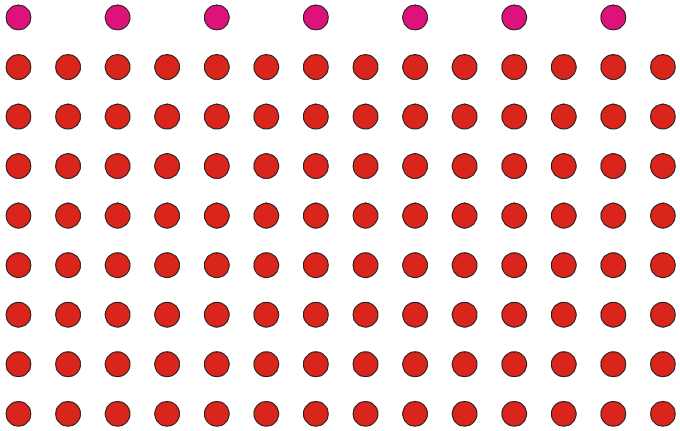


Relaxed surface

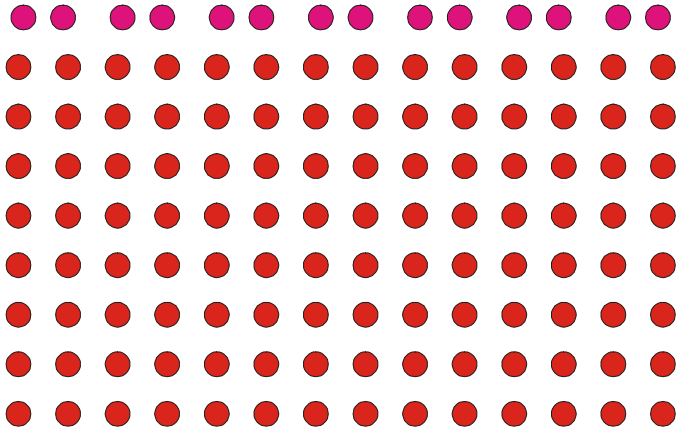


Reconstructed surfaces - examples

2x1 – missing row reconstruction

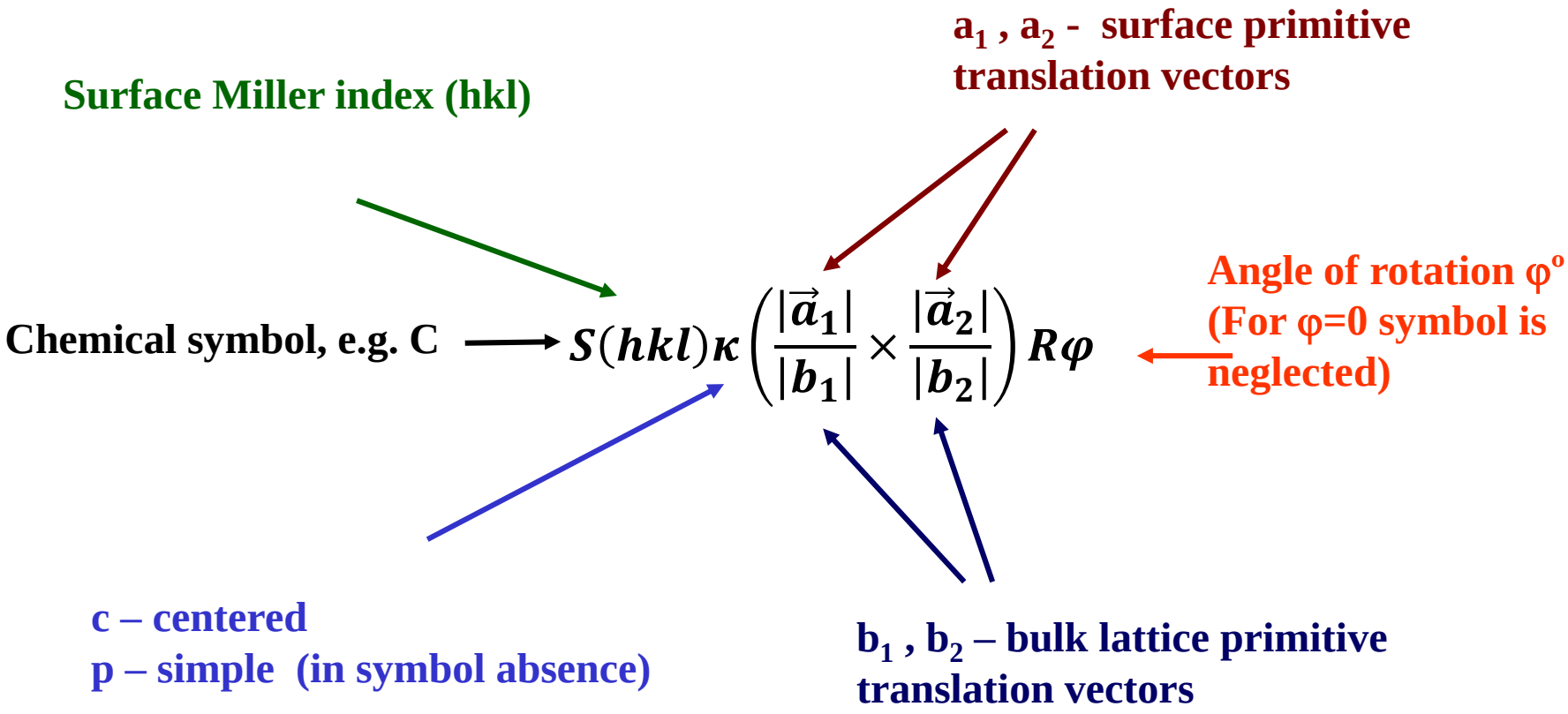


2x1 – pairing reconstruction



Wood notation – description of reconstructed surfaces

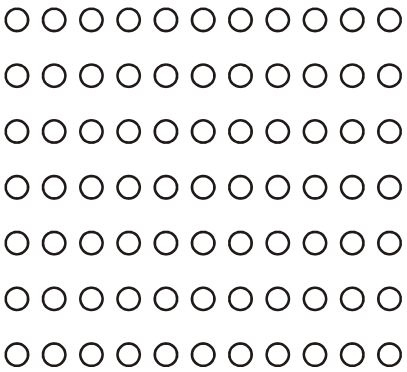
Wood notation (Wood Symbol)



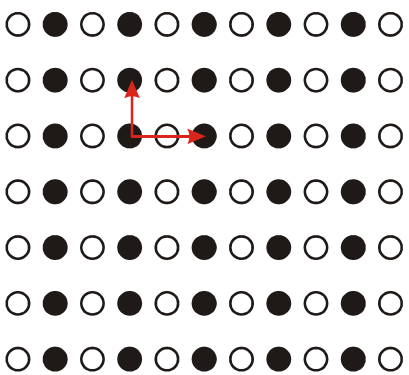
Wood notation is not unique (the same structure may be denoted by different symbols

Wood symbols - examples

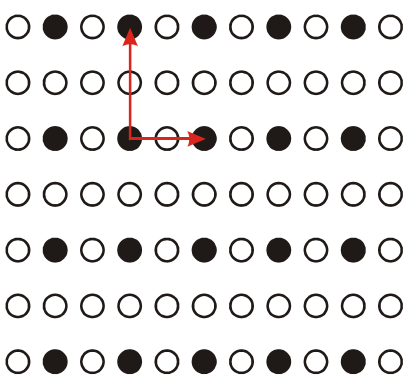
$(1x1)$



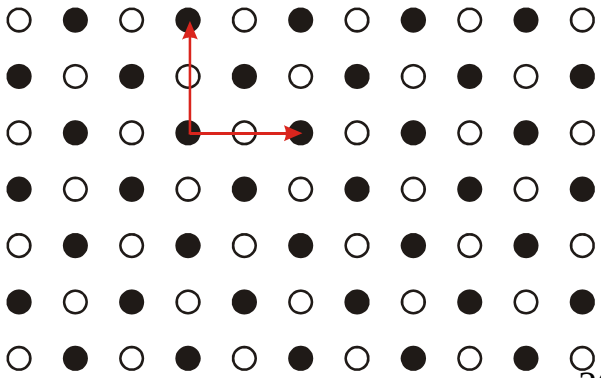
$(2x1)$



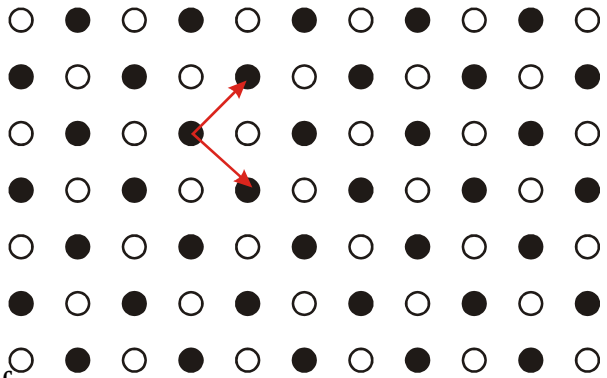
$(2x2)$



$(2x2)$



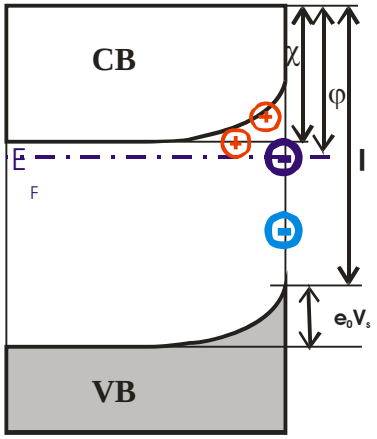
$\left(\sqrt{2}x\sqrt{2}\right)$



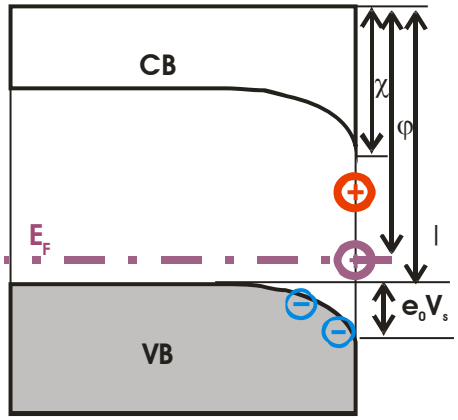
Semiconductor surfaces – reconstruction, charges and fields

- **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

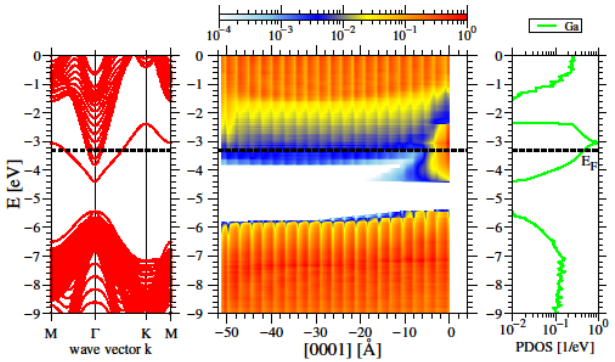
ϕ – work function

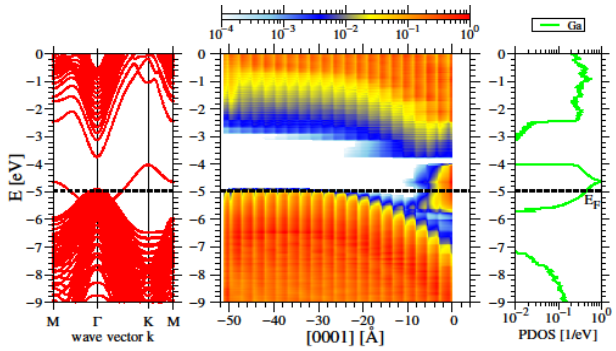
χ – electron affinity

In metal all values are identical

Electronic properties of semiconductor surfaces – GaN(0001) surface

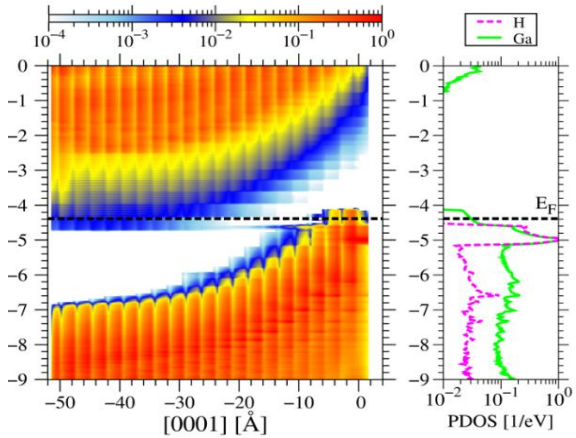
Clean surface



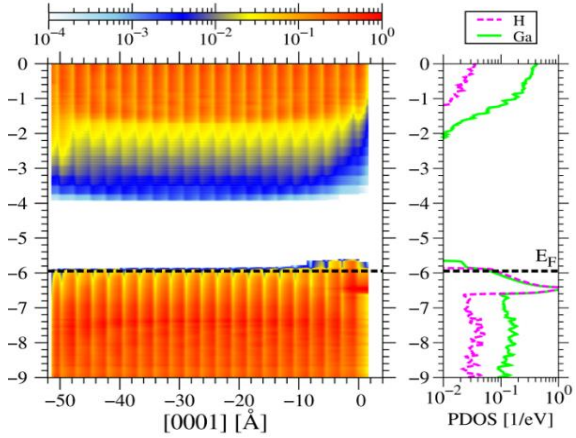


P. Kempisty et al.
AIP Adv. 4 (2014) 117109-1-24.

1 ML coverage

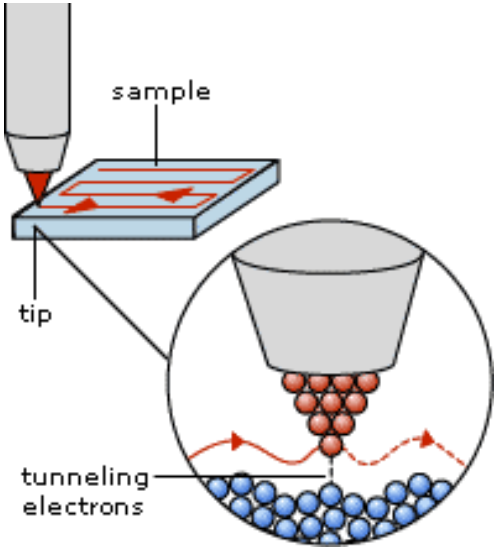


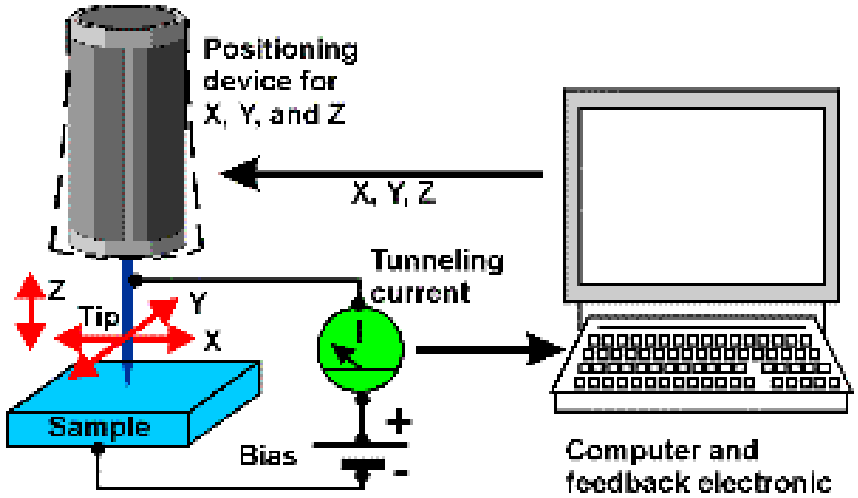
n type



p type

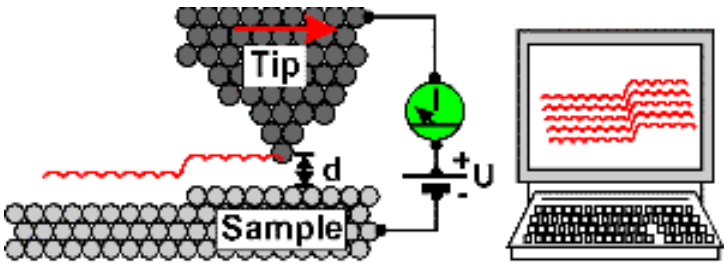
Scanning Tunneling Microscope – STM

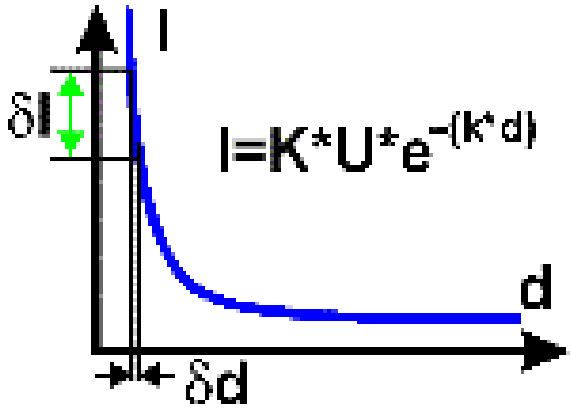




Nobel Laureates:
Heinrich Rohrer and Gerd Binnig 1986

STM work mode





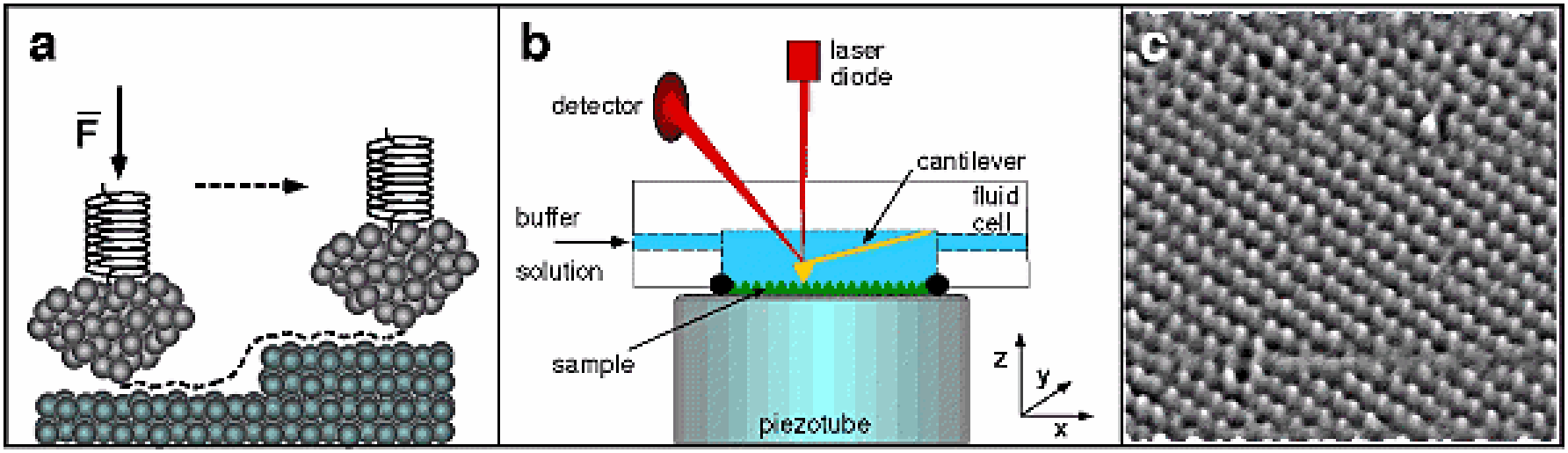
The tip interacts with the surface

Tunneling current vs distance

K and k – constants

STM can achieve atomic resolution!

AFM – measurement technique



AFM tip – surface interaction

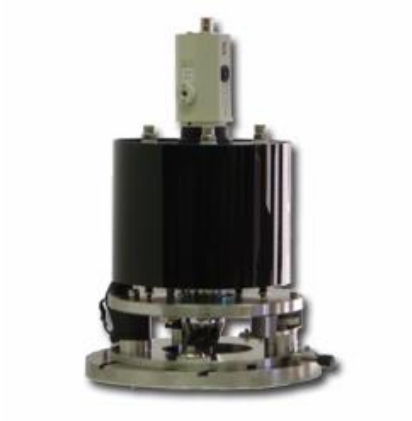
Laser detection of tip motion

Atomic resolution – mica surface (d = 5.4 Å).

AFM – Atomic Force Microscope

Atomic Force Microscope - NovaScan

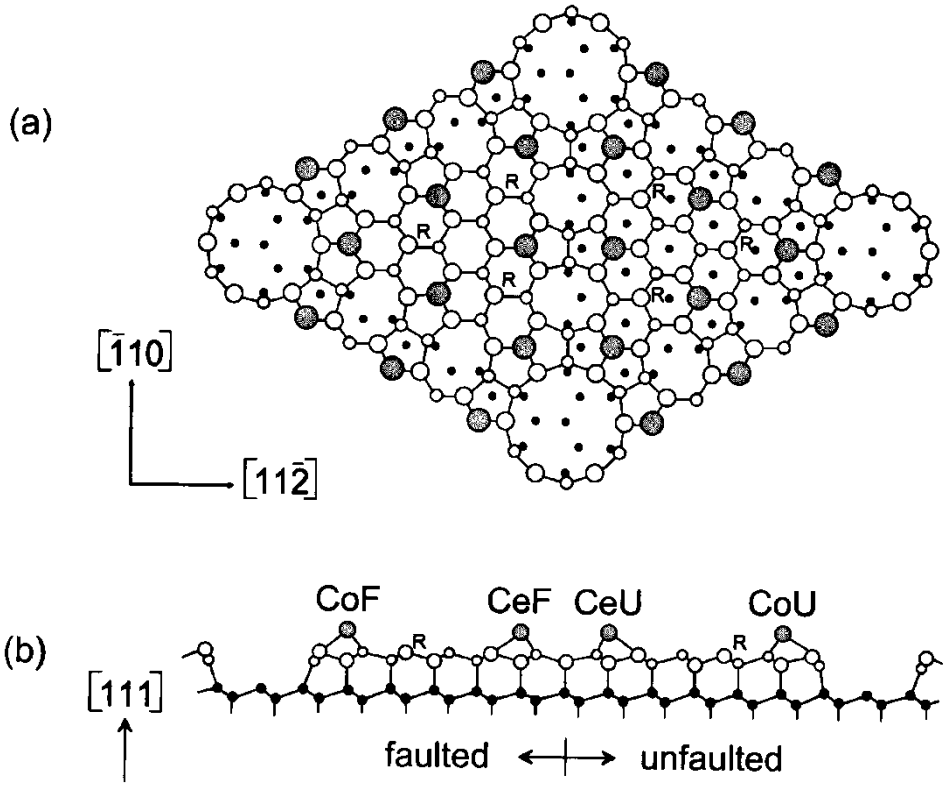
ESPM II



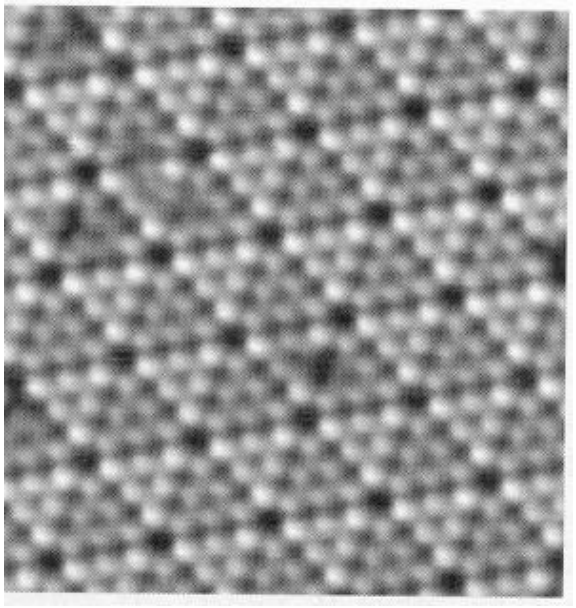
OSPM II

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

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

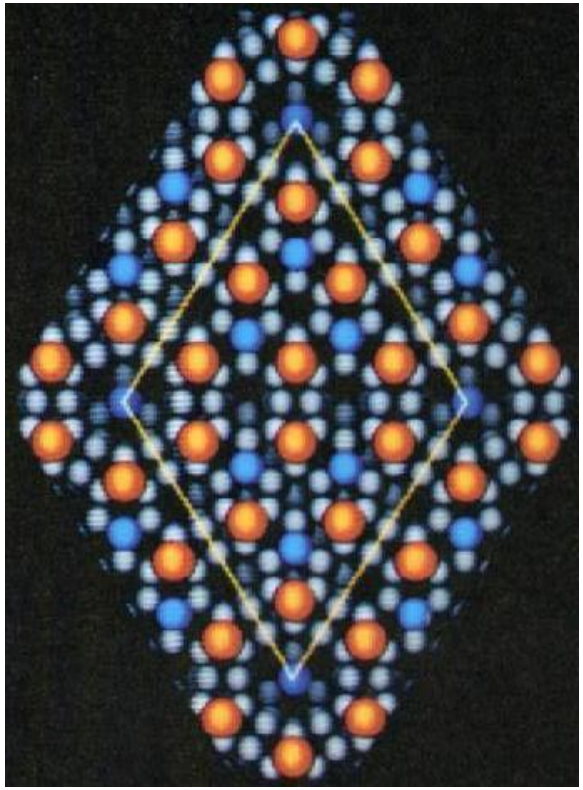


STM picture

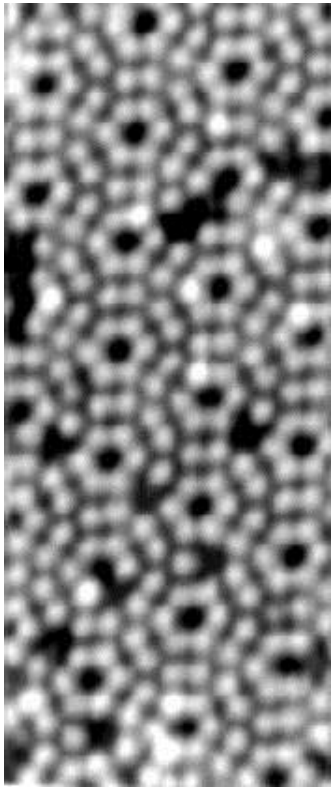


K. Takanayagi et al. Surf. Sci. 164 (1985) 367

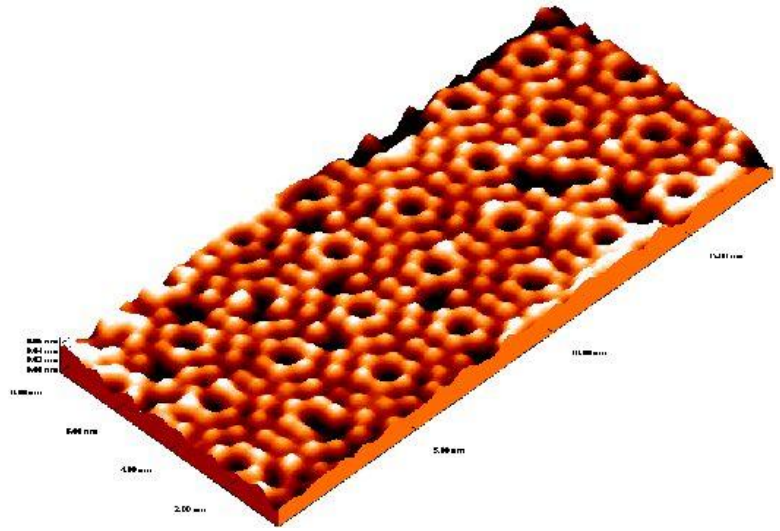
Si(111) (7x7) reconstruction – STM picture



Model -
R.M. Tromp (IBM)



STM picture



3-d model

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- W. Schommers, P. Von Blanckenhagen***, Structure and Dynamics of Surfaces II,*** Ch. 3.2, Springer 1987.
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