For a Kossel crystal (simple cubic, only nearest neighbour interaction) we obtain

$$\gamma(\theta) = \frac{\Phi}{2a^2}(\sin\theta + \cos\theta) \qquad \begin{aligned}\Phi &= \text{bond strength}\\ a^2 &= \text{unit cell area}\end{aligned}$$

In general, this expression is more complicated, if one takes into account more than nearest neighbour interactions and step-step interactions.

As $\sin\theta + \cos\theta > 0 \Rightarrow$ a vicinal surface has $\gamma(\theta) > \gamma(0)$

If we move in the $-\theta$ direction we have

$$\gamma(-\theta) = \frac{\Phi}{2a^2}(\sin(-\theta) + \cos\theta)$$

$$= \frac{\Phi}{2a^2}(-\sin\theta + \cos\theta)$$

Therefore $\gamma(\theta)$ has singularities at $\theta = 0, \pm\frac{\pi}{2}, \pm\pi$. $\gamma(\theta)$ is plotted in Fig. 4.8. $\gamma(\theta)$ is usually plotted as a polar diagram ($\gamma$-plot).

Once the $\gamma$-plot is known, it is possible to construct the equilibrium shape of a crystal using the <u>Wulf-theorem</u>. The Wulff theorem has a non-trivial proof, which may be found in the books of Landau/Lifshitz or Markov.

It states:

<u>The interior envelope of the perpendicular planes through the tip of the radius vector in each point of the $\gamma$-plot is the equilibrium shape.</u>

As visible in Fig. 4.8 the equilibrium shape of a Kossel crystal is a simple cube. A more complicated $\gamma$-plot as shown in Fig. 4.9 gives rise to additional facets.

Equilibrium shapes of metal surfaces can only be created experimentally at high temperatures close to the melting point. At lower temperatures transport is too slow to allow one realization of equilibrium shapes (imagine what the world would look like, if this would not be the

case). The realization of the Fm equilibrium shape is shown in Fig. 10
- This shape shows only small facets and has mostly rounded parts.
The reason is as follows: The step energy $\gamma_L$ is as the surface free energy a free energy $\gamma_e = E_e - TS_e$. Steps posess significant entropy as they meander on the surface between two fixed points

Therefore at high temperatures for steps an certain singular surfaces $\gamma_L = 0$, i.e steps form spontaneously without energy cost
Consequently the singularity in $\gamma(\theta)$ for the singular surface disappears and a rounded (or rough) part appears. The temperature at
- which $\gamma_L$ becomes 0 is called the temperature of the roughening transition. Each crystal orientation has its own roughening temperature.
The equilibrium shape is also defined by the condition that the chemical potential on all faces is identical (otherwise there would be transport). This condition is

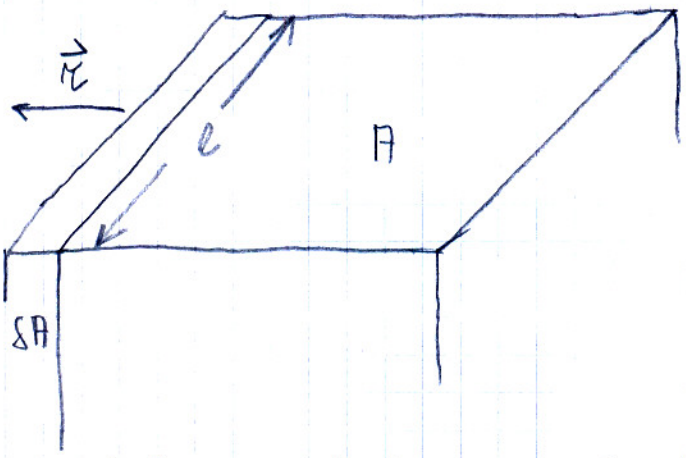
$$\boxed{\Delta\mu = \kappa\, \tilde{\gamma} \cdot v_s}$$ Wulffs-Herring relation

For a rough part of a crystal this equation is easy to understand.
- In the areas around the singular points in the $\gamma$-plot, where the facets are $\tilde{\gamma} = \gamma + \frac{\partial^2\gamma}{\partial\theta^2}$ is negativ. This would imply negativ curvatures which are not possible in an equilibrium shape. Therefore these areas are flat.
In complete analogy to the 3D equilibrium shapes, we may define 2D equilibrium shapes by

$$\int_L \gamma_L(\theta)\, dL \stackrel{!}{=} \min$$

with $\Delta\mu = \kappa\, \tilde{\gamma}_L\, v_s$ . The example is shown in Fig. 11.

Next we try to understand why $\gamma$ is not a force per unit length for a solid. Consider the following situation:




A solid which we cut along a length $\ell$ in a plane normal to the surface. If you remove material to the left we need forces $\vec{f}_i$ to keep the atoms in their positions. The surface stress is then defined as the sum of all those forces per length $\ell$ minus the sum of all forces $\vec{f}_i^{\,0}$ per length $\ell$, which are necessary to keep the atoms in position in the <u>absence</u> of a surface

$$\vec{\kappa} = \frac{1}{\ell} \sum_i \vec{f}_i - \vec{f}_i^{\,0}$$

The difference $\vec{f}_i - \vec{f}_i^{\,0}$ is only $\neq 0$ for atoms in the topmost layers. In the following we calculate for simplicity for a scalar. The work to strain the surface is then

$$\delta W = \kappa \cdot \delta A = \delta(\gamma \cdot A) = \gamma \cdot \delta A + A \cdot \delta\gamma$$

$\gamma \cdot \delta A$: larger surface area; $A \cdot \delta\gamma$: increased $\gamma$ !!

Note that in $\delta W$ we did not include the associated work to elastically strain the solid bulk.

We have

$$\kappa = \gamma + \frac{A}{\delta A}\delta\gamma = \gamma + \frac{\partial\gamma}{\partial\varepsilon}$$

$$\boxed{\mathcal{K} = \gamma + \frac{\partial \gamma}{\partial \varepsilon}}$$ Shuttle worth relation

As the strain derivative $\frac{\partial \gamma}{\partial \varepsilon} \neq 0$ for a solid $\gamma$ is not a surface tension.

In contrast, a liquid does not need forces for deformation and thus $\frac{\partial \gamma}{\partial \varepsilon} = 0$ //

# 5. Clusters

## 5.1. Introduction and Structure of Clusters

Cluster means „a group of similar things" according to the Concise Oxford Dictionary. Here we consider as cluster an aggregation of atoms or molecules with a number N of particles in the range of 3 to $10^5$. The physics of clusters is a field studying the unique properties of objects which may be neither considered as molecules nor as solids. The first technological application is the use of metal clusters to colour glass. Metal atoms in glass precipate and form clusters, with a size dependent on the heat treatment of the glass. Variation of Ag-cluster size from 0.1 – 1.3 μm diameter changes the glas colour from yellow, red, violett, blue to graygreen. Metal additives have been used to colour in this way the windows of churches. The colour is due to the size dependent plasmon resonance. The light electric field $\vec{E}(t)$ induces in a nanoparticle a time dependent polarization

$$\vec{p}(t) = \alpha \, \varepsilon_0 \, \varepsilon_m \, \vec{E}(t)$$

where $\varepsilon_m$ = dielectric constant of the embedding medium and
$\alpha$ = complex polarizability.

$\alpha$ itself is size dependent and depends on the dielectric function of the nanoparticle, which in turn determines absorption, scattering and extinction. See Fig. 5.1

The ratio of surface atoms to the total number of atoms is very large for clusters. Up to N = 12 all atoms are surface clusters (see Fig. 5.2)
Let R be the cluster radius, then

$$V = \frac{4}{3}\pi R^3 = N \cdot \frac{4}{3}\pi r^3 \quad \Rightarrow \quad N = \left(\frac{R}{r}\right)^3 \qquad (*)$$

Here r is not precisely the nn-distance, but a little longer, as (*) assumes 100% packing ratio. The number of surface atoms $N_s$

is determined by

$$S = 4\pi R^2 = N_S \cdot \frac{1}{\gamma} 4\pi r^2 \quad \Rightarrow \quad N_S = \gamma \cdot \frac{R^2}{r^2}$$

The factor $\frac{1}{\gamma}$ takes into account that only a fraction $\frac{1}{\gamma}$ of an atom surface is located at a cluster surface. We have

$$\frac{N_S}{N} = \frac{\gamma \frac{R^2}{r^2}}{\frac{R^3}{r^3}} = \gamma N^{-\frac{1}{3}}$$

For a typical value $\gamma = 4$ Fig. 2 displays the fraction of surface atoms The large surface to bulk atom ratio for clusters makes immediately understandable, why noble metal catalysts are dispersed into small clusters in heterogeneous catalysis.

We distinguish

- small clusters $3 \leq N \leq 12$. All atoms are surface atoms. Concepts of molecular physics are applicable at low T
- medium clusters $13 \leq N \leq 100$. Many isomers. Strong change of properties with N. Molecular concepts unusable.
- large clusters $100 \leq N \leq 1000$. Gradual transition to bulk properties
- micro crystals $N > 1000$.

The structure of clusters is not restricted by the requirement of translational symmetry as for bulk solids.

For metals the rule of Friedel is often valid:

The cluster structure with the largest number of nearest neighbour (nn) bonds has the largest total binding energy and is thus the stable one.

Often cluster take the shape of platonic bodies. Two examples of cluster structure evolution are shown in Figs. 5.3 and 5.4.

In Fig. 5.3 the structure of noble gas clusters are displayed. The cluster with size 7 displays 5-fold symmetry (not possible in bulk),

for N = 13 one obtains the famous ikosaeder structure, a central atom surrounded by a shell of atoms. One may consider this shell as composed of two caps of pentamers, with a central atom above or below. Especially stable ikosaeder structures are obtained for closed shell ikosaeders with magic numbers 13, 55, 147, 309, 561, .. atoms. While the ikosaeder is favored for small noble gas clusters due to the higher packing density, the increased bond length for atoms within a shell eventually causes a transition to the bulk structure with increasing n. The example in Fig 5.4 for Mg exemplifies the complex evolution of crystal structure for another case. It displays already the general way of plotting cluster properties X. X is represented as a function of $N^{-\frac{1}{3}}$, i.e the fraction of surface atoms or the inverse cluster radius.

## 5.2 Preparation of clusters

If we consider for the moment only clusters in a homogenous environment, we may consider two principal methods.

- the chemical method: clusters may be precipated from solution as nanocrystals or colloidal particles, often with a surrounding shell.

By carefully tuning the route of synthesis, astonishingly sharp size distributions may be realized, but they are never atomically sharp. Also the interaction of a cluster with the surrounding liquid can not be neglected. However, the fabrication method in view of throughput

- physical methods: the basic idea is to condense a vapor (e.g. of metal) in a noble gas. Similar to condensation of water vapor in cold air, cluster are formed.

In a first condensation step three atoms have to meet to fulfill conservation of momentum and energy simultaneously.