We may generalize the concept of the Laplace-pressure to arbitrarily shaped surfaces with curvature $\kappa = \frac{1}{r_1} + \frac{1}{r_2}$ where r_1 and r_2 are the two independent radii of curvature. We then have $\Delta p = \gamma \cdot \kappa$ where the large pressure is always found on the convex side.

<u>Example 1</u>: If we perform sputter deposition in a Kr-plasma or if we deposit a thin film under the assistance of energetic Kr-particles, some of the noble gas atoms penetrate into the film. There they are insoluble and precipate as small gas bubbles. For a realistic surface energy of 0.2 eV/Å^2 and a bubble radius of 10 Å we obtain with $P_{out} \approx 0$

$$P_{in} \approx \frac{2\gamma}{r} = \frac{2 \cdot 0.2 \cdot 1.6 \cdot 10^{-19}\,J}{\frac{10^{-20}\,m^2}{10^{-9}\,m}} = 6.4\ GPa$$

Under such pressure noble gases may become solid even at room temperature! See Fig. 3

<u>Example 2</u>: Clusters are small groups of atoms with diameters of a few nm. Thus similar pressures are acting on the atoms inside a cluster. If we compare a typical pressure of 6.4 GPa with a typical modulus of compression $K \approx 100$ GPa we find strains of a few % for the atoms in a cluster, i.e a reduced lattice constant.

$K = -V \frac{dp}{dV}$. Assuming linearity we obtain

$$-\frac{\Delta V}{V} = -3\frac{\Delta L}{L} = \frac{P}{K} \approx \frac{6{,}4}{100} = 6{,}4\% \Rightarrow \frac{\Delta L}{L} \approx 2{,}1\%$$

In fact we observe reduced lattice constants for clusters. However our calculation is just a rough estimate and neglects atomistic details.

Next we derive a formula for the vapor pressure of a liquid or solid phase, which is subject to some additional external pressure not interacting with its vapor (pressure of a noble gas, mechanical pressure)

Through the additional external pressure dP_e the chemical potential of the liquid phase will rise $d\mu_l = v_l \cdot dP_e$ $\quad v_l$ = atomic volume

Keeping the vapor above the liquid in equilibrium will result in an increase

$$d\mu_g = d\mu_l$$

The rise in chemical potential of the vapor is due to a rise in vapor pressure of the solid $\quad d\mu_g = V_g \cdot dp \quad dp$ - rise of vapor pressure

Assuming an ideal gas we have

$$\frac{kT}{p}\, dp = V_l\, dP_e$$

Initially pressure on solid/liquid phase P_0; final pressure $P_0 + \Delta P_e$

we have a vapor pressure p which is unknown

Thus

$$kT \int_{P_0}^{p} \frac{dp'}{p'} = \int_{P_0}^{P_0+\Delta P_e} V_l\, dP_e \approx V_l \cdot \Delta P_e$$

$$\parallel$$

$$kT \cdot \ln \frac{p}{P_0} = V_l \cdot \Delta P_e \quad \Leftrightarrow$$

$$\boxed{p = P_0\, e^{\frac{V_l \cdot \Delta P_e}{kT}}}$$

This is the vapor pressure of a liquid (or solid) phase subject to an additional pressure ΔP_e.

Therefore the vapor pressure of a droplet of radius r is enhanced

$$p = P_0\, e^{\frac{V_l \cdot 2\gamma}{kT \cdot r}}$$

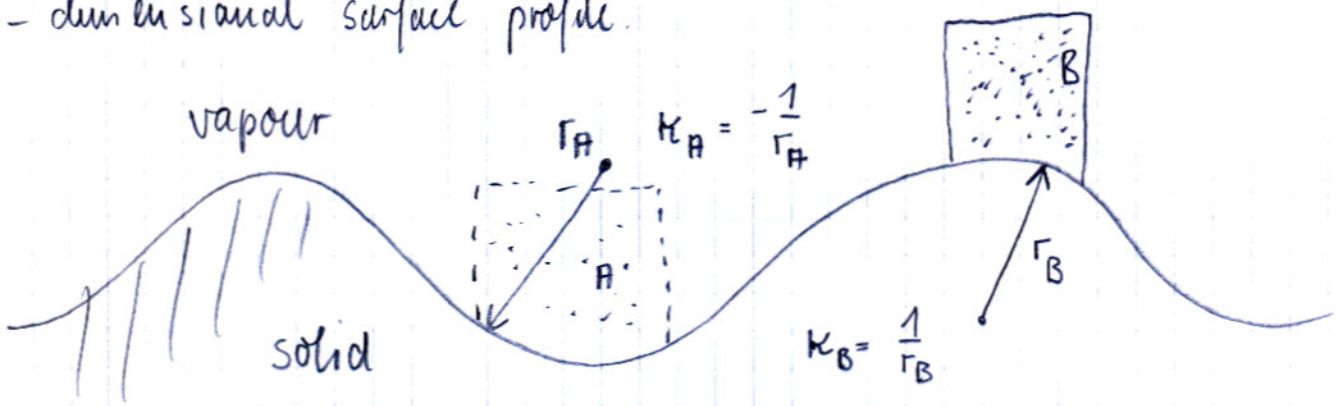
and the one of a bubble is reduced

$$p = P_0\, e^{-\frac{V_l\, 2\gamma}{kT \cdot r}}$$

Note: A CO_2 bubble is under extra pressure $\frac{2\gamma}{r}$ but the water vapor

inside the bubble is reduced by $p = p_0 \, e^{-\frac{2\gamma V_e}{kT \cdot r}}$

Next we consider consequences of surface tension and surface free energy in the liquid-like approximation. Consider for simplicity a one-dimensional surface profile.



If we would enclose the areas A and B then in the enclosure we would obtain different equilibrium vapor pressures p_A and p_B with different deviations $\Delta\mu_A$ and $\Delta\mu_B$ from the one of the flat surface. We have

$$\Delta\mu_{A,B} = k_B \cdot T \ln \frac{p_{A,B}}{p_0} = k_B \cdot T \ln \frac{1}{p_0}\left(p_0 \, e^{\frac{\kappa_{A,B}\gamma V_s}{k_B \cdot T}}\right) = \kappa_{A,B}\gamma \cdot V_s$$

$\kappa_{A,B}$ are the local curvatures and has positive sign for convex portions of the solid and negative for the concave portions of the solid. V_s is the atomic volume of the solid. Note that a factor of 2 is missing in the curvatures, as we consider a one dimensional case. The local vapors are in equilibrium with the local surface areas they are in contact with. Thus with respect to the chemical potential of the infinite bulk phase at the given p,T of μ_0 we are now able to attribute a chemical potential to every surface point

$$\mu = \mu_0 + \Delta\mu = \mu_0 + \kappa\gamma V_s$$

Since particles move from locations of higher chemical potential

to those with lower chemical potential, we are able to predict that particles move from the mountains to the valleys until the surface is flat and all points of the surface have the same chemical potential μ_0. We would have come to the same conclusion by forcing minimization of the surface energy $\gamma \cdot A$ (by minimization of the area), however, without being able to associate a <u>local</u> property to every surface point characterizing its tendency to contribute to transport.

We distinguish two scenarios:

- Transport through the vapor phase: Above the surface we have a unique vapor pressure p^*, as the local redistribution of vapor is rapid (e.g. the mean free path of the atoms is large compared to the surface features).

  Thus mounds receive less atoms from the vapor than they emitted and valleys vice versa. Quantitative analysis shows that the characteristic feature size λ of the surface undulation increases with time according to a power law $\lambda \sim t^{\frac{1}{2}}$

- Transport through surface diffusion: The gradient in the chemical potential leads to a drift velocity v_D of diffusion particles

$$v_D = - \frac{D_s}{k_B T} \frac{\partial \mu}{\partial s} \qquad s = \text{arc length}$$

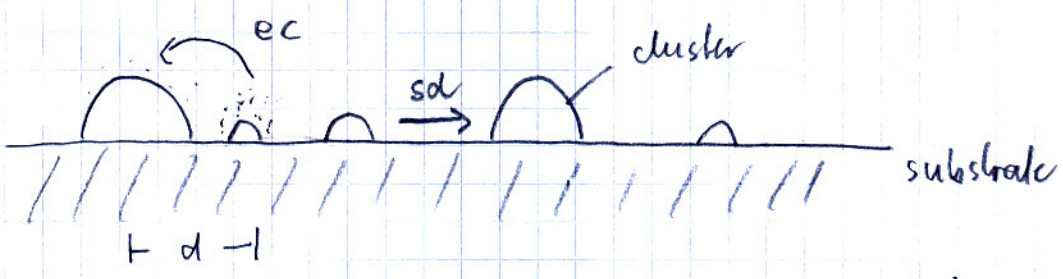
This leads to a differential equation $\frac{\partial h}{\partial t} = B h''''$ or $\left[\frac{\partial h}{\partial t} = B \nabla^4 h \right]$ with B a constant. The characteristic feature size decays with $\lambda \sim t^{\frac{1}{4}}$

A detailed derivation can be found in W.W. Mullins: Theory of Thermal Grooving, Journal of Applied Physics 28 (1957) 333

In both cases also the amplitudes decay with a power law specific for the transport mechanism.

Besides, in the theory of thermal smoothening of surfaces our considerations are relevant for a number of surface phenomena

① <u>Ostwald ripening</u>. Consider islands sitting on a surface. If sufficient temperature is available, the small islands with large radius of curvature will decay and the large ones will grow



typical island separation increases with a power law $d \sim t^{\alpha}$

mechanisms: evaporation - condensation (ec) or surface diffusion (sd)

② <u>Ostwald ripening of monolayer island</u>: The islands have an adatom vapor pressure dependent on their radius of curvature. Small ones especially in the vicinity of large ones disappear first.

Again power laws are observed $d \sim t^{\alpha}$

Compare Fig. 4 and movie

③ <u>Sintering</u>: Many industrial parts of complex shape are formed by pressing powder into the desired shape and heating (e.g. ceramics).

Upon heating diffusion sets, driving material to the locations of low chemical potential

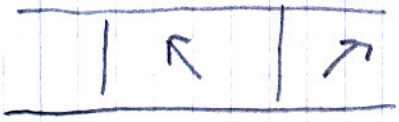
Fig. 5

④ <u>Coarsening during thin film growth or ion beam erosion</u>

Small structures formed during growth or erosion loose material to the larger ones in their vicinity. This results in an increase of the characteristic length scale. See Fig. 6

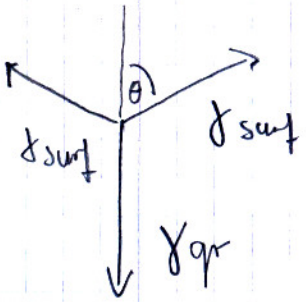
⑤ <u>Grain grooving</u>

One may generalize the concept of surface free energy to general interfaces. Consider the situation a thin film with differently oriented grains. We attribute a grain boundary energy γ_{gr} to a grain boundary



as at grain boundaries the density of atoms and thus the bonding is reduced.

Now consider the equilibrium of surface tensions at a grain boundary



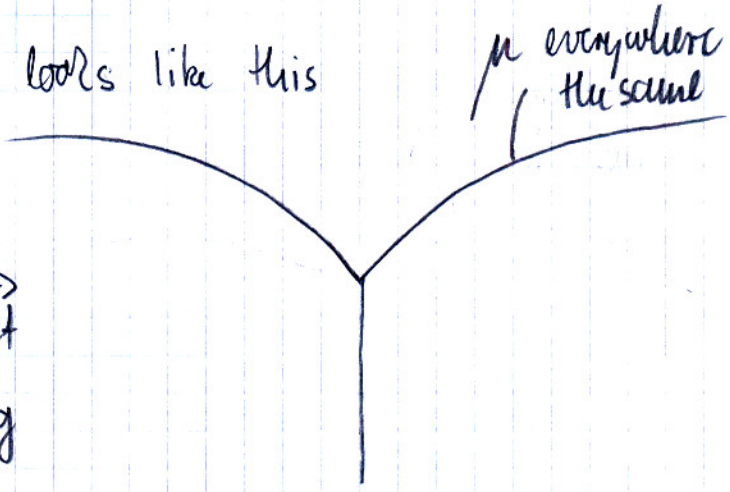
We must have

$$2\,\gamma_{surf} \cdot \cos\theta = \gamma_{gr}$$

(remember: γ is force per unit length)

Therefore initially the surface profile looks like this

transport by heating

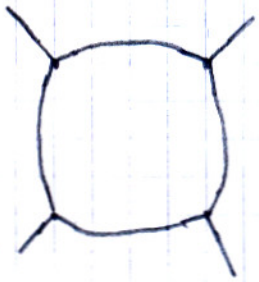


Through this mechanism a groove forms. For thin films this is usually the mechanism of film break-up.

⑥ <u>Grain growth</u>

Consider a top view of a grained thin film. Grains with equivalent grain boundaries form triple junctions with 120°

Now all is about the number of triple junctions. If a grain has only 5 or 4 junctions, its sides will be curved outward. The atoms at the grain surface have a chemical potential $\mu = \mu_0 + \kappa \gamma V_s$



with a positive κ, the atoms at the neighbouring concave surface a chemical potential

$$\mu = \mu_0 - |\kappa| \gamma V_s$$

Thus there is a driving force for dissappearance of this grain through $\Delta\mu = 2\kappa\gamma V_s$

5.3 The equilibrium shape of a crystal and surface stress

Two important factors distinguish the surface free energy γ of a crystal from the one of a liquid.

i) γ is dependent on surface orientation and not isotropic. This implies that the quantity $\gamma = \gamma(\theta)$ for a fixed crystal orientation. This implies also that in the formula $\Delta\mu = \kappa\gamma V_s$ γ has to be replaced by $\tilde{\gamma} = \gamma + \frac{\partial^2\gamma}{\partial\theta^2}$, the surface stiffness.

ii) γ is not a surface tension, i.e. it may no simply regarded as a force per unit length

Let us start with the derivation of γ close to a dense packed surface orientation with $\theta = 0$.

$$\gamma(\theta) = \frac{\gamma_L}{a} \sin\theta + \gamma(0) \cos\theta$$

γ_L is the step free energy per unit length