the $\vec{B}$ - field, its energy will be lower or higher. We thus obtain for every $\vec{k}$ - vector two eigenstates of the wave function with two energy eigenvalues, depending on $s_z = +\frac{1}{2}$ or $s_z = -\frac{1}{2}$ with respect to the z-axis of the $\vec{B}$ - field

Fig 3.35 displays the spin - orbit split band structure resulting for a nearly free electron gas. Fig 3.36 displays experimental ARPES measurements of the spin - orbit split surface state of Au (111)

Now we are in the position to understand a Datta device in the field of spintronics - electronics making use of the additional spin degree of freedom. Take a look at Fig 3.37. The device consists of two ferromagnetic contacts, magnetized along the positive x - direction. In between a 2 dimensional free electron gas is realized through semiconductor epitaxy of materials with different bandgaps. An electrical field may be applied to the 2D electron gas through a gate electrode (just as we have it for free on surfaces). The left electrode acts as spin emitter, the right electrode as a spin analyser. If a spin emitted is travelling without change of its orientation to the right it will enter without scattering into the electrode and the current will be high. If however, the spin rotates by 180° during its flight to the right ferromagnetic electrode, it will be scattered with high probability and not enter the electrode. The current will be small. The density of states at the Fermi edge is either large or small, depending on the spin orientation. By using the gate electrode we are now in fact able to rotate the spin. This means by application of an electrical field the current can be controlled and we have a transistor.

How does this work?

The proper spin - orbit Hamiltonian is also called the <u>Rashba</u> Hamiltonian

$$H_R = \frac{\hbar}{(2m^*c)^2} \nabla V(\vec{r}) \cdot (\vec{\sigma} \times \vec{p})$$

effective e^- mass $\quad -e\phi \quad$ vector of Pauli spin matrices

For the field gradient along the y-direction this simplifies to

$$H_R = \eta \cdot (\sigma_z k_x - \sigma_x k_z)$$

with $\eta = \frac{\hbar^2}{(2m^*c)^2} \cdot \frac{\partial V}{\partial y}$ being the Rashba coupling constant

With $k_z = 0$ this simplifies to

$$H_R = \eta \, \sigma_z \, k_x$$

Now consider an electron with spin along x, that just entered the 2D electron gas. It has a well defined energy E and with respect new quantisation axis of our imaginary B-field along z we have to describe it as a superposition of the two eigenstates of our Rashba Hamiltonian. Thus

$$\left.\begin{aligned} E(z, pol) &= \frac{\hbar^2 k_{x1}^2}{2m^*} - \eta k_{x1} \\ E(-z, pol) &= \frac{\hbar^2 k_{x2}^2}{2m^*} + \eta k_{x2} \end{aligned}\right\} \Rightarrow$$

$$\frac{\hbar^2}{2m^*}\left(k_{x2}^2 - k_{x1}^2\right) + \eta\left(k_{x1} + k_{x2}\right) = 0$$

$$\frac{\hbar^2}{2m^*}\left(k_{x2} + k_{x1}\right)\left(k_{x2} - k_{x1}\right) + \eta\left(k_{x1} + k_{x2}\right) = 0 \Leftrightarrow$$

$$k_{x1} - k_{x2} = \frac{\eta \, 2m^*}{\hbar^2}$$

Our wavefunction in the 2D electron gas is a superposition of two wavefunctions with different wave vectors k_{x1} and k_{x2}. This is similar to the situation for a wave plate. There a wave is decomposed into a superposition of two wave propagating with a different wave vector. After a distance L a phase shift θ results which gives rise to a change in the polarisation of the light (Fig 3.38). Here the phase shift is

$$\theta = (k_{x1} - k_{x2}) \cdot L = \frac{\eta \cdot 2m^* \cdot L}{\hbar}$$

For a phase shift $\theta = \pi$ at L the current will have a minimum. The phase shift is adjusted with the electrical field, since $\eta = \eta(\vec{E})$.

Finally a few words on Tamm states. ARPES and inverse photoemission show three occupied surface states $S_1 - S_3$ and an unoccupied state U_1. The states U_1 and U_2 show hardly any dispersion, implying infinite effective mass of the e^- in these states, i.e. the electrons are well localized. Comparing these measurement with STS and STM images made primarily from e^- out of surface states makes clear: The U_1 and S_1 states are localized at the adatoms (dangling bond states), whereas the S_2 state is localized at the dangling bonds of the rest atoms. The S_3 state is assigned to the back bonds of the adatoms. See Figs. 3.39 - 3.41.

4. Thermodynamic Aspects of Surfaces

4.1 Processes Far From and Close To Thermodynamic Equilibrium

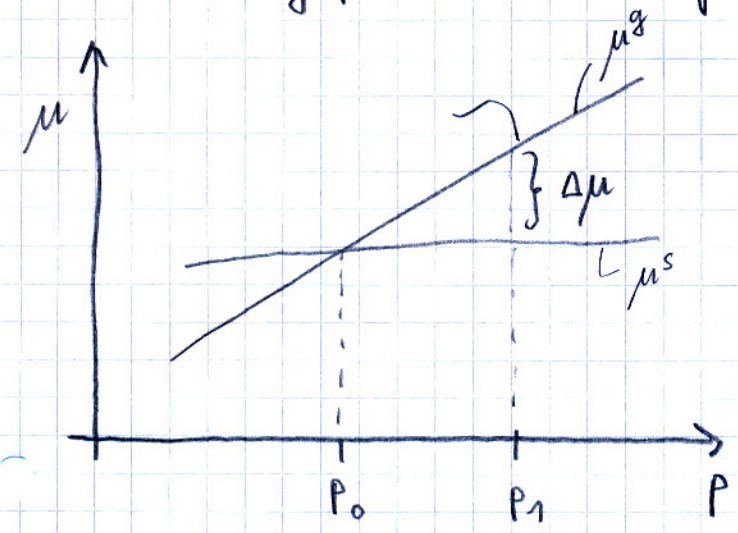
Surface and nanostructure processes are often performed far from thermodynamic equilibrium. In order to quantify what we mean by this let us consider a simple one component two phase system.
As a function of state variables p and T we describe the system by its Gibb's free energy

$$G(p,T) = U + p \cdot V - TS = n^s \mu^s + n^g \mu^g$$

Here the indices s and g indicate solid (or liquid) and gas phase for example. The symbol μ is the chemical potential which is for a one component system nothing but the Gibb's free energy per particle generally

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{p,T}$$

In phase equilibrium at a given temperature T_0 and pressure p_0 we have $\mu^s = \mu^g$, since then G can not be lowered by transfer of atoms between the phases. If we increase now p from p_0 to p_1 at fixed temperature T a difference in the chemical potentials will arise, driving particles from the gas phase to the solid phase



We then have

$$\Delta\mu = \left[\mu^g(p_1) - \mu^g(p_0)\right] - \left[\mu^s(p_1) - \mu^s(p_0)\right]$$

$$= \int_{p_0}^{p_1} \frac{\partial \mu^g}{\partial p}\, dp - \int_{p_0}^{p_1} \frac{\partial \mu^s}{\partial p}\, dp$$

$$= \int_{p_0}^{p_1} (v^g - v^s)\, dp$$

$$\cong \int_{p_0}^{p_1} v^g\, dp$$

Here we used that at fixed temperature

$$d\mu^g = \underbrace{v^g}_{\text{volume per particle}} dp - \underbrace{s^g dT}_{=0} \quad \text{and} \quad d\mu^s = \underbrace{v^s}_{\text{small compared to } v^g} dp \approx 0$$

If we treat the vapor phase as an ideal gas with $pv^g = kT$ we obtain by integration

$$\boxed{\Delta\mu = kT \ln \frac{p_1}{p_0}} \quad \underline{\text{supersaturation}}$$

where p_0 is the equilibrium vapor pressure of the solid phase at T. A similar expression may be derived for a liquid in coexistence with the solid with melting temperature T_m:

$$\Delta\mu = \frac{\Delta T}{T_m} \cdot L$$

Here L is the latent heat of melting and ΔT is the temperature <u>undercooling</u> of the melt under T_m.

Supersaturation and undercooling drive crystallization. In typical crystal growth conditions $\Delta\mu \approx 10^{-3}$ eV/atom, in typical thin film and nanostructure growth conditions $\Delta\mu \approx 1$ eV/atom. To get some more insight consider the hypothetical situation in Fig. 1. Two Si-Wafers on different temperatures are separated by a small gap. The vapor pressure of the „growth-wafer" at 900 K is $p(900K) \approx 10^{-13}$ Pa the one of the evaporator-wafer" at 1350 K is $p(1350K) \approx 5 \cdot 10^{-4}$ Pa

$\frac{5 \cdot 10^{-4}}{10^{-13}} = 5 \cdot 10^{9}$ more often particles from the evaporator wafer hit the growth wafer than vice versa. Growth is thus irreversible and

$$\Delta\mu = k \cdot 900\,K \cdot \ln 5 \cdot 10^{9} \approx 2\,eV/atom$$

Under these conditions the growth rate is about 1 ML/s, a typical value in technology.

If we would limit supersaturation to a value typical for crystal growth (e.g. 10^{-3} eV/atom), then we would obtain $\frac{P_1}{P_0} \approx 1{,}01$.

This means that a particle crosses the phase boundary about 100 times before it is incorporated into the growth wafer. Only if the atom arrives at the optimum binding site at the growth-wafer there is a chance that it stays – growth is reversible.

In growth far from equilibrium a particle passing through the phase boundary may be trapped in a metastable state well above equilibrium. Still it will not return. This is the key point, which enables us to create a rich manifold of metastable structures. Consider Fig. 2

Even for a metastable situation full of defects we may define partial equilibria, in which we are able to apply thermodynamic concepts. However this has to be done with care.

5.2 Surface Tension of Liquids and the Laplace Pressure

Although the considerations in the present section are strictly only valid for liquids, they are in many cases a good approximation for solids when effects of anisotropy can be neglected.

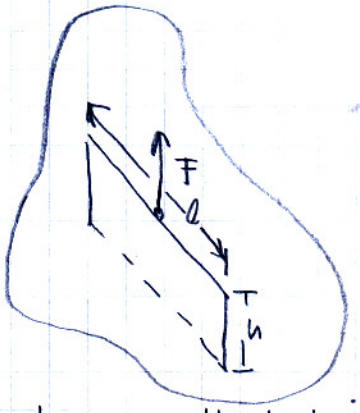
If we increase the surface of a liquid being in equilibrium with its vapor work needs to be done being proportional to the area increase dA

$$dW = \gamma \, dA$$

γ is the specific surface tension (energy per area) and is a temperature dependent quantity. Evidently it vanishes above T_c (γ is a free energy, later)

One may not only imagine γ as an energy per unit area but also as a force per unit length. Consider a wire frame being pulled out of soap solution, such that a lamella of liquid is increased in area:

$$dW = F\,dh = \gamma \cdot dA = \gamma \cdot \underset{\substack{\uparrow \\ \text{two sides of} \\ \text{lamella}}}{\ell} \cdot 2\,dh$$



Thus $\frac{F}{2\ell} = \gamma$ force per unit length

You may imagine γ as a thin rubber membrane that tries to reduce the surface area.

|| γ is a free energy per unit area or a force per unit length.

In the absence of external forces the shape of a liquid in equilibrium with its vapor and for fixed particle number, T and p is

$$\int_S \gamma\, dA = \min ! \quad T, p, N = \text{const}$$

For a liquid this condition is met by a sphere. Consider now a gas bubble in a liquid (e.g. CO_2 in water). Its radius is constant, i.e it is in equilibrium) if the forces acting inward (resulting from surface tension and outside pressure) are balanced by the forces acting outward (resulting from inside pressure).

If we would shrink the bubble by dr we would gain work derived from shrinking the surface area

$$dW_\gamma = 4\pi r^2 \cdot \gamma - 4\pi (r - dr)^2 \gamma \approx \underbrace{8\pi r \gamma}_{= F_\gamma}\, dr$$

The force balance thus reads

$$4\pi r^2 p_{in} = 4\pi r^2 p_{out} + 8\pi r \gamma \quad \Leftrightarrow$$

<u>Laplace pressure</u> $\boxed{p_{in} = p_{out} + \frac{2\gamma}{r}}$ or $\boxed{\Delta p = \frac{2\gamma}{r}}$