

# Surface Thermodynamics and general crystal shape

Internal energy of a homogeneous thermodynamic system, having in mind the bulk crystal. This is given by the Euler equation

$$U = TS - PV + \mu N.$$

Now suppose that this crystal is cleaved and a surface area is created. Suppose further that this process is carried out reversibly at a constant temperature, system volume and chemical potential. The creation of the surface adds a term to the energy which must be proportional to the amount of surface area created and positive because otherwise bulk crystals would cleave spontaneously. The energy is then

$$U = TS - PV + \mu N + \gamma A,$$

where the constant  $\gamma$  has the dimension of energy per surface area and is called the **surface tension**. Unfortunately, it is very difficult to measure the surface tension (or energy) of a solid/vacuum interface.

Some hint about the magnitude of the quantity can be taken from measurements of the liquid gas interface but this is not sufficient to test the interesting details in the theory.

When we think about the microscopic origin of  $\gamma$  it is obvious that it will be different for the various possible surface planes of a crystal.

As we shall see below, the number of bonds which have to be broken to generate a certain surface plane depends on the **orientation** of the plane. A surface with many steps might be particularly unfavourable because several of bonds have to be broken to create a low-coordination step atom.

Therefore we write  $\gamma$  with a **directional dependence**  $\gamma(\vec{n})$ .

These considerations have important consequences on the macroscopic shape of crystals.

While **liquids** are always found in the shape of **smallest surface area** (a sphere) this is not the case for solids.

The solid crystal wants to have a shape where a large fraction of the surface area is given by crystal planes with a low  $\gamma$ . More formally, if we look for the minimum in the free energy (but **at zero temperature**) we have to require that

$$\int_A \gamma(\vec{n}) = \text{minimum}.$$

This requirement leads to quite complex equilibrium shapes of crystals.

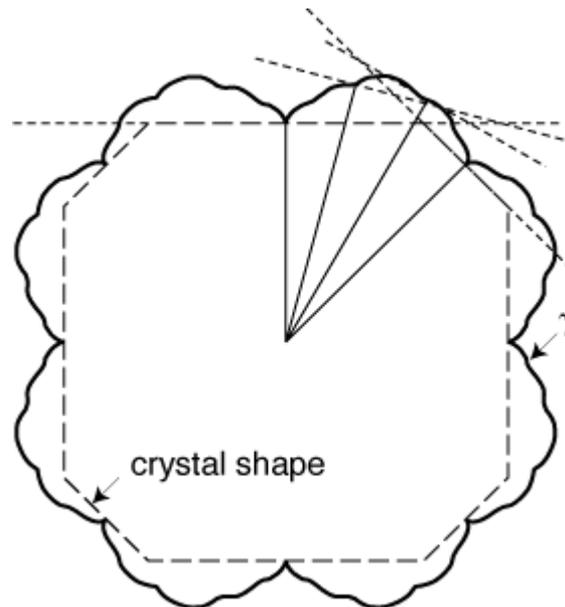
If  $\gamma(\vec{n})$  is known, the problem can be solved graphically by the so-called Wulff construction shown in Figure.

The procedure for finding the equilibrium crystal shape at 0K is as follows:

Draw  $\gamma(\vec{n})$ .

Draw a plane perpendicular to the radius vector which intersects  $\gamma(\vec{n})$  at each point.

The inner envelope of all these planes is the equilibrium crystal shape.



In a simple tight-binding picture, the energy per bond can be assumed to scale with  $(N_c)^{1/2}$ . If we denote the surface energy per atom by  $\sigma$ , we can estimate it by

$$\sigma = \frac{\sqrt{N_c^{bulk}} - \sqrt{N_c^{surf}}}{\sqrt{N_c^{bulk}}} E'_{coh} :$$

where  $N_c^{bulk}$  and  $N_c^{surf}$  are the coordination number of the bulk and the surface, respectively, and  $E'_{coh}$  is the cohesive energy related to a *non-magnetic* atom for a non-magnetic surface.

It is interesting to consider this crystal shape if we want to prepare a surface by cleaving a crystal.

The cleaving process will only work (if at all) for surfaces which also appear on the **equilibrium crystal**. If we attempt a cleavage in another direction, the result will be a surface with **facets** of low-energy planes.

At **finite temperature** the situation changes. Now excitations which do not cost much energy but increase the entropy of the system become important. Such excitations are steps and other defects.

As the temperature is raised, the free energy for the steps decreases. The sharp edges of the Wulff-crystal disappear and the facets decrease.

Eventually, the facets will vanish completely and the crystal will have a **round shape**.

This behaviour can be described by **a phase transition**, the so-called roughening transition

Another process worth mentioning is the phenomenon of **surface melting**.

This is the formation of a thin, liquid-like phase on the surface below the melting temperature of the bulk. The most important example of this phenomenon is the surface melting of ice which permits for example skating. The existence of surface melting can be made plausible by considering the Lindemann formula for bulk melting. It states that

$$T_m \propto \Theta_D^2$$

where  $T_m$  is the melting temperature and  $\Theta_D$  is the Debye temperature.

The latter is often found to be much **smaller at the surface**.

A rule of thumb is that the surface Debye temperature is about a factor of  $\sqrt{2}$  smaller than its bulk counterpart.

This simply means that the **surface atoms** vibrate more strongly than the bulk atoms at a given temperature and this eventually leads to melting.

But one has to keep in mind that this point of view is much too simple. Note that also the completely counter-intuitive phenomenon of surface overheating is found in which the bulk melts at a lower temperature than the surface.

# Surface geometry: truncated bulk, relaxation, reconstruction, defects and super-structures

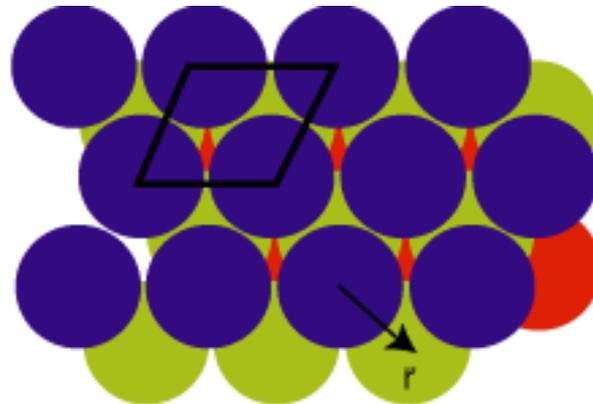
## General phenomena

The simplest picture of a microscopic surface structure is that of the truncated bulk (the so-called ideal surface).

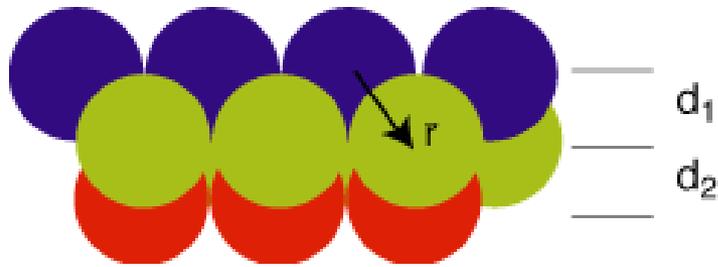
Suppose the crystal is cleaved along a plane specified by its Miller indices  $(hkl)$ .

In the truncated bulk model, all the atoms on the cleaved crystal's surface stay exactly where they have been in the bulk crystal. This means that one can immediately draw the surface geometry of the crystal.

Figure shows the surface geometry for the fcc(111) surface.



*The (111) surface of an fcc crystal*



*The (111) surface of an fcc crystal  
Side view*

When looking at a surface, we think of the bulk as being made of planes parallel to the surface plane.

We define a unit cell in the first plane and, if required, a basis.

We define furthermore a vector  $\vec{r}$  connecting the atoms in successive planes.

A "plane" does of course not necessarily mean that all the atoms have the same  $z$  value ( $z$  being the distance perpendicular to the surface). We can extend the unit cell over several layers if we want to.

In Figure however, we have chosen a primitive unit cell and all the atoms in one layer are at the same height. We call the  $z$  component of  $\vec{r}$  the distance between the planes. In the side view of the surface in Figure we can see the familiar ABCABC... stacking sequence of the fcc lattice.

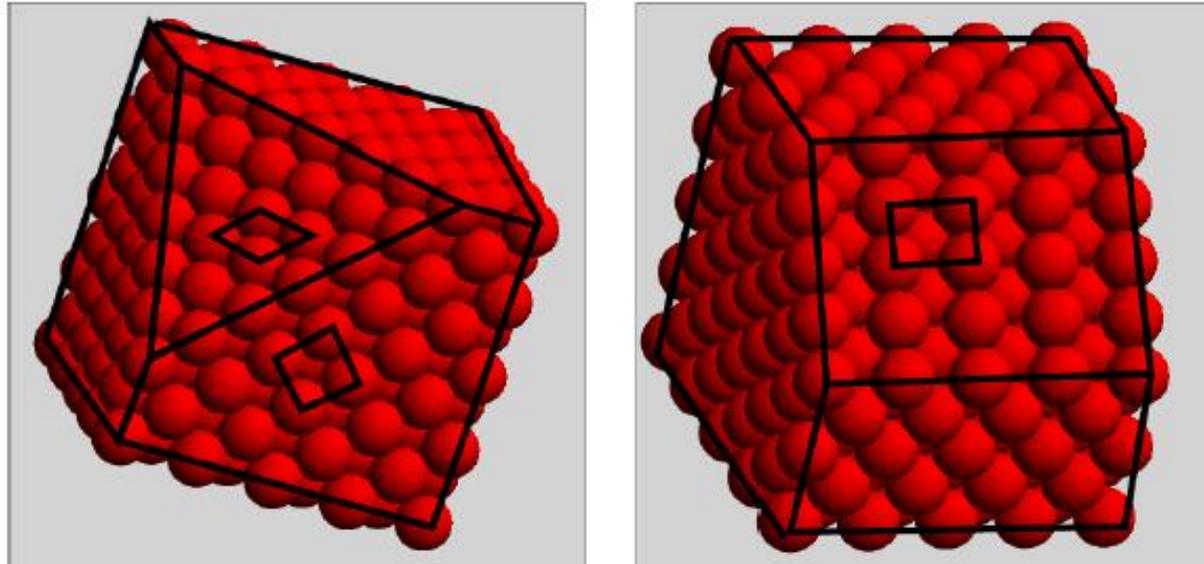
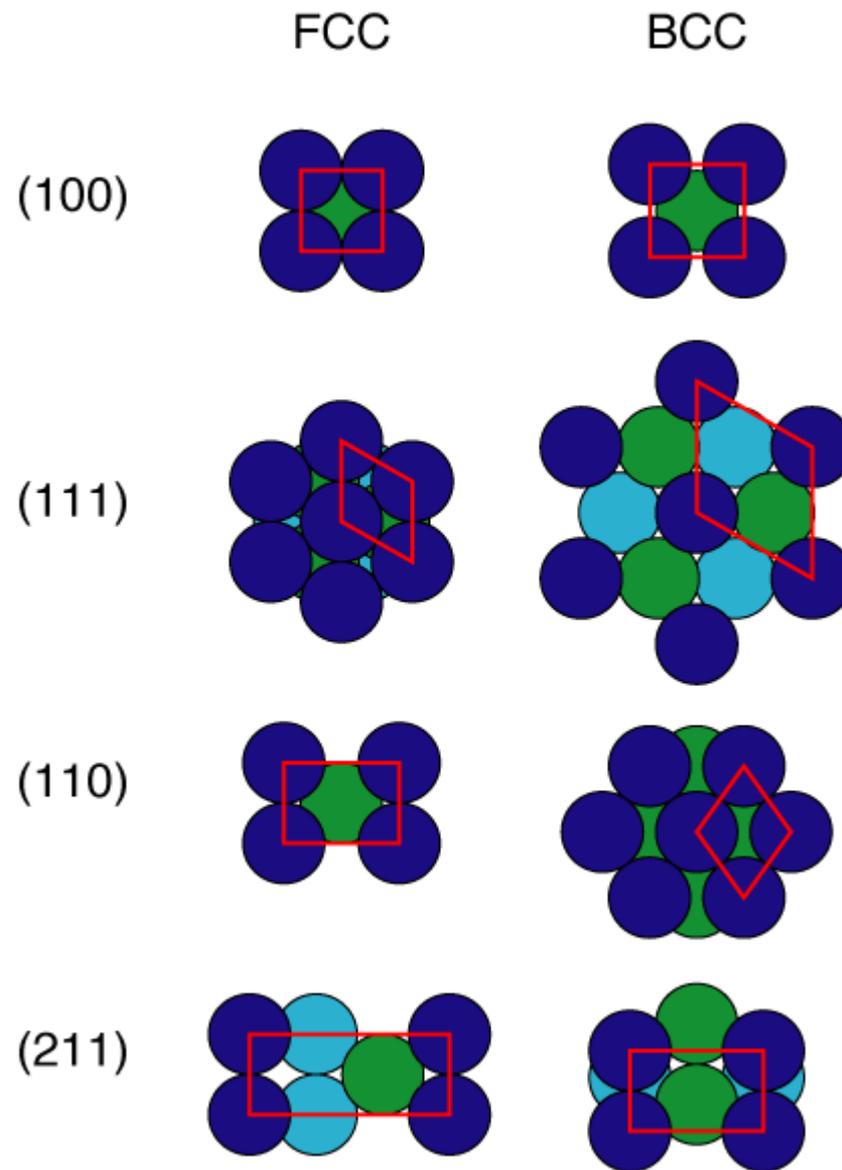


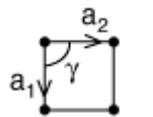
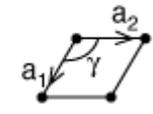
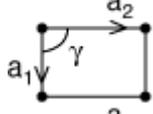
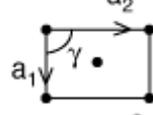
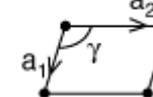
Figure 2: Structure of surfaces. Left panel: fcc crystal with (100) faces and one (111) face, right panel: fcc crystal with (100) faces and one (110) face. The surface unit cells of the corresponding faces are also indicated in the figure.

In Figure the truncated bulk surfaces of a few important cases are shown.



The concepts for lattice and reciprocal lattice on surfaces are very similar to what we know from the bulk. In any case, it is worth repeating them!

The 14 possible Bravais lattices of the bulk are reduced to 5 two-dimensional surface Bravais lattices which are shown below:

	square	$a_1 = a_2$	$\gamma = 90^\circ$
	hexagonal	$a_1 = a_2$	$\gamma = 120^\circ$
	rectangular	$a_1 \neq a_2$	$\gamma = 90^\circ$
	centered rectangular	$a_1 \neq a_2$	$\gamma = 90^\circ$
	oblique	$a_1 \neq a_2$	$\gamma \neq 90^\circ, 120^\circ$

The two-dimensional lattice is then the combination of one of the Bravais lattices and a basis. It is important to notice that since a surface is not two-dimensional, the basis atoms need not be in one plane. Once the basis is assigned one can find out the two-dimensional point group of the lattice.

The point group will be some sub-group of the highest possible symmetry compatible with the Bravais lattice under consideration. The final symmetry of the system, the space group, is then formed by a combination of the translation group (i.e. the Bravais lattice) and the point group. Like in the three dimensional case this combination can lead to entirely new symmetry elements which are glide-lines in the two-dimensional case. In total, there are 17 possible two-dimensional space groups.

The reciprocal lattice of the surface is defined in the same way as that of the three-dimensional crystal:

$$\vec{g}_1 = \frac{2\pi(\vec{a}_2 \times \vec{n})}{|\vec{a}_1 \times \vec{a}_2|}, \vec{g}_2 = \frac{2\pi(\vec{n} \times \vec{a}_1)}{|\vec{a}_1 \times \vec{a}_2|},$$

This means that

$$\vec{a}_i \vec{g}_j = 2\pi \delta_{ij}.$$

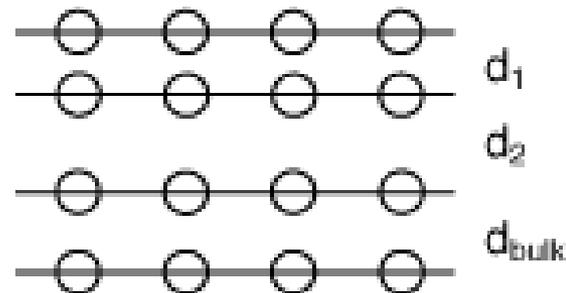
and

$$|\vec{g}_i| = \frac{2\pi}{a_i \sin \angle(\vec{a}_i, \vec{a}_j)}, \quad i, j = 1, 2.$$

The two last equations also give a simple recipe to construct the reciprocal lattice.

The most severe problem with the truncated bulk model is that it completely neglects the dramatic change in the coordination and potential due to the abrupt termination of the crystal in the direction normal to the surface. This change will for almost all surfaces lead to a phenomenon called *relaxation*

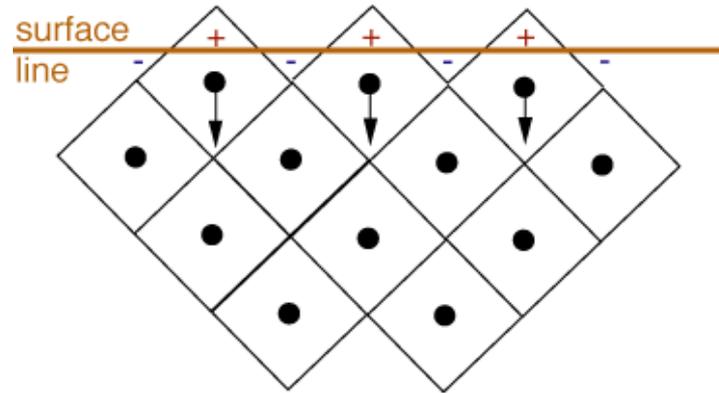
side view



A relaxation is a change in the distances between the first few layers with respect to the bulk values.

For most surfaces the distance  $d_1$  is smaller than the corresponding bulk value.

This can be made plausible by the model of Finnis and Heine shown below:



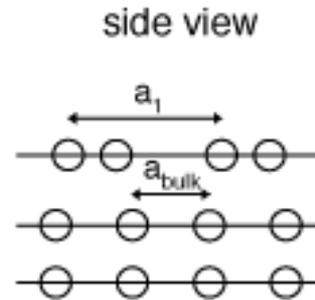
In the bulk (of a metal) the ion cores are screened by the conduction electrons around them. If we divide up the crystal in Wigner-Seitz cells, it is easy to see what happens in the surface case: the original distribution of electrons in the Wigner-Seitz cells would lead to a highly corrugated electron distribution at the surface.

This is, however, very unfavourable because of the **high kinetic energy** of "bent" wave functions.

The electrons at the surface will re-distribute themselves leading to a **smooth charge density** at the surface. This creates an asymmetric screening of the ion cores in the first layer and a net electrostatic force which pushes them "into" the crystal and thus reduces  $d_1$ .

The charge smoothing at the surface is called the Smoluchowski effect

A more severe change of structure is the phenomenon of surface *reconstruction*



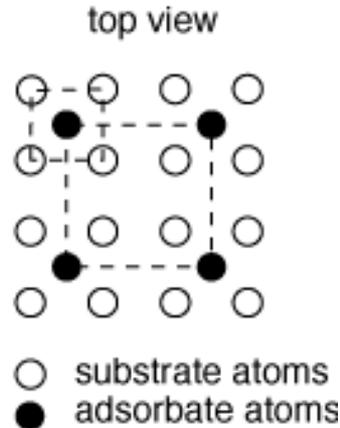
In a reconstruction the periodicity parallel to the surface is changed with respect to that of the bulk.

Surface reconstructions are the rule in the case of **semiconductors**. There the bonds are **highly directional**. Cleaving the crystal leaves the structure in an unfavourable elastic state and also gives rise to half-occupied **"dangling" bonds**.

Reconstructions give a considerable **gain in energy** and **reduce** the number of dangling bonds. The resulting structures can be rather complicated (the bond strength varies with the coordination number: for a low-coordinated atom the single bonds are stronger than for a high-coordinated atom.).

**Most metals surfaces do not reconstruct** but some do. In most cases, this happens for metals where localized *d* or *f* electrons take part in the bonding for reasons similar as on the semiconductor surfaces. But there are also a few simple metal surfaces which reconstruct.

Another phenomenon, somewhat similar to reconstruction, happens when atoms or molecules are adsorbed on a surface. The adsorbates often form ordered structures (due to their mutual interaction) which have unit cells larger than the substrate unit cell.



In most cases, however, there is still a simple ratio between the substrate and adsorbate unit cell (due to the adsorbate - substrate interaction). Adsorbates will in general change the structure of the underlying substrate. In particular, they can induce **a lift of the reconstruction** of the clean surface.

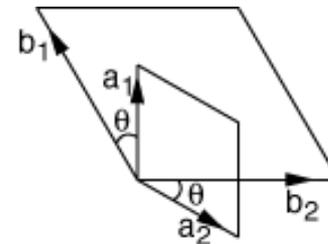
Apart from these simple phenomena there are many things which can make life much more complicated: adsorbate structures have domains and domain boundaries, the surface may have many imperfections such as steps and terraces, the atoms and molecules which are adsorbed on the surface do not show any long-range order and so on.

The phenomena of reconstruction and ordered overlayers make it necessary to have a nomenclature which describes the periodicity and symmetry of the surface with respect to that of the bulk.

Suppose the two-dimensional lattice vectors of the bulk are  $\vec{a}_1$  and  $\vec{a}_2$ . By "two-dimensional lattice vectors of the bulk" we mean the lattice vectors for the bulk-truncated crystal or, equivalently, the vectors which represent the lattice of the bulk projected onto the surface.

Let the lattice vectors of the surface including possible adsorbate overlayers be  $\vec{b}_1$  and  $\vec{b}_2$ . A simple nomenclature of surface structures is that of Woods. The surface structure is described by

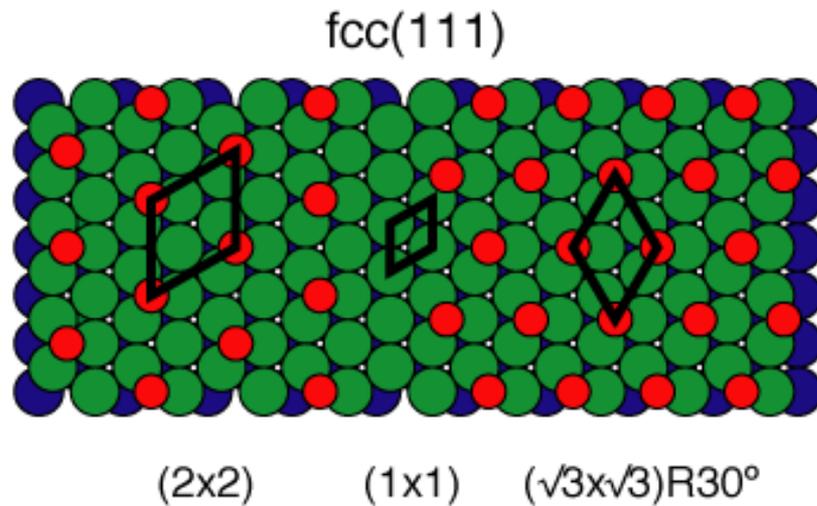
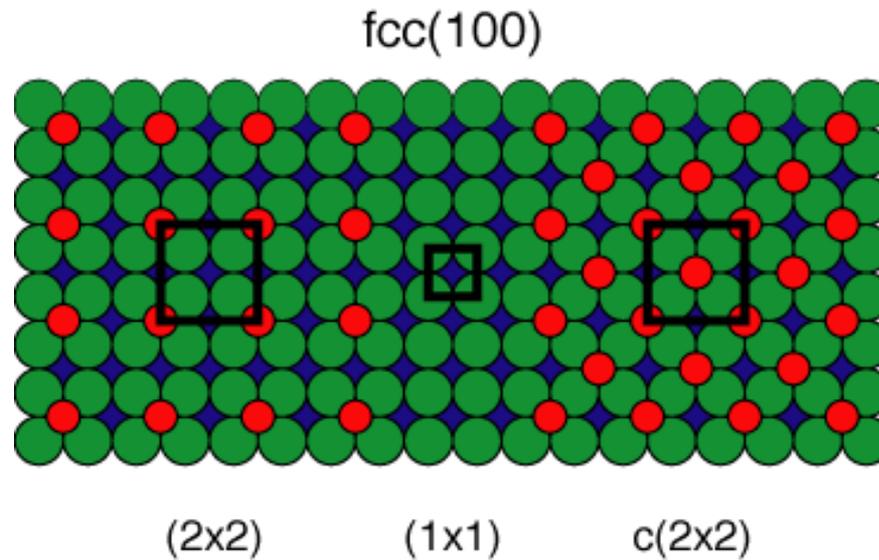
$$N \begin{pmatrix} \vec{b}_1 & \vec{b}_2 \\ \vec{a}_1 & \vec{a}_2 \end{pmatrix} R^\Theta$$



where  $N$ ="p" or "c" for primitive or centred cells, respectively, and  $\Theta$  is the angle by which the surface vectors have to be rotated with respect to those of the bulk

The nomenclature of Woods has the advantage of simplicity. It is, however, not possible to describe all surface structures because the rotation angle might not be the same for both vectors.

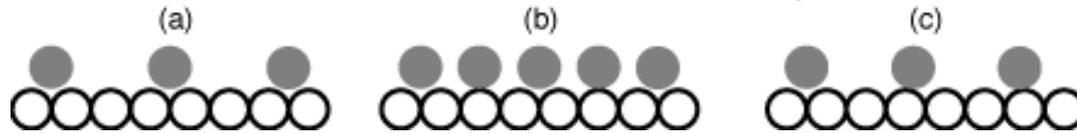
Some examples for the application of the Woods nomenclature are given in Figure.



A more general description of the surface structure is the so-called matrix notation

$$\begin{aligned} \vec{b}_1 &= m_{11} \vec{a}_1 + m_{12} \vec{a}_2, \\ \vec{b}_2 &= m_{21} \vec{a}_1 + m_{22} \vec{a}_2. \end{aligned} \quad \text{or, in other words} \quad \begin{pmatrix} \vec{b}_1 \\ \vec{b}_2 \end{pmatrix} = \begin{pmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{pmatrix} \begin{pmatrix} \vec{a}_1 \\ \vec{a}_2 \end{pmatrix}.$$

The inspection of the matrix directly allows the classification of the overlayer structures into three types which are illustrated in Figure



(a) simply related to the substrate, (b) rationally related and (c) an incommensurate structure with no common periodicity

- All the matrix elements are integer: the adsorbate and substrate lattices are called simply related and the lattice of the whole surface (adsorbate and substrate) has the same translational symmetry as the adsorbate lattice.
- Some matrix elements are rational: the adsorbate and substrate lattices are called rationally related. The lattice of the whole surface (adsorbate and substrate) has a translational symmetry which is given by the distance it takes before adsorbate lattice and substrate lattice come into coincidence again.
- Some matrix elements are irrational. In this case the adsorbate lattice is incommensurate with the substrate and no true lattice for the whole surface (adsorbate plus substrate) exists.

It is obvious that the relative strength of the substrate-adsorbate and adsorbate-adsorbate interactions will favour one type of structure over the others.

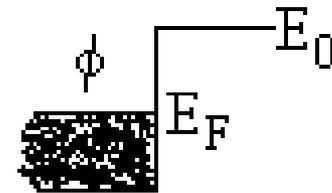
# The electronic structure of surfaces: basic ideas

## Work function

All materials have a work function, i.e. that one has to pay some energy in order to extract an electron from a solid.

The workfunction of a metal is defined as the smallest energy needed to extract an electron at 0 K

This is the energy, typically a few eV, required to move an electron from the *Fermi Level*,  $E_F$ , to the vacuum level,  $E_0$ . The **work function** depends on the **crystal face** {hkl} and **rough surfaces** typically have lower work function.



# The electronic structure of surfaces: basic ideas

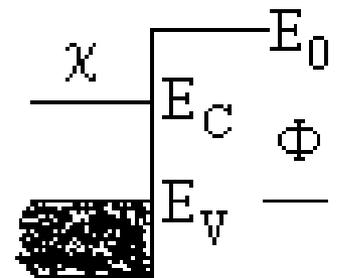
## Electron Affinity and Ionisation Potential

Both of these would be the same for a metal, and equal to  $\phi$ , but for a semiconductor or insulator, they are different.

The **electron affinity** is the difference between the vacuum level  $E_0$ , and the bottom of the *Conduction Band*  $E_C$ .

The **ionisation potential** is  $E_0 - E_V$ , where  $E_V$  is the top of the valence band.

These terms are not specific to surfaces: they are also used for atoms and molecules generally, as the energy level which a) the next electron goes into, and b) the last electron comes from.

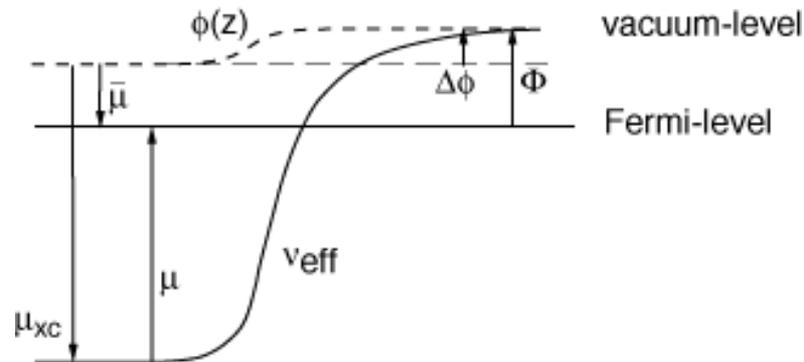


# The electronic structure of surfaces: basic ideas

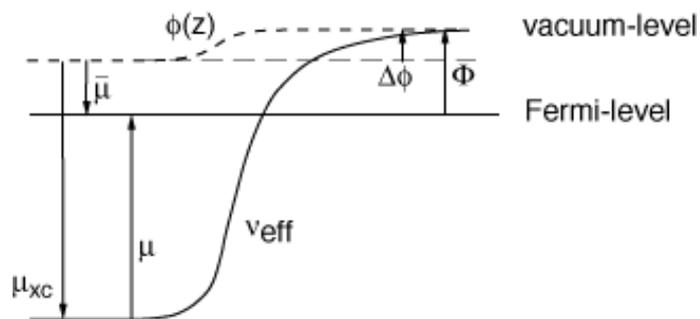
## Work function

All materials have a work function, i.e. that one has to pay some energy in order to extract an electron from a solid.

The workfunction of a metal is defined as the smallest energy needed to extract an electron at 0 K. Formally, this definition is made for an infinitely large crystal plane. One takes an electron from infinitely deep inside the crystal and brings it through the surface, infinitely far away into the vacuum. In practice, one wishes to avoid external fields and fields set up by the edges of the crystal. The definition is modified such that one brings the electron far away from the surface compared to atomic dimensions but not far compared to crystal dimensions. The energetics involved in this is displayed in Figure



There are two potentials displayed. The first is the electrostatic potential  $\phi(z)$ . This potential changes a little when going into the crystal. The change is due to the surface dipole layer which is caused by the spill-out of the conduction electrons

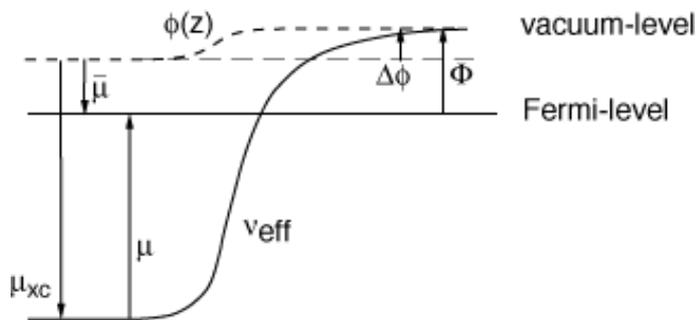


The potential difference between inside and outside the crystal is called  $\Delta\phi$ . The other potential is the full one-electron potential  $v_{eff}(z)$ . This is obtained from the electrostatic potential by adding the exchange-correlation potential  $\mu_{xc}$ .  $v_{eff}(z)$  shows that the electron reaches a much lower total potential energy inside the crystal than that caused by the electrostatic part. This must be so, because the exchange and correlation will cause the electrons to go out of each others way and therefore their potential energy will decrease.

The zero for the kinetic energy in the bulk is different from the zero outside. The difference is the so-called inner potential  $V_0 = \mu + \Phi$ , i.e. the occupied band width plus the work function.

The chemical potential can now be referenced to the  $v_{eff}(z)$  or to  $\phi(z)$ . It is called  $\mu$  or  $\bar{\mu}$ , respectively.

The workfunction, finally, is the difference between the Fermi level and the vacuum level. It is called  $\Phi$ . We can write down an expression for the workfunction:



$$\Phi = \phi(+\infty) - \mu = \Delta\phi - \bar{\mu}.$$

The right hand side of this equation now allows us to think about the workfunction as being made of two parts.

A surface-part  $\Delta\phi$  and a bulk-part  $\bar{\mu}$ .

Workfunctions of metals have values between about 1.5 eV and 5.5 eV.

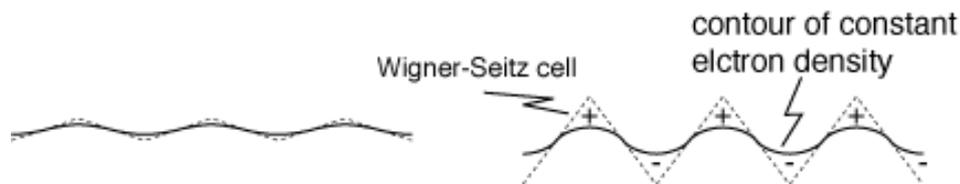
The surface part of the workfunction is of interest here because any change of the surface in terms of morphology or adsorption will be changing the workfunction. The workfunction (change) can be used as a fingerprint of the state the surface is in.

Workfunction changes upon adsorption can be in the range of 100 meV to 1.5 eV for a full monolayer.

One can measure workfunction changes within about 1 meV.

We just give give two examples for workfunction changes.

First we illustrate how the workfunction for a specific material depends on the surface orientation. Consider a closed packed and an "open" surface of some material. On the open surface we find the Smoluchowski effect of charge smoothing

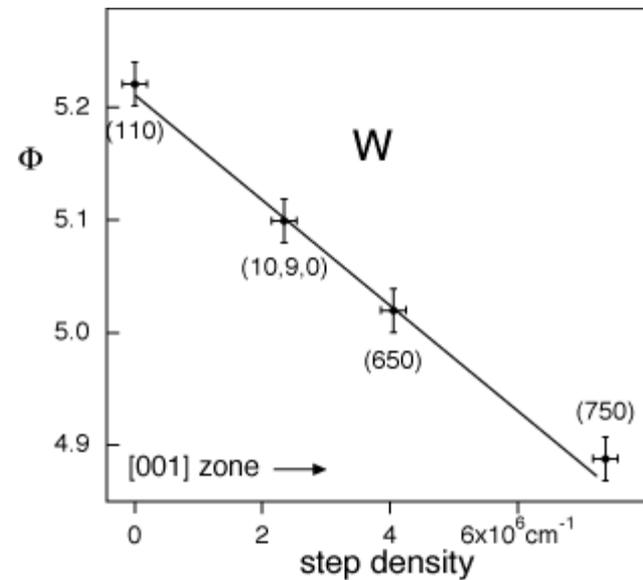


*Charge distribution at a closed packed (left) and at an open (right) surface.*

This smoothing leads to a **dipole moment** which **opposes** the dipole created by the flow-out of the electrons.

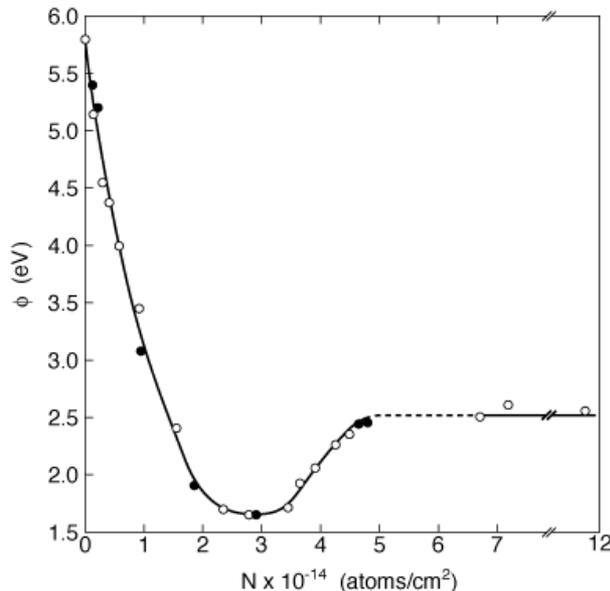
Hence, the work function of a closed packed surface will be higher than that of an open surface.

This is illustrated in Figure for a number of W surfaces. The closed packed (110) surface has the highest workfunction.



Another important example is the change of the workfunction upon adsorption. A famous case is the adsorption of alkali metals which drastically lowers the workfunction.

In very simple terms, the bond is ionic and the alkali metal gives an electron to the surface. This does also lead to a dipole moment which also opposes the spill-out of the electrons and reduces the workfunction. At low coverage, the dipole-dipole interaction between the alkali atoms will keep them far apart and the workfunction decreases linearly as a function of coverage. At high coverage, the same interaction causes a depolarization of the dipoles and leads to a metallic bond. This increases the workfunction again by a small amount. Figure shows the workfunction change upon the adsorption of potassium on tungsten.



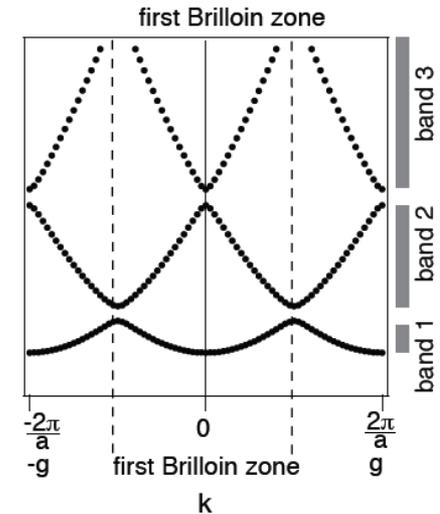
Alkali metal adsorption can be used to lower the workfunction of tungsten filaments such that they do not have to be heated so much to produce the same amount of electrons and therefore live longer.

*Workfunction change upon the adsorption of K on W(110)*

# Surface States and related ideas

In an infinite periodic solid the electron states are described by Bloch functions giving rise to allowed bands and forbidden gaps.

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \quad \varepsilon_n(\mathbf{k} + \mathbf{G}) = \varepsilon_n(\mathbf{k})$$



Bloch states are by definition non-localized, that is, they are extended over the all real space.

As a surface is introduced, the crystal becomes finite in at least one dimension. The original Bloch states will be modified along the corresponding coordinate.

The energy states of the allowed bands will not be affected strongly since the surface represents only a small fraction of the total crystal but the wavefunctions may be considerably modified near the interface. New states may be allowed at the surface and, if their energy, correspond to a band gap in the bulk, such states are termed *surface states*.

# Surface States and related ideas

Surface states are therefore trapped at the crystal-vacuum interface. Consequently they are called localized states with the understanding that they may be well delocalized (Bloch-like) in the two dimensions parallel to the surface.

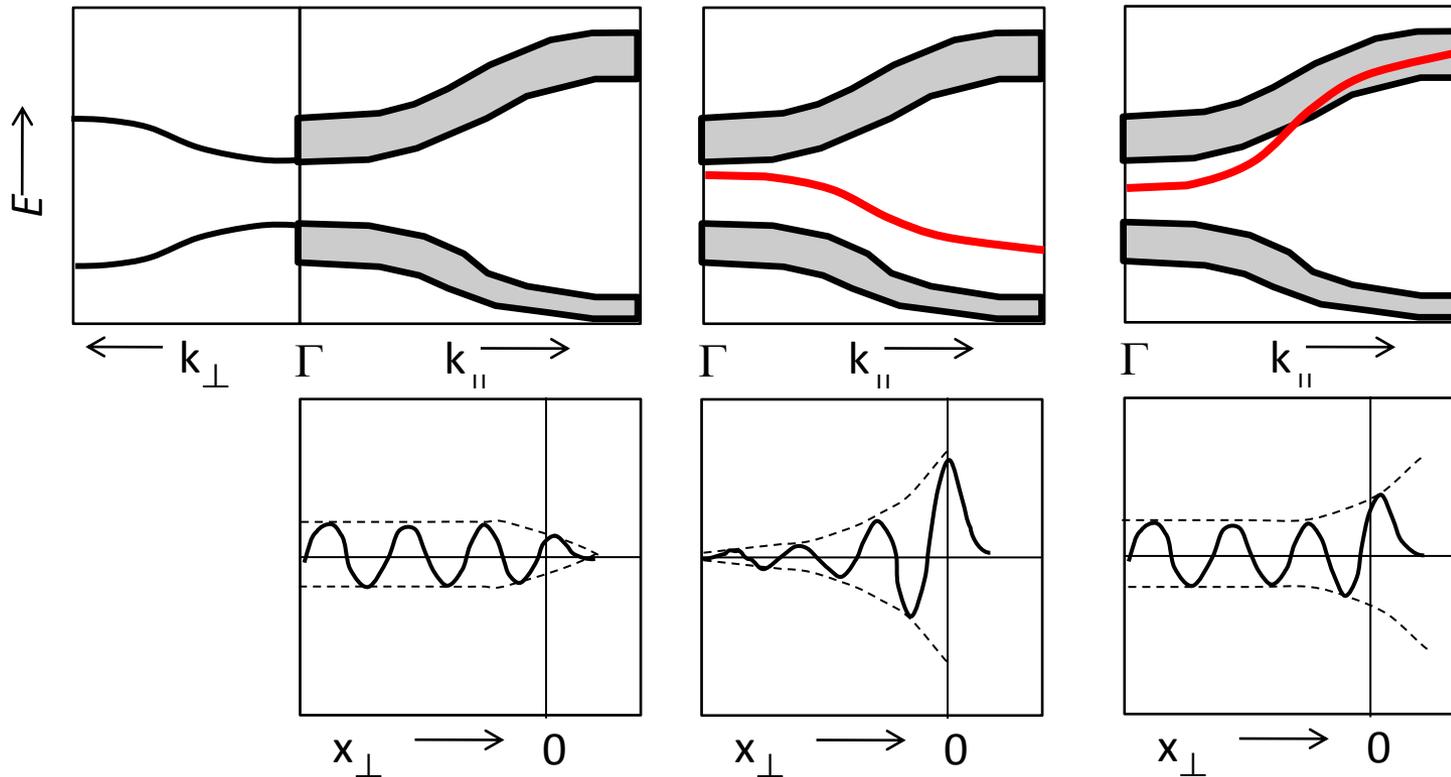
In this case surface states form band analogous of bulk bands, in the two-dimensional reciprocal space of wavevectors parallel to the surface  $\mathbf{k}_{||}$ .

All electron states at the surface, that is, bulk states that extend to the surface as well as localized states, are described by **local** density of states at the surface.

$$N(E, \mathbf{r}) = N(E) |\Psi_E(\mathbf{r})|^2$$

where  $\Psi_E$  is an eigenstate of the system at energy  $E$ . If the real space coordinate  $\mathbf{r}$  is limited to the surface, the above equation defines a **surface local density of states**.

# Surface States and related ideas



Schematic illustration of the electron states and wavefunctions near an interface.

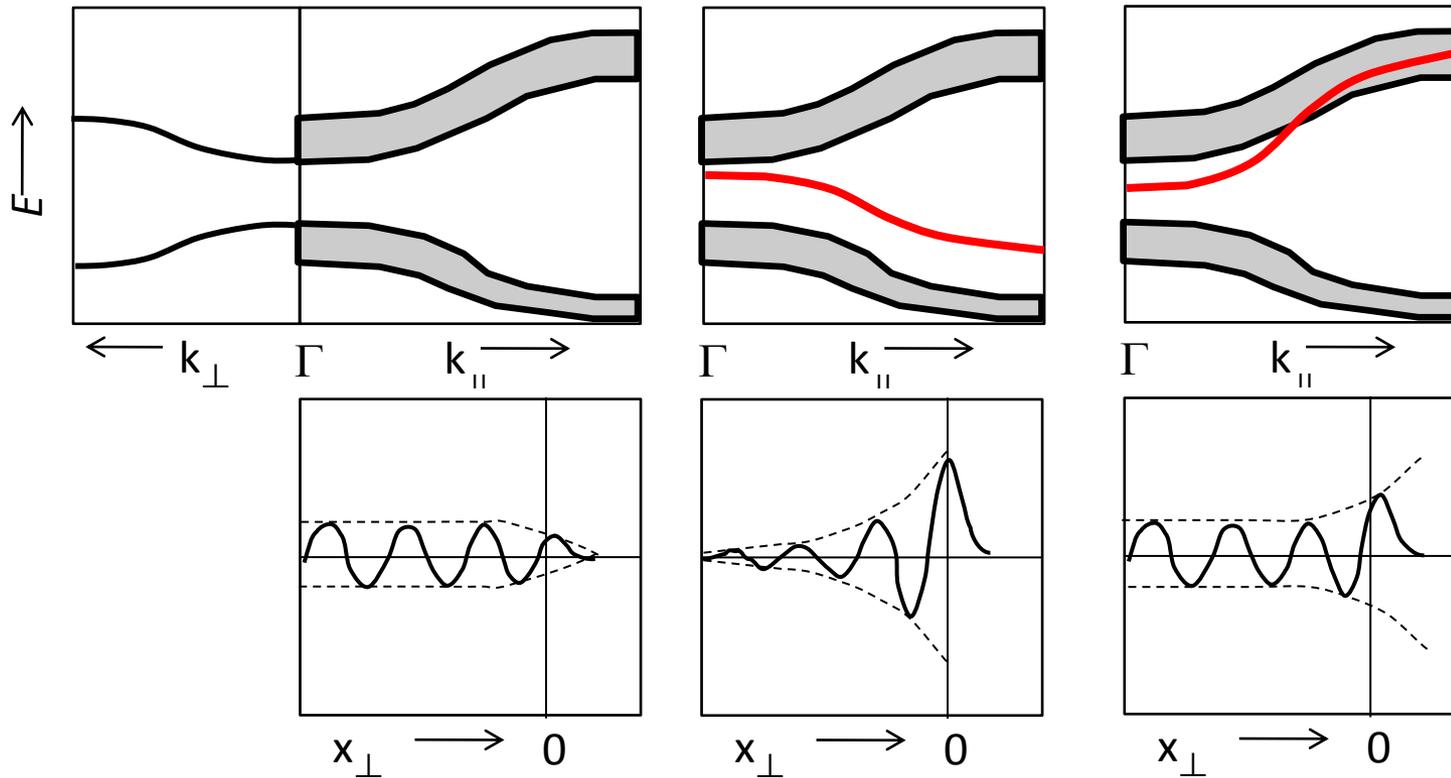
The top left diagram shows **bulk band states at the surface**.

The normal  $\mathbf{k}$ -vector component ( $\mathbf{k}_{\perp}$ ) is not a good quantum number at the surface due to the lack of periodicity normal to it, while  $\mathbf{k}_{||}$  is.

So for each value of  $\mathbf{k}_{||}$  a range of states is possible for different allowed values of normal momentum, as shown by the dashed area.

For  $\mathbf{k}_{||} = 0$  the behaviour of bulk states inside the solid is shown as a function of  $\mathbf{k}_{\perp}$ .

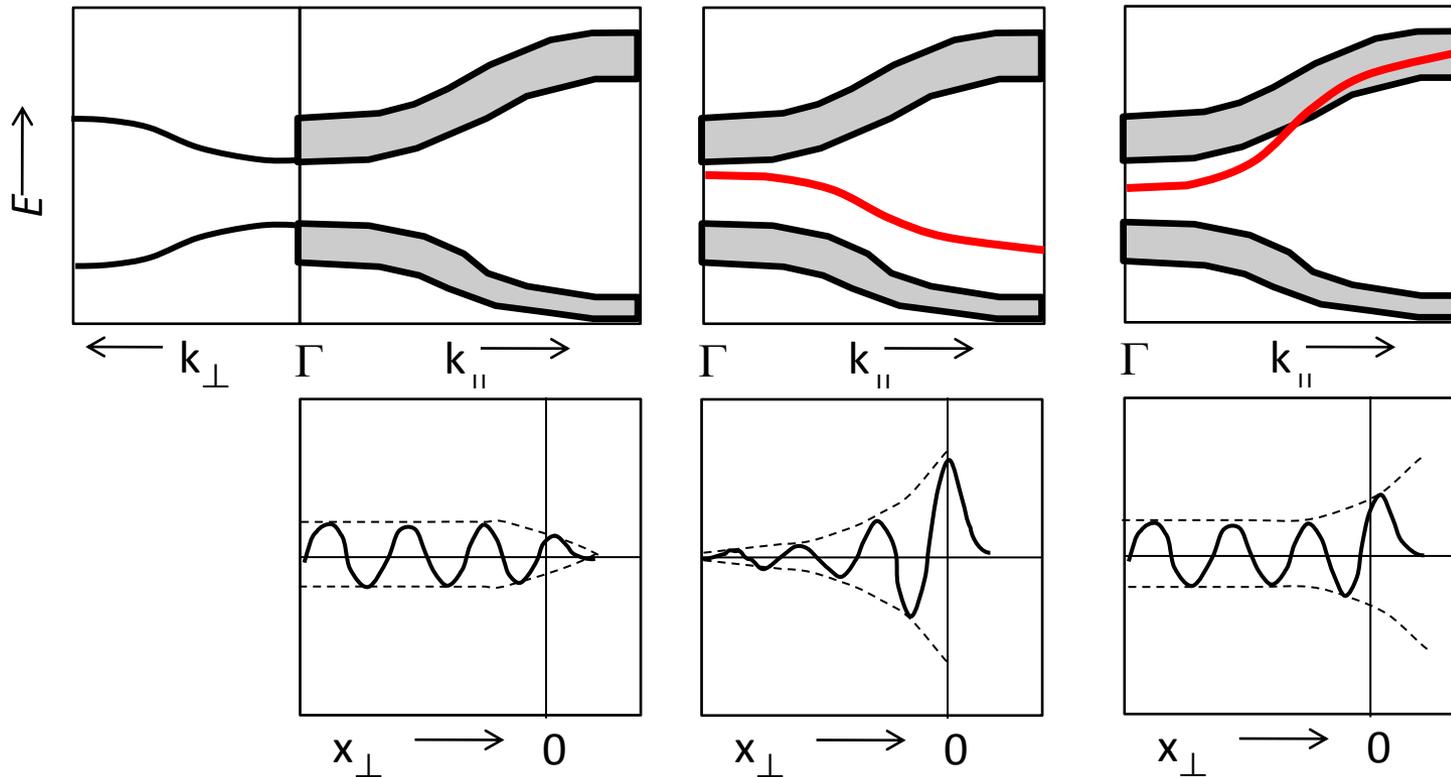
# Surface States and related ideas



Schematic illustration of the electron states and wavefunctions near an interface.

The width of this band gives the quasi-continuum of allowed states at the surface. The density of states of these “bulk” states at the surface is in general not the same as in the volume. The wavefunction amplitude (lower diagram on the left) can be different near the surface leading to different **local** density of states

# Surface States and related ideas

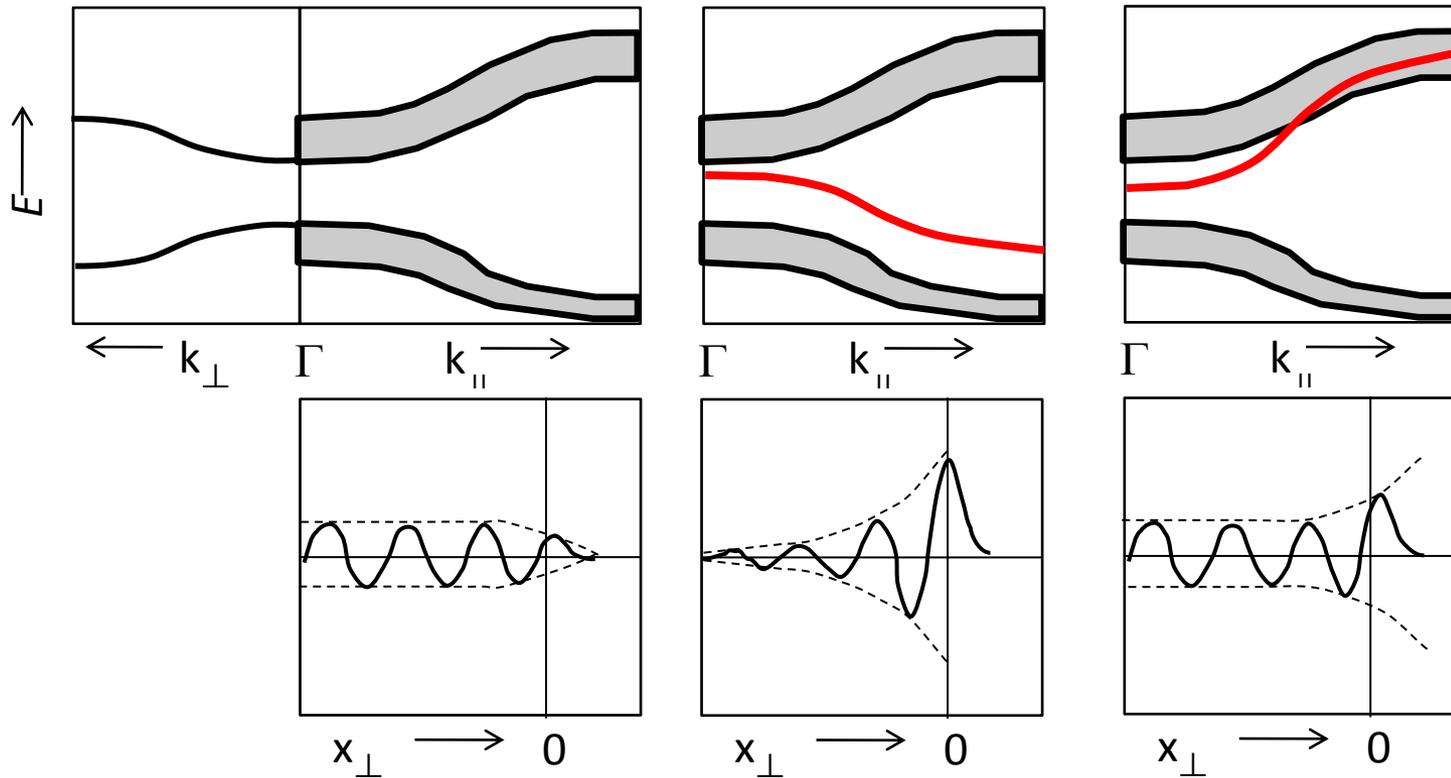


Schematic illustration of the electron states and wavefunctions near an interface.

The situation for the surface states is shown in the two centre diagrams.

Surface states may occur only in a bulk band gap for any particular  $\mathbf{k}_{||}$ , but may well overlap with bulk states for other parallel wavevectors, since  $\mathbf{k}_{||}$  is a good quantum number. The wavefunction of the surface state is concentrated near the surface plane, decaying both into the bulk and into the vacuum (bound state).

# Surface States and related ideas



Schematic illustration of the electron states and wavefunctions near an interface.

In the last two diagrams of the figure an example is shown of a state that exists as a surface state only for a limited range of  $k_{||}$  and is degenerate with bulk bands for other  $k_{||}$ . The corresponding wavefunction is enhanced near the surface, but extends into the volume of the crystal and is therefore called a *surface resonance*.

# Surface States and related ideas

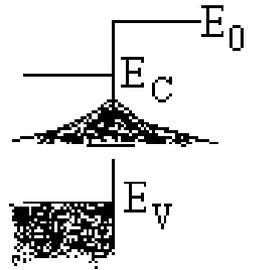
One can obtain new solutions to the Schrödinger equation caused by the introduction of the surface. Inside the crystal they have the form

$$\psi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}} u_{\mathbf{k}}(\mathbf{r}) \longrightarrow \psi_{\vec{k}}(\vec{r}) = u_{\vec{k}_{\parallel}}(\vec{r}_{\parallel}) e^{i\vec{k}_{\parallel}\vec{r}_{\parallel}} e^{-\kappa r_{\perp}}$$

with a complex wave-vector  $k_{\perp}$  perpendicular to the surface, leading to decay away from the surface on both sides.

$u_{\mathbf{k}_{\parallel}}(\mathbf{r})$  has the two-dimensional periodicity of the surface.

The new solutions decay exponentially both into the vacuum and into the bulk and are thus located at the surface and called surface states.



They are characterized by the quantum number  $\vec{k}_{\parallel}$  and an energy  $E(\vec{k}_{\parallel})$ .

$k_{\perp}$  is not a good quantum number any more because of the broken periodicity in the direction perpendicular to the surface.

We have assumed a perfect surface in the sense that the periodicity parallel to the surface remains the same as in the bulk

# Surface States and related ideas

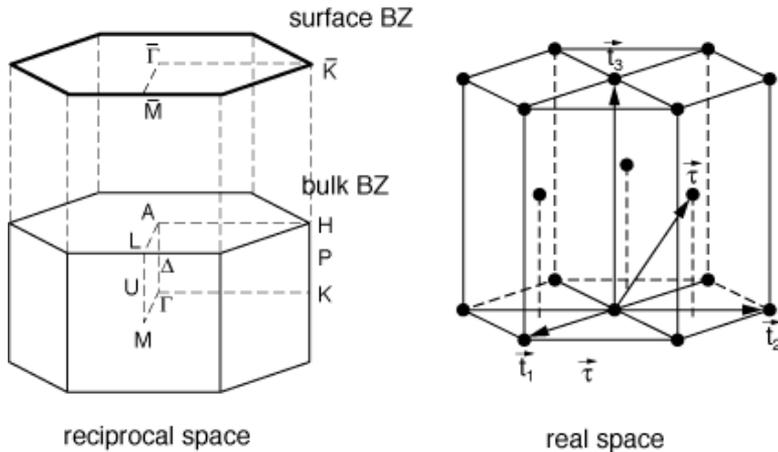
It is important to realize that **a true surface state** can not be degenerate with any bulk state.

By this we mean the following: For a true surface state with  $\vec{k}_{||}^+$  and  $E(\vec{k}_{||}^+)$  there can not be any bulk state with the same energy and  $\vec{k}_{||}^+$  for any value of  $k_{\perp}$ , i.e. on the whole  $k_{\perp}$ -rod of the surface state.

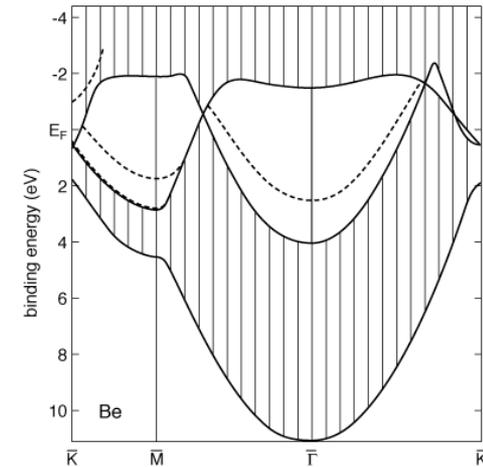
If there was such a state, the surface state could couple to it and penetrate infinitely into the bulk. It would not be a surface state any more (surface resonance, increased amplitude at the surface, but evolves continuously into a bulk state).

**The translational symmetry parallel to the surface results in selection rule of the conservation of the wavenumber parallel to the surface in analogy with the case of the three-dimensional periodicity in the theory of optical properties of solid (vertical transitions).**

This requirement gives a necessary condition for the existence of a surface state. We can illustrate it by introducing the concept of the projected bulk band structure. Figure shows the structure and Brillouin zone of the hcp metal Be and the surface Brillouin zone for the closed packed Be(0001) surface.



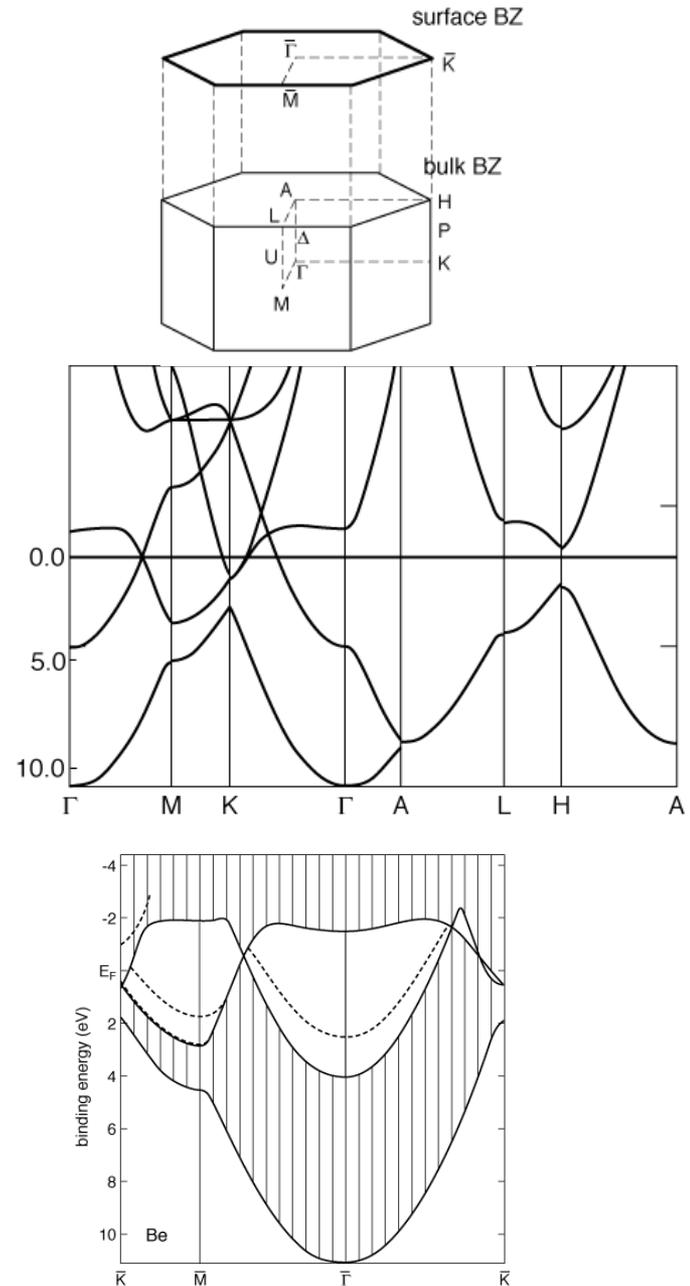
Real space structure and Brillouin zone of Be. The surface Brillouin zone of Be(0001) is the projection of the bulk Brillouin zone in the (0001) direction.



Projected bulk band structure and electronic surface states for Be(0001). For the shaded areas there are bulk states with the same  $k_{||}$  and energy for a  $k_{\perp}$  somewhere in the bulk Brillouin zone.

Every point in the surface Brillouin zone is characterized by a  $\vec{k}_{||}$ . For every point we can ask: at which binding energies are there bulk electronic states with this particular  $\vec{k}_{||}$  and an arbitrary  $\vec{k}_{\perp}$  somewhere in the bulk Brillouin zone. The answer to this question for many points along high-symmetry lines of the surface Brillouin zone is the so-called projected band structure. For Be(0001), it is shown in Figure

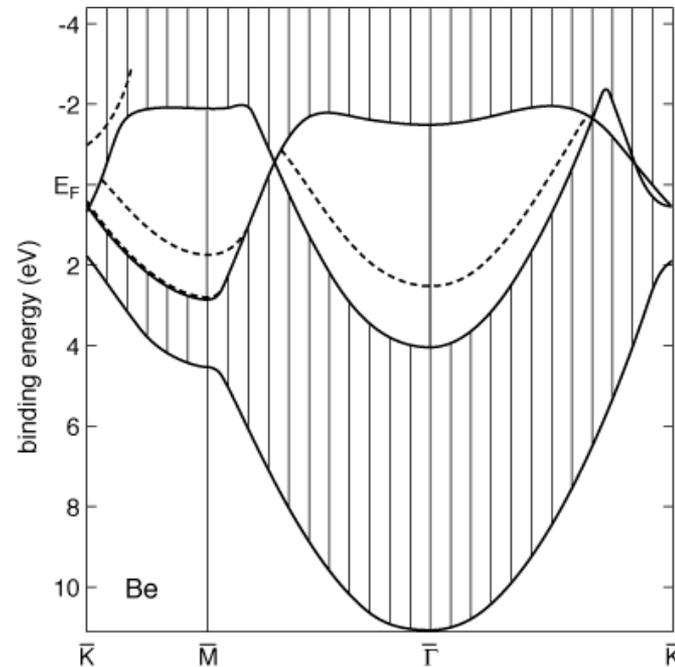
In order to illustrate again how the projected band structure is formed, we calculate it for just one point,  $\vec{k}_{\parallel} = (0, 0) = \bar{\Gamma}$ , i.e. the centre of the surface Brillouin zone. For this point we have to consider all the k-points in the bulk Brillouin zone with the same  $\vec{k}_{\parallel}$ . These points lie all along the  $\Gamma - A$  direction of the bulk Brillouin zone. Now let us look at the bulk band structure in this direction in Figure. There is a free-electron like band going from  $\Gamma$  to A, being folded back to  $\Gamma$ . For all energies between the bottom of the valence band and a binding energy of about 4 eV it is possible to find a value of  $k_{\perp}$  such that there is a bulk state with  $\vec{k}_{\parallel} = (0, 0)$  at that energy. So there can not be any surface states. This energy range is also shaded for the  $\bar{\Gamma}$  point, i.e. for  $\vec{k}_{\parallel} = (0, 0)$  in Figure. At higher energies, up to the Fermi level, there are no bulk states in the  $\Gamma - A$  direction. There is a gap in the projected bulk band structure where a surface state could "live". Figure before does indeed show one as a dashed line.



A close inspection of Figure shows that there are also dashed lines (meaning surface states) which do go into the projected bulk band continuum, in contrast to what we have said above.

They are the so called surface resonances introduced above.

These are bulk states with a high amplitude at the surface..

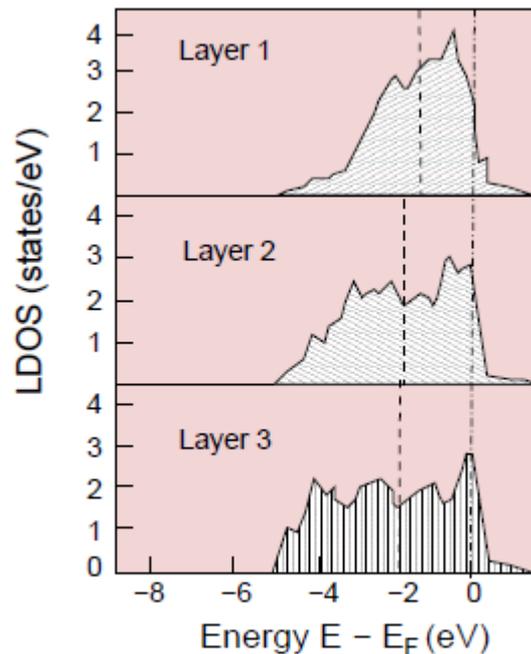


# Surface States and related ideas

In metals absolute band gaps are in general not present. Surface states are expected to exist in relative gaps, that is, for specific values of  $k_{\parallel}$ .

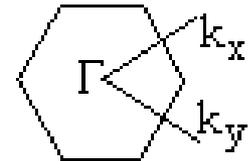
Calculations of bulk bands extended to a local density of states at the surface show a pronounced **narrowing** of the bulk bands near the surface, the width being roughly proportional to the **square root** of the number of neighbouring atoms (coordination number).

The narrowing is occurring at the bottom of the band (lowest energies).



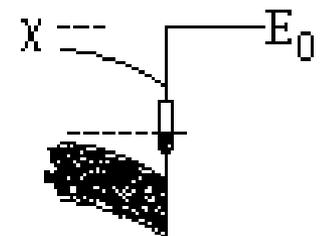
# Surface Brillouin Zone

A surface state takes the form of a *Bloch wave* in the 2-dimensions of the surface, in which there can be energy dispersion as a function of the  $k_{//}$  (parallel) vector. For electrons crossing the surface barrier,  $k_{//}$  is conserved,  $k_{\perp}$  (perpendicular) is not. The  **$k_{//}$  conservation is to within a 2D reciprocal lattice vector, i.e.  $\pm\mathbf{G}_{//}$** . This is the theoretical basis of (electron and other) diffraction from surfaces.



## Band Bending, due to Surface States

In a semiconductor, the bands can be bent near the surface due to surface states. Under zero bias, the **Fermi level** has to be 'level', and this level typically **goes through the surface states** which lie in the band gap. Thus you can convince yourself that a p-type semiconductor has bands which are bent downwards as you approach the surface. This leads to a reduction in the electron affinity. Some materials (eg Cs/p-type GaAs) can even be activated to **negative electron affinity**, and such materials form a potent source of electrons, which can also be spin-polarised as a result of the band structure.



## Optical properties of solids:

$M_{fi} = \langle f | \mathbf{A} \cdot \mathbf{p} + \mathbf{p} \cdot \mathbf{A} | i \rangle$ : matrix element, Fermi Golden rule.

Normally  $\nabla \cdot \mathbf{A} = 0$  everywhere in a medium with constant dielectric properties. This allows to simplify  $M_{fi} = \langle f | \mathbf{A} \cdot \mathbf{p} | i \rangle$  (dipole matrix element).

Now:  $\nabla \cdot \mathbf{A} = c/\epsilon\omega \mathbf{E} \cdot \nabla \epsilon$

At an interface, where there is a discontinuity in the dielectric properties of the medium, the divergence of the vector potential may take appreciable values.

This is particularly relevant in for the optical properties, since the gradient of the dielectric constant will vanish except within a few ångstrom from the interface.

$\nabla \cdot \mathbf{A} \neq 0 \rightarrow \mathbf{p} \cdot \mathbf{A}$  has to be considered too, in the matrix element. This is termed divergence term or surface-field term, being surface specific (surface selection rules).

Very important in photoemission.

## Photoemission from surfaces

At surface, the non-periodicity normal to the solid-vacuum interface can supply normal momentum as required during the electron-escape process. The surface can be regarded as a momentum source.

The simplest way to visualize this is by use of the Heisenberg uncertainty principle. Localization of the wave function near the solid-vacuum interface imposes limitation on the  $z$ -coordinate of the electron, so its momentum spread normal to the surface increases. A spatial limitation into the lattice layer in the surface results in a normal momentum uncertainty equal to the size of the Brillouin zone in the bulk, so optical transition may be excited between electron states without consideration of wavevector selection rules.

**In other words, the surface offers a continuous spectrum of normal  $k$ -vectors, from which the energy selection rule picks the appropriate one for the optical excitation.**

## Escape across the surface

The electrons capable of escaping are those whose component of kinetic energy normal to the surface is sufficient to surmount the potential barrier.

This means  $\hbar \mathbf{k}_{\perp}^2/2m \geq \phi$ .

This condition defines a cone (escape cone). If  $\theta$  denotes the angle between  $\mathbf{k}$  and the normal at the surface, the condition above becomes:

$$\cos\theta = \mathbf{k}_{\perp} / k \geq (\phi/E)^{1/2}$$

where  $E$  equal  $\hbar k^2/2m$ , the kinetic energy inside the metal (works well at high energy).

But we have to apply the  $\mathbf{k}_{\parallel}$  conservation law (single crystal faces or flat surface as a consequence of wavefunction continuity) together with  $\partial E/\partial k_{\perp} > 0$ . Due to the energy conservation  $k_{\text{out}} \neq k_{\text{in}}$ , the electron is refracted into direction  $\mathbf{k}_{\text{out}}$  outside.

The normal momentum difference inherent in the in the refraction process is taken up by the surface.

Even more: the surface can act both as a source or a sink of normal momentum!. It supplies the momentum required to fulfil both  $\mathbf{k}_{\parallel}$  and energy conservation laws. There is no minimum positive group velocity ( $\partial E/\partial k_{\perp}$ ) necessary for emission, which explains the puzzling observation that photoelectron spectra “see” electron at the centre or border of the Brillouin zone, where the group velocity vanishes.

## The Image Force

There is also a completely different type of surface states which we should mention in a few words. Consider an electron in front of a metal surface. The screening properties of the metal can be described by a positive image charge in the metal which has an attractive interaction with the electron. One can describe this as if the electron moves inside an attractive Coulomb potential in front of the surface. Such a potential can actually support unoccupied bound states, so-called image potential states. These states lie above the Fermi energy of the solid but below the vacuum energy. This means that image potential states can be populated but the electrons in these states can not leave the solid.

You will recall from elementary electrostatics that a charge outside a conducting plane has a field on it equivalent to that produced by a fictitious 'image charge'.

The corresponding potential felt by the electron,  $V(z) = -e/4z$ .

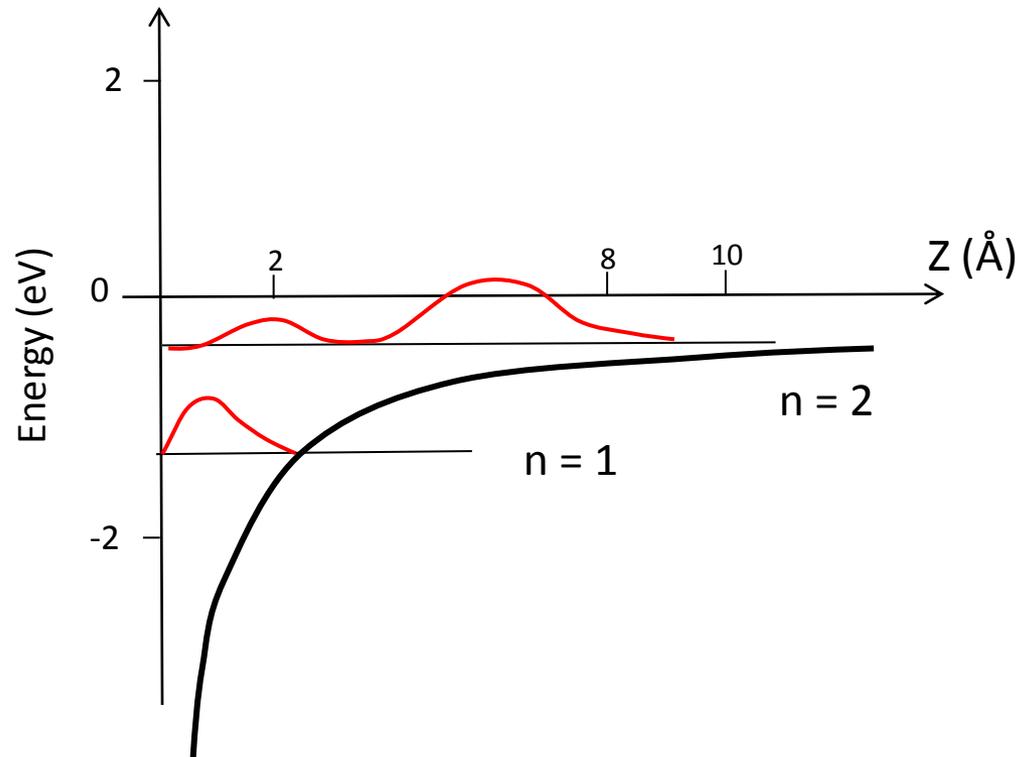
For a dielectric, with permittivity  $\epsilon$ , there is also a (reduced) potential

$$V(z) = -(e/4z) (\epsilon-1)/(\epsilon+1).$$

It is often useful to think of metals as the limit  $\epsilon \rightarrow \infty$ , and vacuum as  $\epsilon \rightarrow 1$ .

- An electron can be trapped by its own image potential.
- The problem is similar to the radial Schrödinger equation for the hydrogen atom with the boundary condition  $\Psi = 0$  at  $z = 0$  (potential infinitely repulsive at  $z = 0$ ).
- Binding energies are given by:

$$- e_n = 1/16 n^2 \cdot (\epsilon - 1)^2 / (\epsilon + 1)^2 \quad n = 1, 2 \dots$$



# Plasmons

**Plasmon:** The quanta of waves produced by collective effects of large numbers of electrons in matter when the electrons are disturbed from equilibrium.

The quantum of Plasma Oscillation is called Plasmon

Metals provide the best evidence of plasmons, because they have a high density of electrons free to move.

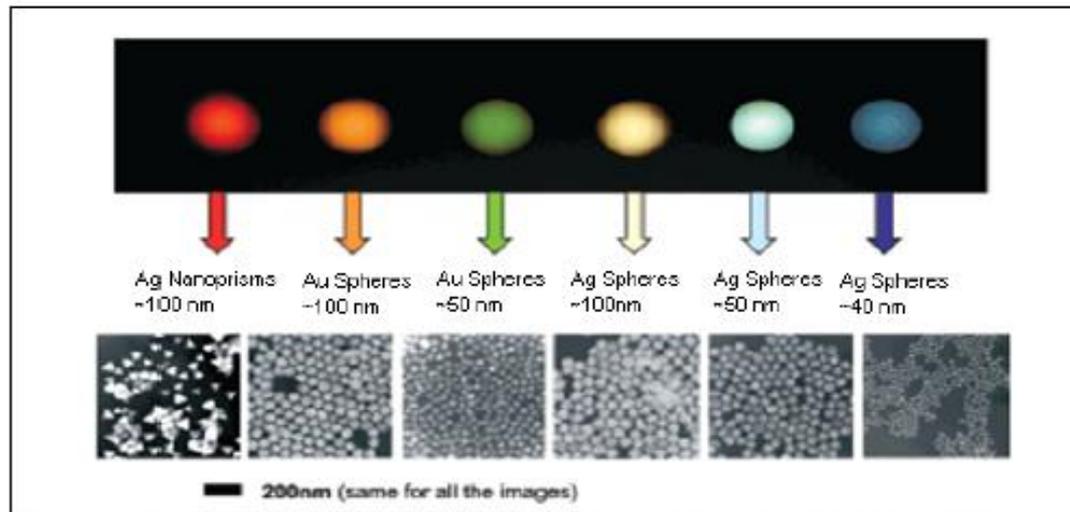
The name plasmon derives from the physical plasma as a state of matter in which the atoms are ionized. At the lowest densities this means an ionized gas, or classical plasma; but densities are much higher in a metal, the atoms of a solid metal being in the form of ions. In both types of physical plasma, the frequency of plasma-wave oscillation is determined by the electronic density. In a quantum plasma the energy of the plasmon is its frequency multiplied by *Planck's constant*, a basic relationship of quantum mechanics.

Plasmons play a large role in the optical properties of metals. Light of frequency below the **plasma frequency** is reflected, because the electrons in the metal screen the electric field of the light. Light of frequency above the plasma frequency is transmitted, because the electrons cannot respond fast enough to screen it. In most metals, the plasma frequency is in the ultraviolet, making them shiny (reflective) in the visible range. On the other hand, some metals, such as copper, have a plasmon frequency in the visible range, yielding their distinct color.

**The geometry of the metal film plays an important** role in plasmon frequency. For example gold, has plasmon frequency in the deep ultraviolet, but geometric factors bring it close to the visible.

In doped semiconductors, the plasma frequency is usually in the infrared.

Sizes, shapes, and compositions of metal nanoparticles can be systematically varied to produce materials with distinct light-scattering properties.



The plasmon energy for most metals corresponds to that of an ultraviolet photon. However, as mentioned above for **some metals like silver, gold, the alkali metals**, and a few other materials, the plasmon energy can be sufficiently low to correspond to that of a visible or near-ultraviolet photon. **This means there is a possibility of exciting plasmons by light.**

**If plasmons are confined upon a surface**, optical effects can be easily observed. In this case, the quanta are called **surface plasmons, SP**, and they have the bulk plasmon energy as an upper energy limit.

Surface plasmons were first proposed to explain energy losses by electrons reflected from metal surfaces. Since then, numerous experiments have involved coupling photons to surface plasmons. Potential applications extend to new light sources, solar cells, holography, Raman spectroscopy, microscopy, and sensors.

## Drude theory: why are metals shiny?

- Drude's theory, or rather a theory with free electrons, gives an explanation of why metals do not transmit / reflect light.

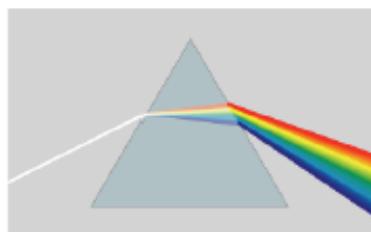
## Some relations from basic optics wave propagation in matter

plane wave  $\mathbf{E}(z, t) = \mathbf{E}_0 e^{i(kz - \omega t)}$

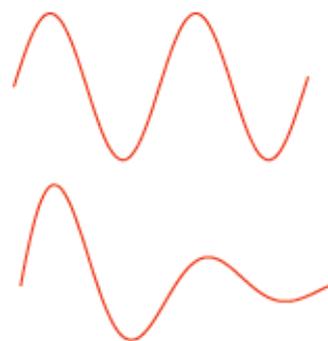
$$k = \frac{2\pi N}{\lambda_0}$$

complex index  
of refraction

$$N = n + i\kappa$$



$$\mathbf{E}(z, t) = \mathbf{E}_0 e^{i\left(\frac{2\pi n}{\lambda_0} z - \omega t\right)} e^{-\left(\frac{2\pi \kappa}{\lambda_0}\right) z}$$



Maxwell relation  $N = \sqrt{\epsilon} = \sqrt{\epsilon_r + i\epsilon_i}$

$$\mathbf{E}(z, t) = \mathbf{E}_0 e^{i\left(\frac{2\pi N}{\lambda_0} z - \omega t\right)} = \mathbf{E}_0 e^{i\left(\frac{\omega \sqrt{\epsilon}}{c} z - \omega t\right)}$$

all the interesting physics in in the dielectric function!

# Free-electron dielectric function

one electron in  
time-dependent field

$$m_e \frac{d^2 x(t)}{dt^2} = -eE(t)$$

we write

$$E(t) = Ee^{-i\omega t}$$
$$x(t) = xe^{-i\omega t}$$

$$-m_e \omega^2 x = -eE$$

and get

$$x = \frac{eE}{m_e \omega^2}$$

the dipole moment  
for one electron is

$$P = -ex$$

and for a unit volume  
of solid it is

$$P = -nex = -\frac{ne^2 E}{m_e \omega^2}$$

## Free-electron dielectric function

$$P = -nex = -\frac{ne^2 E}{m_e \omega^2}$$

we use

$$D = \epsilon \epsilon_0 E = \epsilon_0 E + P$$

to get

$$\epsilon = 1 + \frac{P}{\epsilon_0 E}$$

so the final  
result is

$$\epsilon = 1 - \frac{ne^2}{\epsilon_0 m_e \omega^2} = 1 - \frac{\omega_P^2}{\omega^2}$$

$$\omega_P^2 = \frac{ne^2}{m_e \epsilon_0} \quad \text{is called} \\ \text{the plasma frequency}$$

# Meaning of the plasma frequency

the dielectric function in the Drude model is

$$\epsilon(\omega) = \left(1 - \frac{\omega_P^2}{\omega^2}\right) \quad \text{with} \quad \omega_P^2 = \frac{ne^2}{m_e \epsilon_0}$$

remember

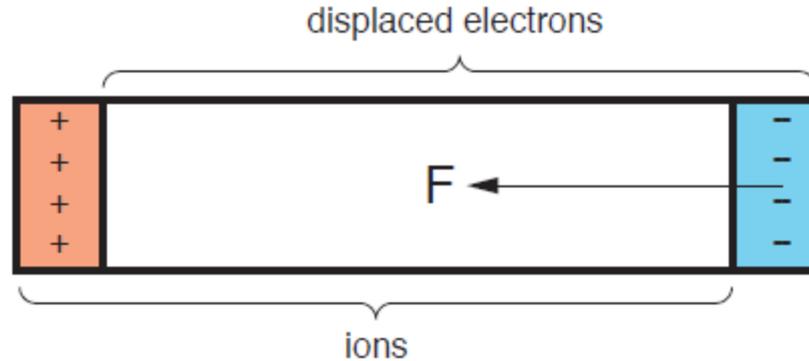
$$\vec{E} = \vec{E}_0 e^{i\left(\frac{2\pi N}{\lambda_0} x - \omega t\right)} = \vec{E}_0 e^{i\left(\frac{\omega \sqrt{\epsilon}}{c} x - \omega t\right)}$$

$$\begin{array}{ll} \omega < \omega_P & \epsilon \text{ real and negative, no wave propagation} \\ & \text{metal is opaque} \\ \omega > \omega_P & \epsilon \text{ real and positive, propagating waves} \\ & \text{metal is transparent} \end{array}$$

We can distinguish between two cases: if  $\omega < \omega_P$  then  $\epsilon$  is real and negative and Eq. above, gives only **exponentially damped solutions**. This means that an electric field can not penetrate a metal, the metal **is reflecting all the light**.

Above the plasma frequency Eq. above does permit propagating solutions of the electric field. For simple metals, there is a good agreement with the calculated plasma frequency  $\omega_P$ , or plasmon energy  $\hbar\omega_P$ , and the experimental values.

# plasma frequency: simple interpretation



values for the plasma energy  $\hbar\omega_P$

	measured	calculated
K	3.72 eV	4.29 eV
Mg	10.6 eV	10.9 eV
Al	15.3 eV	15.8 eV
Si	16.6 eV	16.0 eV
Ge	16.2 eV	16.0 eV

- longitudinal collective mode of the whole electron gas

Surface plasmons (SPs), are coherent electron oscillations that exist at the interface between any two materials where the real part of the dielectric function changes sign across the interface (e.g. a metal-dielectric interface, such as a metal sheet in air).

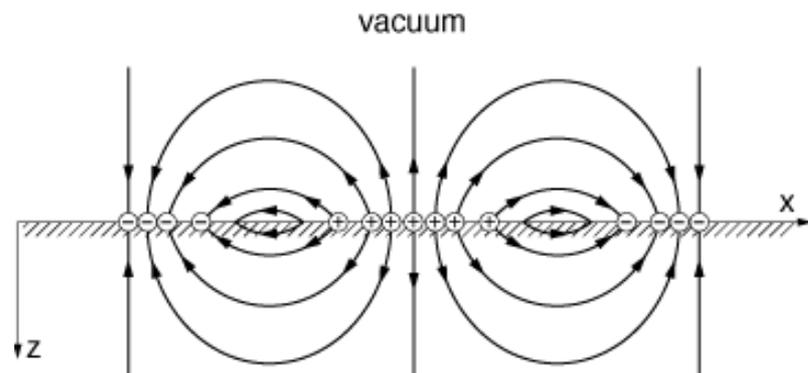
SPs have lower energy than bulk (or volume) plasmons which quantise the longitudinal electron oscillations about positive ion cores within the bulk of an electron gas (or plasma).

A Surface plasmon mode is localized at a metal surface and decays exponentially towards both metal and dielectric can be described as a longitudinal wave

$$\Phi(\vec{r}) = \Phi_0 e^{iq_{\parallel} r_{\parallel}} e^{-q_{\parallel} |z|}.$$

A plasmon propagates along the metal-dielectric interface.

Figure shows the field and charge distribution for such a mode.



*Charge and field distribution for a surface plasmon*

The planar component of the  $\vec{E}$  field associated with this is continuous but the perpendicular component is not. Just above and below the surface it is

$$E(z+0) = \Phi_0 q_{||} e^{iq_{||} z} \quad \text{and} \quad E(z-0) = -\Phi_0 q_{||} e^{iq_{||} z}$$

Now the  $\vec{D} = \epsilon \vec{E}$  field must be continuous.

This gives us the condition for the existence of the surface plasmon

$$\epsilon(\omega_{SP}) = -1$$

and hence

$$\omega_{SP} = \omega_P / \sqrt{2} \quad \text{In case of air}$$

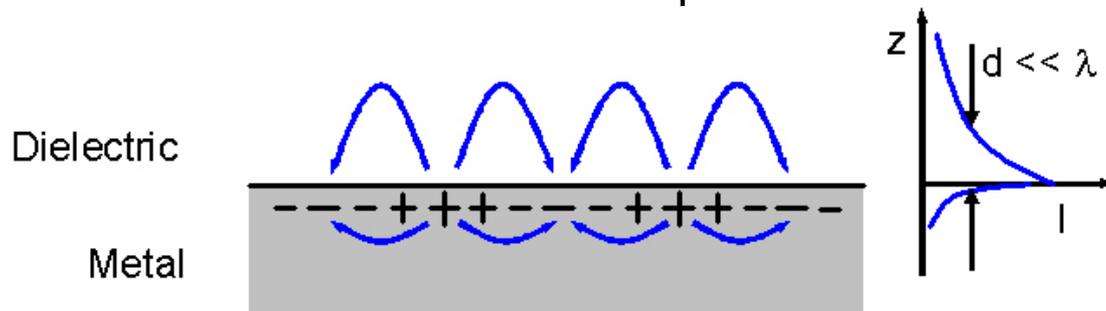
$$\omega_{SP} = \omega_P / \sqrt{1 + \epsilon_2}. \quad \text{For a general dielectric}$$

A **surface plasmon** is a collective excitation located at the surface, with frequency typically  $\omega_{SP} = \omega_P / \sqrt{2}$ . or more in general  $\omega_{SP} = \omega_P / \sqrt{1 + \epsilon_2}$ .

Surface plasmons are those plasmons that are confined to surfaces and that interact strongly with light resulting in a polariton.

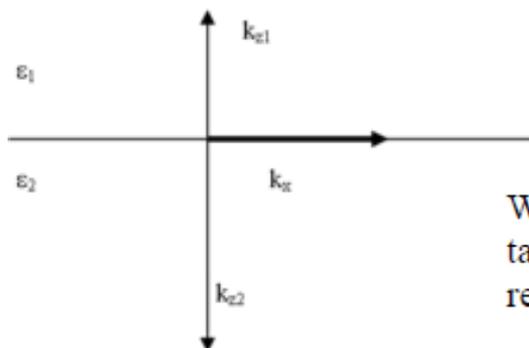
When SPs couple with a photon, the resulting hybridised excitation is called a surface plasmon polariton (SPP). This is a surface mode trapped at the interface which will have electromagnetic fields decaying into both media, but which tied to the oscillating surface charge density propagates along the interface.

This SPP can propagate along the surface of a metal until energy is lost either via absorption in the metal or radiation into free-space.



A propagating wave has the mathematical form  $E_1 = A \exp[i(k_x x - \omega t)]$

$k_x$  is a complex function;  $k_x = k_x' + ik_x''$ . The real part is that of a travelling wave while the imaginary part is a damping term due to real metals having resistive scattering. Therefore as the surface plasmon propagates in the x direction it will decay in amplitude. The propagation length depends on the frequency of the SPP (Surface Plasmon Polariton) mode and the plasma frequency. For silver it is around 100  $\mu\text{m}$



$$E = E_0 \exp[i(k_x x + k_z z - \omega t)]$$

We can apply the boundary conditions at  $z = 0$ . Tangential  $\mathbf{H}$  is continuous and so is tangential  $\mathbf{E}$  thus  $H_{y1} = H_{y2}$  and  $E_{x1} = E_{x2}$  leading to a simple relationship between the relative permittives and the normal components of the wave vectors.

$$\frac{k_{z1}}{\epsilon_1} + \frac{k_{z2}}{\epsilon_2} = 0 \quad k_{xi}^2 + k_{zi}^2 = \epsilon_i \left(\frac{\omega}{c}\right)^2 \quad i = 1, 2$$



$$k_x = \frac{\omega}{c} \left( \frac{\epsilon_1 \epsilon_2}{\epsilon_1 + \epsilon_2} \right)^{1/2} .$$

The requirement for a propagating wave mode is that  $k_x$  is real with  $\epsilon_2$  negative, we can see that  $|\epsilon_2| > \epsilon_1$ . Thus  $|\epsilon_2| > \epsilon_1$  and  $\epsilon_2 < 0$

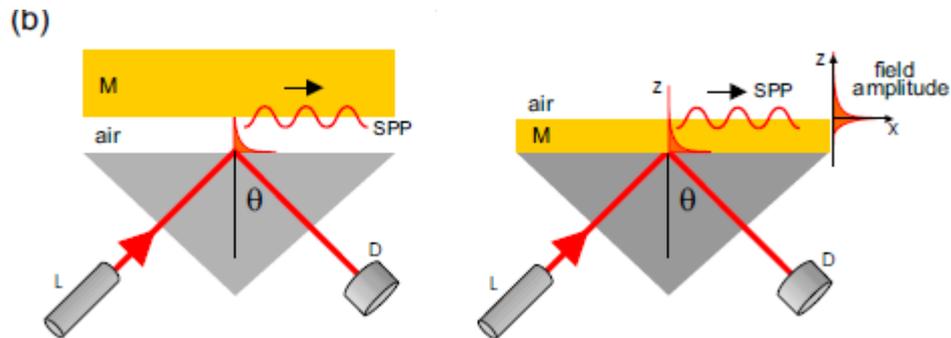
# Surface Plasmon Resonance

The excitation of surface **plasmons** by light is denoted as a **surface plasmon resonance** (SPR) for planar surfaces or **localized surface plasmon resonance** (LSPR) for nanometer-sized metallic structures.

**Surface plasmon polaritons (SPP)**, ( coupling between photon and an excitation of a material) are surface electromagnetic waves that propagate parallel along a metal/dielectric interface. **For surface plasmons to exist, the complex dielectric constants of the two media must be of opposite sign.** This condition is met in the IR-visible wavelength region for air/metal and water/metal interfaces (where the real dielectric constant of a metal is negative and that of air or water is positive). Typical metals that support surface plasmons are silver and gold, but metals such as copper, titanium, or chromium can also support surface plasmon generation.

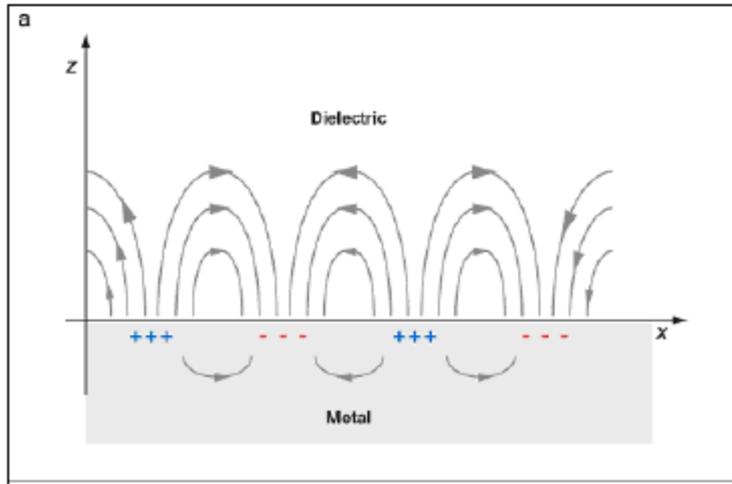
## Excitation of surface plasmons

At an interface between two transparent media of different refractive index (glass and water), light coming from the side of higher refractive index is partly reflected and partly refracted. Above a certain critical angle of incidence, no light is refracted across the interface, and total internal reflection is observed. While incident light is totally reflected the electromagnetic field component penetrates a short (tens of nanometers) distance into a medium of a lower refractive index creating an **exponentially attenuating evanescent wave**. If the interface between the media is coated with a thin layer of metal (gold), and light is monochromatic and TM-polarized, the intensity of the reflected light is reduced at a specific incident angle producing a sharp shadow (called surface plasmon resonance) due to the resonance energy transfer between evanescent wave and surface plasmons.

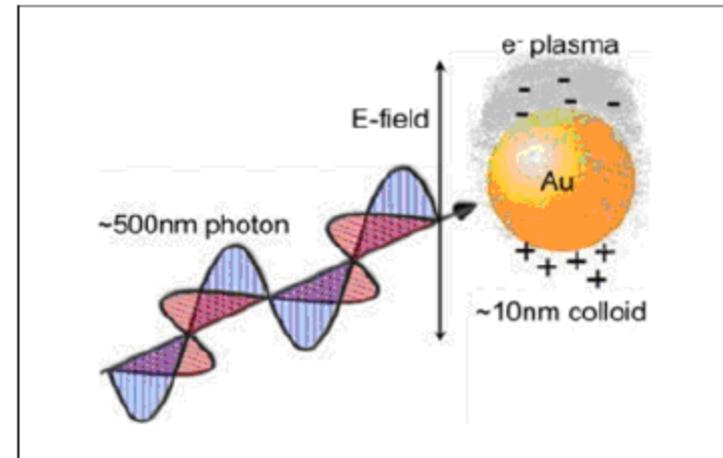


Surface plasmons on a plane surface are non-radiative electromagnetic modes, that is, SPP cannot be generated directly by light nor can they decay spontaneously into photons. The origin of the non-radiative nature of SPP is that the interaction between light and SP cannot simultaneously satisfy energy and momentum conservation. This restriction can be circumvented by relaxing the momentum conservation requirement by roughening or corrugating the metal surface. Other method is to increase the effective wave vector (and hence momentum) of the light by some means (discussed later).

# Surface Plasmon and Localized Surface Plasmon Resonance

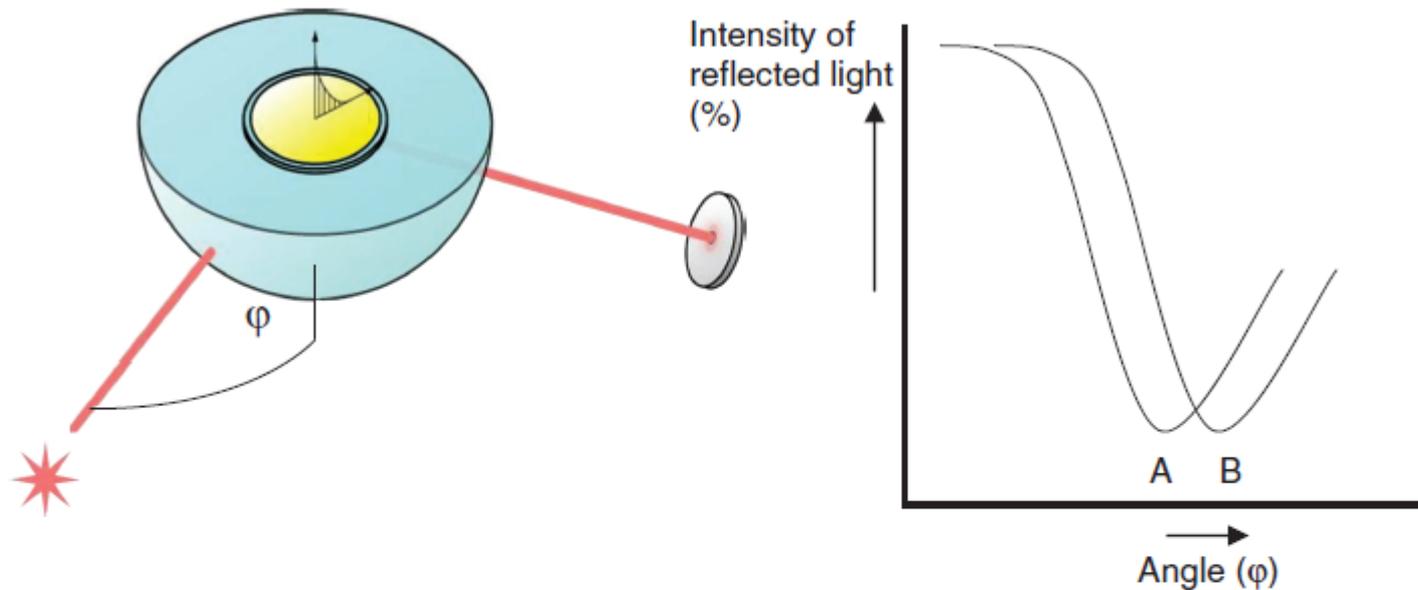


- Surface Plasmon (SP): Charge density wave that exists at the interface between metal and dielectric - Plasmons propagate along metal dielectric interface
- Excitation of SP: momentum of incident photon = that of plasmon  $\rightarrow$  resonance
- Sensing; measurement of absorption: function of angle of incidence or function  $\lambda$  (we used the latter)



- Light at certain  $\lambda$  causes conduction electrons oscillate around the nanoparticles
- LSPR is similar to SPR but it is localized – refers to the frequency at which plasmons oscillate around the nanoparticle – or when light is in resonance with collective oscillation of electrons
- Sensing; measurement of absorption: function of angle of incidence or function  $\lambda$  (we used the latter)

During the last two decades many researches devoted to develop optical sensors for the measurement of chemical and biological quantities. In the beginning, the optical chemical sensors were based on the measurement of changes in absorption spectrum and were developed for the measurement of CO<sub>2</sub> and O<sub>2</sub> concentrations. Since then, a large variety of optical methods have been used in chemical and biosensors, among them, Surface Plasmon Resonance. In these sensors, a desired quantity is determined by measuring the refractive index, absorbance and fluorescence properties of analyte molecules.



**Figure 1.1** Schematic experimental set-up of surface plasmon resonance excitation. A sensor chip with a gold coating is placed on a hemisphere (or prism). Polarized light shines from the light source (star) on the sensor chip. Reflected light intensity is measured in the detector (disk). At a certain angle of incidence ( $\phi$ ), excitation of surface plasmons occurs, resulting in a dip in the intensity of the reflected light (A). A change in refractive index at the surface of the gold film will cause an angle shift from A to B.

Surface plasmon resonance is an excellent method to monitor changes of the refractive index in the near vicinity of the metal surface. When the refractive index changes, the angle at which the intensity minimum is observed will shift as indicated in Figure