F7360 Characterization of thin films and surfaces

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3. Chapter - Introduction to Surface Processes
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Outline

- 3. Introduction to Surface Processes
- 3.1 Thermodynamics of Clean Surfaces
- 3.2 Electronic Structure of Clean Surfaces
- 3.3 Work Function
- 3.4 Thermoemission
- 3.5 Gas Adsorption to Surfaces
- 3.6 Surface Relaxation & Reconstruction
- 3.7 Methods for Preparation of Clean Surfaces

Introduction

We need to introduce the concept of **surface (free) energy**, **surface tension** and **surface stress**. The essential features of bulk thermodynamics (e. g. Callen, 1985)

- in equilibrium, a one-component system is characterized completely by internal energy, U
- U is a unique function of extensive parameters, entropy S, volume V and particle number of the system N and extensive property can be written as $U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N)$

$$U = U(S, V, N) \qquad \mathrm{d}U = |\frac{\partial U}{\partial S}|_{V,N}\mathrm{d}S + |\frac{\partial U}{\partial V}|_{S,N}\mathrm{d}V + |\frac{\partial U}{\partial N}|_{S,V}\mathrm{d}N,$$

It defines intensive parameters, the temperature T, pressure p and chemical potential μ

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \mu\mathrm{d}N.$$

that are function of independent extensive parameters S, V and N.
Differentiating the **Euler equation**

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

we can derive a relation among the intensive variables, the **Gibbs-Duhem equation**

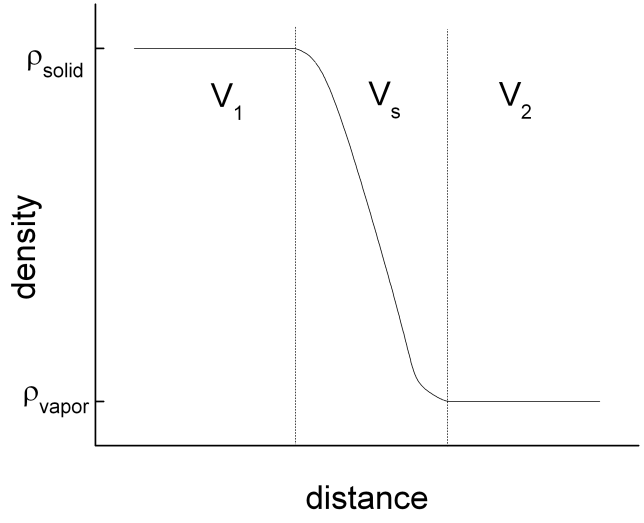
$$S\mathrm{d}T - V\mathrm{d}p + N\mathrm{d}\mu = 0$$

Surface Tension γ

Let's create a surface of area A from the infinite solid by a cleavage process. The total energy of the system must increase by amount proportional to A. The constant of proportionality, γ, is called **surface tension** ($[\gamma] = \mathrm{J/m^2}$)

$$U = TS - pV + \mu N + \gamma A.$$

In equilibrium, at any finite T and p, the semi-infinite solid coexists with its vapor. Gibbs ascribed definite amounts of the extensive variables to a given area of surface.



There is nothing unique about the particular choice of the boundary positions

$$V = V_1 + V_2 + V_s,$$
$$S = S_1 + S_2 + S_s,$$
$$N = N_1 + N_2 + N_s.$$

Once the surface volume is chosen, the other surface quantities are defined as excesses. Changes of surface quantities are completely determined by changes in the bulk quantities

$$\Delta S_s = -\Delta S_1 - \Delta S_2,$$
$$\Delta V_s = -\Delta V_1 - \Delta V_2,$$
$$\Delta N_s = -\Delta N_1 - \Delta N_2.$$

Surface Tension γ and Surface Energy f_s

We can take Gibbs G (used for constant p, T, N processes) or Helmholtz F (used for constant V, T, N processes) free energy

$$\mathrm{d}F_\mathrm{b} = -p\mathrm{d}V - S\mathrm{d}T + \Sigma_i \mu_i \mathrm{d}N_i \qquad \mathrm{d}G_\mathrm{b} = -V\mathrm{d}p - S\mathrm{d}T + \Sigma_i \mu_i \mathrm{d}N_i$$

No operational need to distinguish between F and G for the purpose of measurements (see R. J. Good, J. Colloid Interface Sci. 59, 1977, 398). At constant V and T

According to previous definition the surface tension γ is the reversible work done in creating unit area of new surface.

$$\gamma = \left(\frac{\mathrm{d}F_\mathrm{total}}{\mathrm{d}A}\right)_{V,T}$$

How is it related to the **surface free energy f_s**?

$$\mathrm{d}F_\mathrm{total} = f_\mathrm{s}\mathrm{d}A + \Sigma_i \mu_i \mathrm{d}N_i \qquad \Rightarrow \qquad \gamma\mathrm{d}A = f_\mathrm{s}\mathrm{d}A + \Sigma_i \mu_i \mathrm{d}N_i$$

In one component system, e.g. metal - vapor, we can choose the dividing surface such that $\mathrm{d}N_i = 0 \Rightarrow$ **γ and f_s are the same**

Surface Stress σ_{ij} and Strain ϵ_{ij} Tensors

Consider the effect of small variations in the area of the system, e.g., by **stretching**. The energy change can be described by linear elasticity theory (Landau & Lifshitz, 1970). Accordingly,

$$\mathrm{d}U = \frac{\partial U}{\partial S}|_{V,N,A}\,\mathrm{d}S + \frac{\partial U}{\partial V}|_{S,N,A}\,\mathrm{d}V + \frac{\partial U}{\partial N}|_{S,V,A}\,\mathrm{d}N + \sum_{i,j}|\frac{\partial U}{\partial \epsilon_{ij}}|_{S,V,N}\,\mathrm{d}\epsilon_{ij}$$

where $\sum \mathrm{d}\epsilon_{ij}\delta_{ij} = dA/A$ is the **surface strain tensor**.

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}N + A\sum_{i,j}\sigma_{ij}\mathrm{d}\epsilon_{ij}$$

where σ_{ij} is the **surface stress** in units J/m^2 = N/m.
Differentiation of Euler eq. $U = TS - pV + \mu N + \gamma A$ and its combination with above equations gives Gibbs-Duhem equation for the whole system including surface

$$A\sum_{i,j}\sigma_{ij}\,\mathrm{d}\epsilon_{ij} = S\mathrm{d}T - V\mathrm{d}p + N\mathrm{d}\mu + A\mathrm{d}\gamma + \gamma\mathrm{d}A$$

Using Gibbs-Duhem equations for both the bulk phases separately it can be reduced to quantities describing only the surface ⇒ **Gibbs adsorption equation**

$$A\mathrm{d}\gamma + S_{\mathrm{S}}\mathrm{d}T - V_{\mathrm{S}}\mathrm{d}p + N_{\mathrm{S}}\mathrm{d}\mu + A\sum_{i,j}(\gamma\delta_{ij} - \sigma_{ij}\mathrm{d}\epsilon_{ij}) = 0$$

Gibbs adsorption equation

At first glance it seems that there 5 independent variables, γ, μ, p, T and ϵ in

$$A\mathrm{d}\gamma + S_\mathrm{S}T - V_\mathrm{S}\mathrm{d}p + N_\mathrm{S}\mathrm{d}\mu + A\sum_{i,j}(\gamma\delta_{ij} - \sigma_{ij}\mathrm{d}\epsilon_{ij}) = 0$$

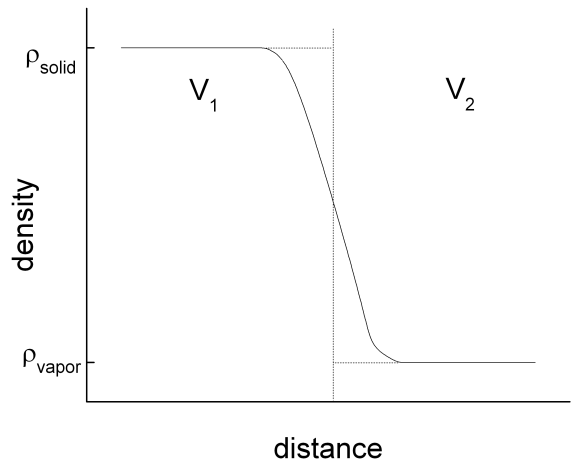
However, the two bulk phase Gibbs-Duhem relations reduce this number to 3. We define particle density $\rho_{i,j}$ and density of entropy $s_{i,j}$ for phase 1 and 2 as $N_i = \rho_i V_i$ and $S_i = s_i V_i$. Then,

$$\mathrm{d}\mu = -\frac{s_1 - s_2}{\rho_1 - \rho_2}\mathrm{d}T \qquad \mathrm{d}p = s_1\mathrm{d}T + \rho_1\mathrm{d}T - \frac{s_1 - s_2}{\rho_1 - \rho_2}$$

$$A\mathrm{d}\gamma + \left[S_\mathrm{S} - V_\mathrm{S}\frac{s_1\rho_2 - s_2\rho_1}{\rho_2 - \rho_1} + N_\mathrm{S}\frac{s_1 - s_2}{\rho_2 - \rho_1}\right]\mathrm{d}T + A\sum_{i,j}(\gamma\delta_{ij} - \sigma_{ij})\mathrm{d}\epsilon_{ij} = 0$$

It can be shown that the term in square brackets is independent of the arbitrary boundary positions defining N_S, V_S and $S_\mathrm{S} \Rightarrow V_\mathrm{S} = N_\mathrm{S} = 0$ gives simple form of **Gibbs adsorption equation**

$$A\mathrm{d}\gamma + S_\mathrm{S}\mathrm{d}T + A\sum_{i,j}(\gamma\delta_{ij} - \sigma_{ij})\mathrm{d}\epsilon_{ij} = 0$$



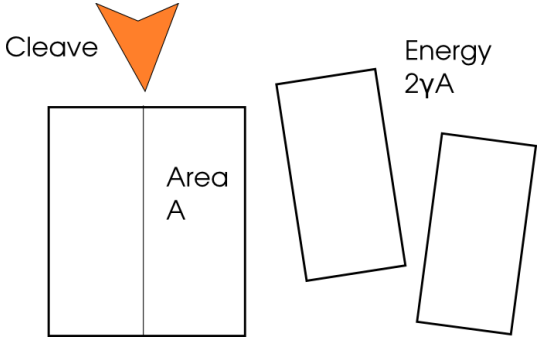
It follows from Gibbs adsorption equation that

$$\sigma_{ij} = \gamma\delta_{ij} + \frac{\partial\gamma}{\partial\epsilon_{ij}}|_T, \qquad S_{\mathrm{S}} = -A\frac{\partial\gamma}{\partial T}|_\epsilon$$

$\Rightarrow$ surface tension and stress are **identical only if $\partial\gamma/\partial\epsilon = 0$**
i. e. only if the system is free to rearrange in response to a perturbation, as in a liquid.

If $\partial\gamma/\partial\epsilon < 0$ atomic dislocations and elastic buckling of the surface can be expected.

Estimation of γ - energy cost/unit area to cleave a crystal, i. e. break bonds



. . . from bulk cohesive energy $E_{\mathrm{coh}} \approx 3\,\mathrm{eV}$,
fractional number of bonds broken $Z_{\mathrm{S}}/Z \approx 0.25$,
areal density of surface atoms $N_{\mathrm{S}} \approx 10^{15}\,\mathrm{cm}^{-2}$

$$\gamma = E_{\mathrm{coh}}\frac{Z_S}{Z}N_{\mathrm{S}} \approx 1.2\,\mathrm{J/m^2}$$

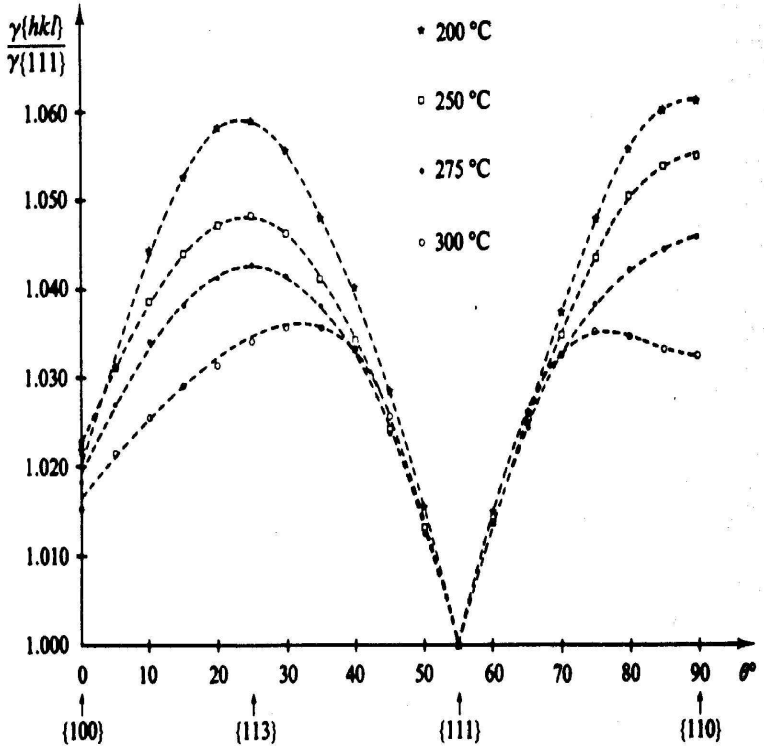
material	γ [J/m^2]
mica	4.5
gold	≈ 1
PTFE	0.019

The **surface tension can be regarded as an excess free energy/unit area**. High energy surfaces tend to **reduce energy by adsorption** of contaminants from environment.

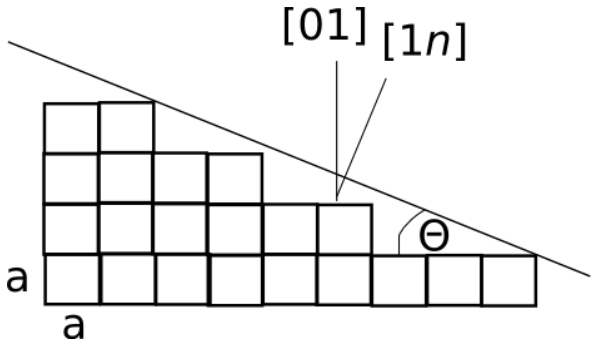
Annisotropy of γ and Wulff theorem

The tendency to minimize surface energy is a defining factor also in the morphology of surfaces and interfaces:

- Spherical equilibrium shape in an isotropic liquid (in the absence of gravity),
- In crystalline solids, the surface tension depends on the crystallographic orientation $\Rightarrow$ **minimization of** $\int \gamma(hkl)\mathrm{d}A(hkl)$ even if it implies a larger surface area.



anisotropy of γ relative to {111} for lead
Heyraud, Metois, Surf. Sci. 128, 334 (1983)

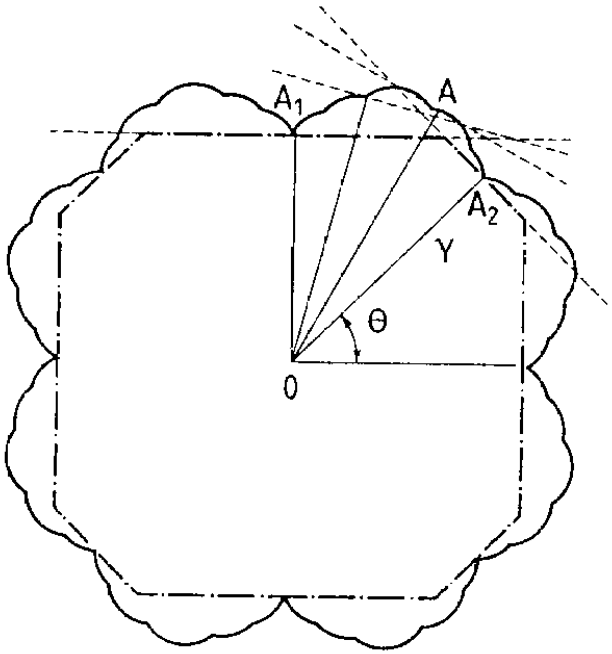


step width ... $n.a$,
step free energy ... β
tension in direction [01] ... $\gamma(0)$
for large n ... $\theta \simeq \tan\theta = a/(n.a) = 1/n$

tension in direction [1n]

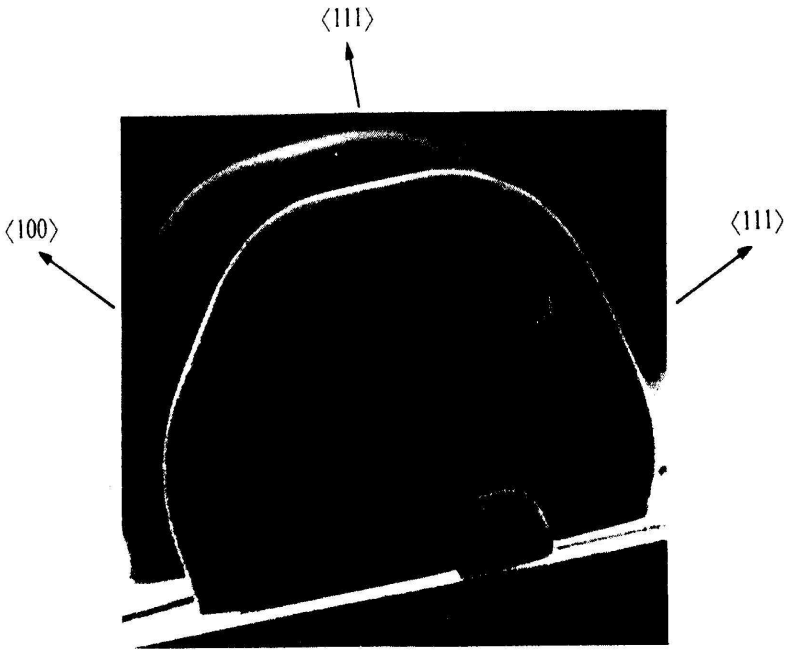
$$\gamma(\theta) = \gamma(0) + \frac{\beta}{na} = \gamma(0) + \frac{\beta}{a}|\theta|$$

Equilibrium shapes can be calculated but it is easier to use a graphics method, the **Wulff construction**.



The surface tension is plotted in polar coordinates vs. the angle.
The minimization: construction the surface from the inner envelope of planes perpendicular to the radius vector.

Faceting is energetically favored for crystals, shown example is lead at 473 K *Heyraud, Metois, Surf. Sci. 128, 334 (1983)*.



It is important to note that the formation of the equilibrium shape requires sufficient mobility (or fast kinetics), not just thermodynamics.

Roughening Transition

At finite T, the discussion must be supplemented to include entropy effects.

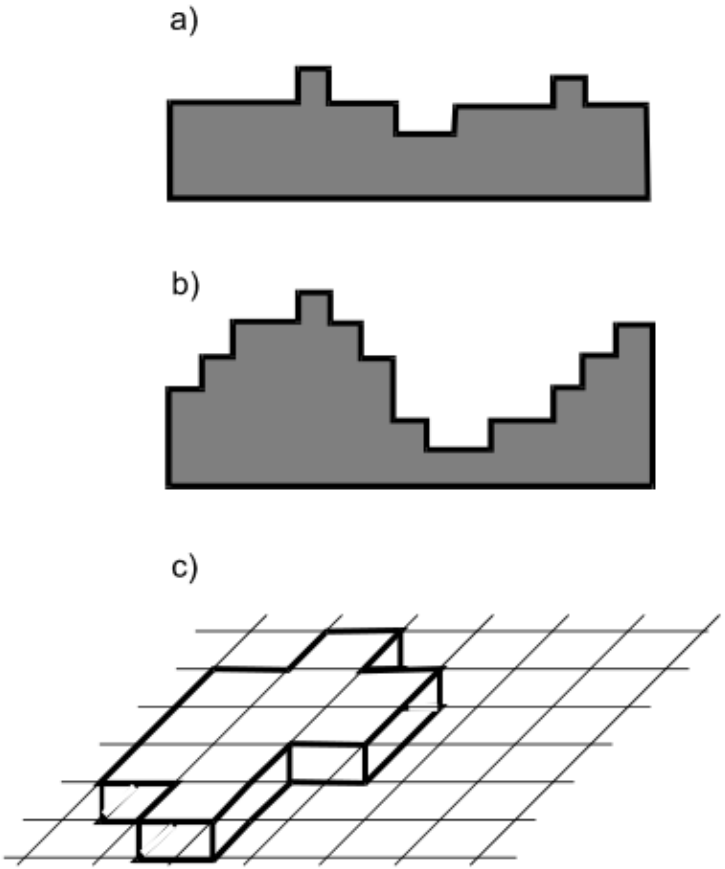


fig. a At very low T any given facet is microscopically flat with only a few thermally excited surface vacancies.

fig. b At higher T more and more energetic fluctuations in the local height of the surface can occur leading to delocalized interface with long wavelength variations in height (step free energy $\beta \downarrow$).

At certain **roughening temperature**, T_{r}, $\beta < 0$, i. e. the facets disappear and only a smoothly rounded macroscopic morphology remains (phase transition for $T = T_{\mathrm{r}}$).

Approaches to Quantum Mechanical Calculations

Knowing the positions of all the atoms in the semi-infinite crystal (described by the set of $\vec{R}$) and ignoring ion motion (Born-Oppenheimer approx.), the Hamiltonian for N electrons is

$$\hat{H} = \sum_{i=1}^{N} -\frac{\hbar^2 \nabla_i^2}{2m} - \sum_{\vec{R}} \sum_{i=1}^{N} \frac{Ze^2}{\vec{r}_i - \vec{R}} + \frac{1}{2} \sum_{i \neq j}^{N} \frac{e^2}{\vec{r}_i - \vec{r}_j} = \sum_{i=1}^{N} \hat{H}_i + \frac{1}{2} \sum_{i \neq j}^{N} \hat{V}_{ij}$$

The wave function describing the set of N electrons has the general form

$$\Psi(\vec{r}_1, S_{z1}, \vec{r}_2, S_{z2}, \ldots, \vec{r}_i, S_{zi}, \ldots \vec{r}_N, S_{zN})$$

where S_{zi} is electron spin in a chosen z-direction, with measurable values $\frac{1}{2}\hbar$ and $-\frac{1}{2}\hbar$.

Approximate methods for systems with many electrons:

- Hartree-Fock approximation - a particular case of the variational method

$$\delta J = \delta \int \Psi^* \hat{H} \Psi \mathrm{d}\tau = 0$$

  in which the trial wave function is constructed from single-electron functions
- density functional theory (DFT) - application of variational method to the energy as functional of electron density (does not need to find a trial wave function)
- simple models: nearly-free electrons, tight-binding model

Hartree-Fock Method of Self-Consistent Field

The wave function in the ground state is constructed from a set of orthonormal **single-electron functions** $\psi_i(\vec{x})$, each a product of a spatial orbital function $\phi_i(\vec{r})$ and a spin function $\sigma(S_z)$, i. e. $\vec{x} \equiv \vec{r}, S$.
Single-electron functions are combined into **multi-electron antisymmetric function** (Pauli exclusion principle has to be fulfilled) by forming products in the form of $N \times N$ Slater determinant:

$$\Psi_0 \approx \Psi_{\mathrm{HF}} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{x}_1) & \psi_2(\vec{x}_1) & \dots & \psi_N(\vec{x}_1) \\ \psi_1(\vec{x}_2) & \psi_2(\vec{x}_2) & \dots & \psi_N(\vec{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\vec{x}_N) & \psi_2(\vec{x}_N) & \dots & \psi_N(\vec{x}_N) \end{vmatrix}$$

The **Hartree-Fock method** needs to solve a set of coupled integro-differential equations that was obtained from the variational principle

$$[\hat{H}_i + \sum_{j(j\neq i)} \int \phi_i^* \hat{V}_{ij} \phi_i \mathrm{d}\tau_j - \epsilon_i]\phi_i = 0$$

in which the potential energy $\sum_{j(j\neq i)} \int \phi_i^* \hat{V}_{ij} \phi_i \mathrm{d}\tau_j$ is determined self-consistently starting from zero approximation of wave functions ϕ_i^0 of hydrogen-type atom.

$\Rightarrow$ used in quantum chemistry but is quite awkward for use in extended systems like solid surfaces

Density Functional Theory

The **electron density** is the central quantity in DFT. It is defined as the integral over the spin coordinates of all electrons and over all but one of the spatial variables, $\vec{r}_1 \equiv \vec{r}$,

$$n(\vec{r}) = N \int |\Psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N,)|^2 \mathrm{d}S_1 \mathrm{d}S_2 \ldots \mathrm{d}S_N \mathrm{d}\vec{r}_2 \mathrm{d}\vec{r}_3 \ldots \mathrm{d}\vec{r}_N$$

- The **first Hohenberg-Kohn theorem**: For any system of interacting particles in an external potential $V_{\mathrm{ext}}(\vec{r})$, $n(\vec{r})$ uniquely determines the Hamiltonian operator ($V_{\mathrm{ext}}(\vec{r})$ is a unique functional of $n(\vec{r})$) and thus all the properties of the system.
- The **second Hohenberg-Kohn theorem**: The energy of the many-body problem can be written as **functional** of the density, $E[n]$. The exact ground state is the global minimum value of this functional.

A popular form of DFT functional was introduced by Nobel laureate W. Kohn and L. Sham

$$E[n(\vec{r})] = T[n(\vec{r})] + \sum_{\vec{R}} Ze \int d\vec{r} \frac{n(\vec{r})}{|\vec{R} - \vec{r}|} + \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} + E_{\mathrm{xc}}[n(\vec{r})]$$

- $T[n(\vec{r})]$ is the **kinetic energy of a non-interacting** inhomogeneous electron gas.
- The second term is **ion-electron interaction**.
- The third term is the average **electrostatic interactions between the electrons**.
- $E_{\mathrm{xc}}[n(\vec{r})]$ is **exchange-correlation** term that represents all quantum mechanics many-body effects $E_{\mathrm{xc}}[n(\vec{r})] = \Delta E_{\mathrm{ee}} + \Delta T$.

Density Functional Theory (contin.)

The great advantage of this formulation is that the density that minimizes the energy is found by solution of a set of ordinary differential equations (Kohn-Sham)

$$\left[-\frac{1}{2}\nabla^2 + V_{\mathrm{eff}}(\vec{r})\right]\psi_i(\vec{r}) = \epsilon_i\psi_i(\vec{r})$$

$$V_{\mathrm{eff}}(\vec{r}) = Z\mathrm{e}^2\sum_{\vec{R}}\frac{1}{|\vec{r}-\vec{R}|} + \int \mathrm{d}\vec{r}'\,\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|} + V_{\mathrm{xc}}(\vec{r})$$

where $n(\vec{r}) = \sum|\psi_i|^2$.

Many-body interactions are hidden in the **exchange-correlation potential** $V_{\mathrm{xc}}(\vec{r}) = \delta E_{\mathrm{xc}}[n(\vec{r})]/\delta n(\vec{r})$ and **practical implementation requires a good approximation** for this quantity.

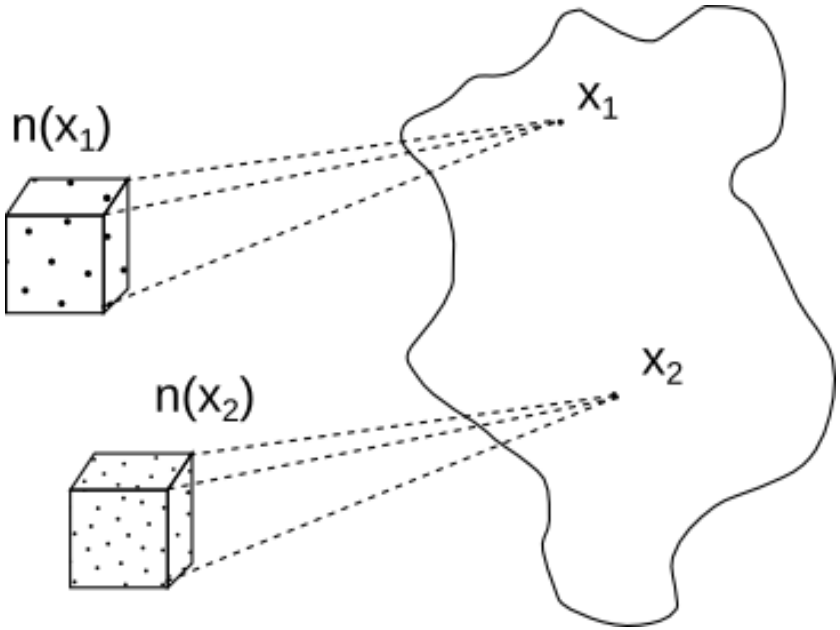
The electron density appears in the effective potential which means that the Kohn-Sham equations needs to be solved self-consistently.

The parameters ϵ_i and $\psi_i(\vec{r})$ that enter the Schrödinger-like equation formally have no physical meaning. Nevertheless, they are frequently interpreted as one-particle excitation energies and eigenfunctions, respectively.

Density Functional Theory - Local Density Approximation

It is necessary to introduce an approximation of $V_{\mathrm{xc}}(\vec{r})$
- **local density approximation (LDA)**:

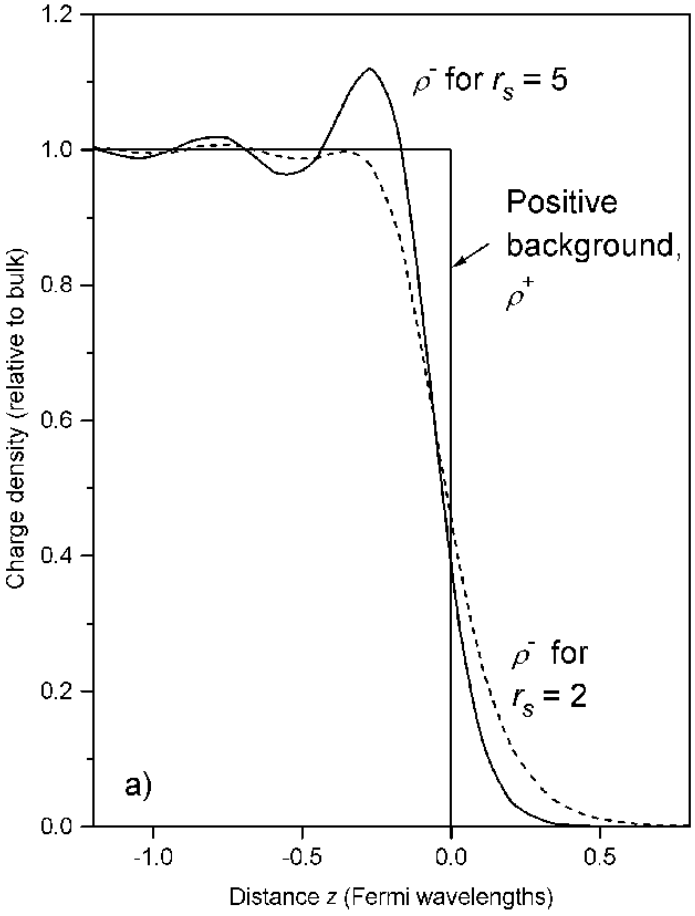
- The exchange-correlation energy density of each infinitesimal region of the **imhomogeneous** electron distribution, $n(\vec{r})$, is taken to be precisely equal to the exchange-correlation energy density of a **homogeneous electron gas (HEG)** with the same density as the corresponding infinitesimal volume element.



The LDA is easy to apply because $V_{\mathrm{xc}}(\vec{r})$ is known very precisely for the homogeneous electron gas at all densities of physical interest (*Ceperley, Alder, Phys. Rev. Lett. 45 (1980) 566*).

Density Functional Theory - Jellium Model

- The discrete ion cores are replaced by a uniform, positive background charge with density equal to the spatial average of the ion charge distribution.
- For the analogous surface problem, the semi-infinite ion lattice is smeared out as



$$n_+(\vec{r}) = \begin{cases} \overline{n} & z \leq 0, \\ 0 & z > 0 \end{cases}$$

where $\overline{n}$ is expressed in terms of an inverse sphere volume

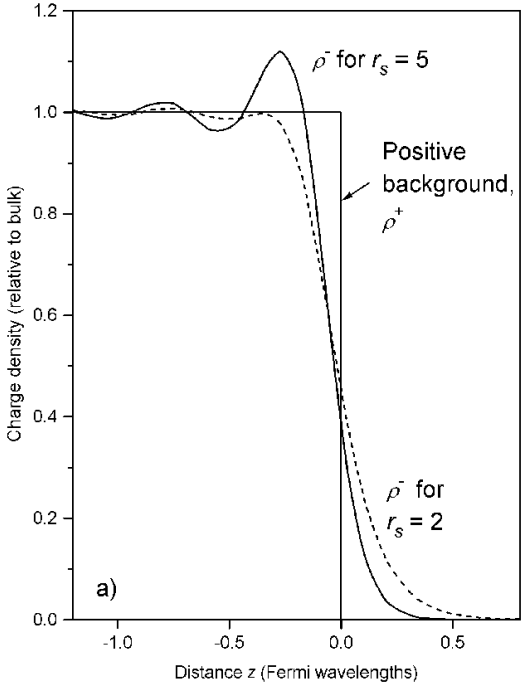
$$\frac{1}{\overline{n}} = \frac{4}{3}\pi r_s^3.$$

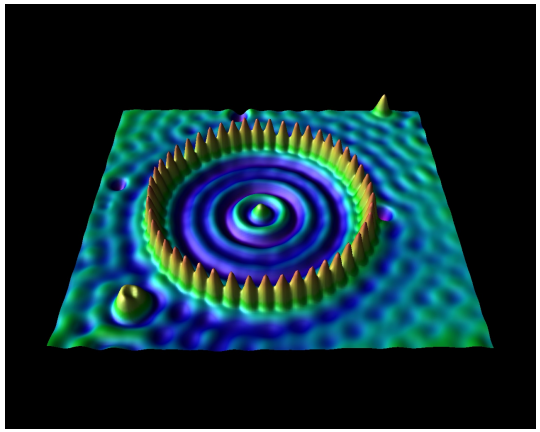
Typical r_s values are 2–5a_0 (a_0 being Bohr radius).

The density variation perpendicular to the surface, $n(z)$, reveals two features:

1. electrons spill out into vacuum region ($z > 0$) $\Rightarrow$ **electrostatic dipole layer** at the surface.
2. $n(z)$ **oscillates** as it approaches an asymptotic value that exactly compensates the uniform (bulk) background charge.

Density Functional Theory - Friedel Oscillations





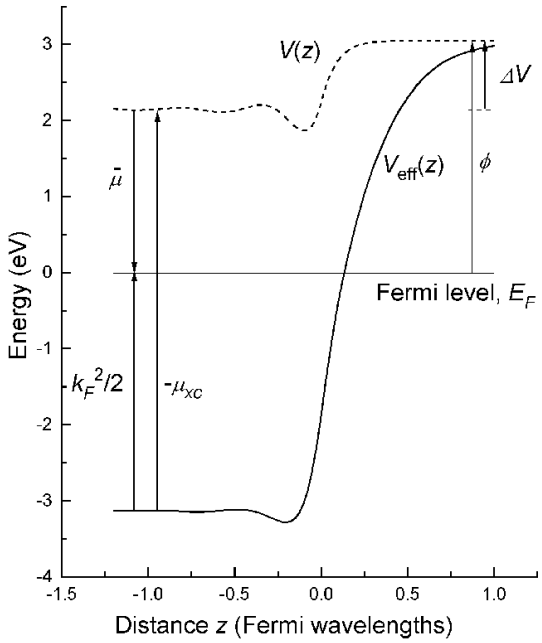
Electron oscillation arise because the electrons (with standing wave vectors between zero and k_{F}, radius of Fermi sphere) try to screen out the positive background charge distribution which includes **step** at $z = 0$.

Screening in metals is so effective that there are ripples in the response, corresponding to overscreening
$\Rightarrow$ **Friedel oscillations** with wavelength π/k_{F}, where $k_{\mathrm{F}} = (3\pi^2\overline{n})^{1/3}$

In 1993, electron density oscillations were observed in STM images of individual adsorbed atoms on surfaces (Eigler's IBM group). By assembling adatoms at low T into particular shapes, these 'Quantum Corrals' produce stationary waves of electron density on the surface.

$\Leftarrow$ Left corral is created from 48 iron atoms (the sharp peaks) on a copper surface. The wave patterns are formed by copper electrons confined by the iron atoms.

Density Functional Theory - Work Function



No sharp edge of the electron density - effective surface at

$$d_{\parallel} = \frac{1}{\bar{n}} \int_{-\infty}^{\infty} \mathrm{d}z\, z \frac{\mathrm{d}n(z)}{\mathrm{d}z}$$

The formation of a dipole layer means that the electrostatic potential far into vacuum is greater than the mean electrostatic potential deep in the crystal.

Potential step

$$\Delta V = V(\infty) - V(-\infty)$$

keeps the electrons within the crystal. It is **surface property**.

The remainder of the surface barrier comes from short range Coulomb interactions - exchange and correlation. It is **bulk effect**.

The **work function** is, therefore, divided into the part related to the bulk properties (band structure) and surface contribution

$$\phi = \Delta V - E_{\mathrm{F}}$$

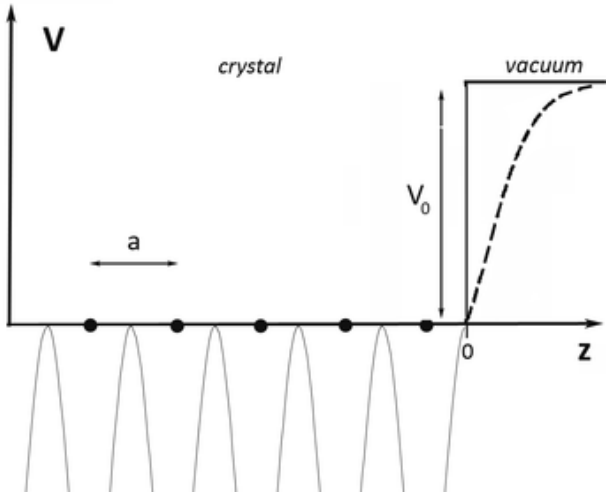
where V and chemical potentail μ are referenced to the mean electrostatic potential deep in the bulk. The surface part is responsible e. g. for different work function from different crystal planes.

Nearly-Free Electron Model

- The jellium description of a metal surface - 1D model that neglects the details of electron-ion interaction and emphasizes the nature of the smooth surface barrier.
- The band structure approaches emphasize the lattice aspects and simplify the form of the surface barrier.

1D nearly-free electron model (appropriate to a **metal surface**): neglects e-e interaction and self-consistency effects present in LDA Schrödinger-like equation, i. e. effective potential includes only the ion cores and a crude surface barrier:

$$\left[-\frac{\mathrm{d}^2}{\mathrm{d}z^2} + V(z)\right]\Psi(z) = E\Psi(z).$$



The effect of the screened ion cores is modelled with a weak periodic pseudopotential

$$V(z) = -V_0 + 2V_g \cos gz$$

where $g = 2\pi/a$ is the shortes **reciprocal lattice** vector of the chain.

For solution see e. g. *Kittel, 1966*. A two-plane-wave trial function is sufficient:

$$\Psi_k(z) = \alpha e^{\mathrm{i}kz} + \beta e^{\mathrm{i}(k-g)z}$$

Nearly-Free Electron Model (contin.)

Substituing the trial function into Schrödinger equation leads to the secular equation

$$\begin{bmatrix} k^2 - V_0 - E & V_g \\ V_g & (k-g)^2 - V_0 - E \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = 0$$

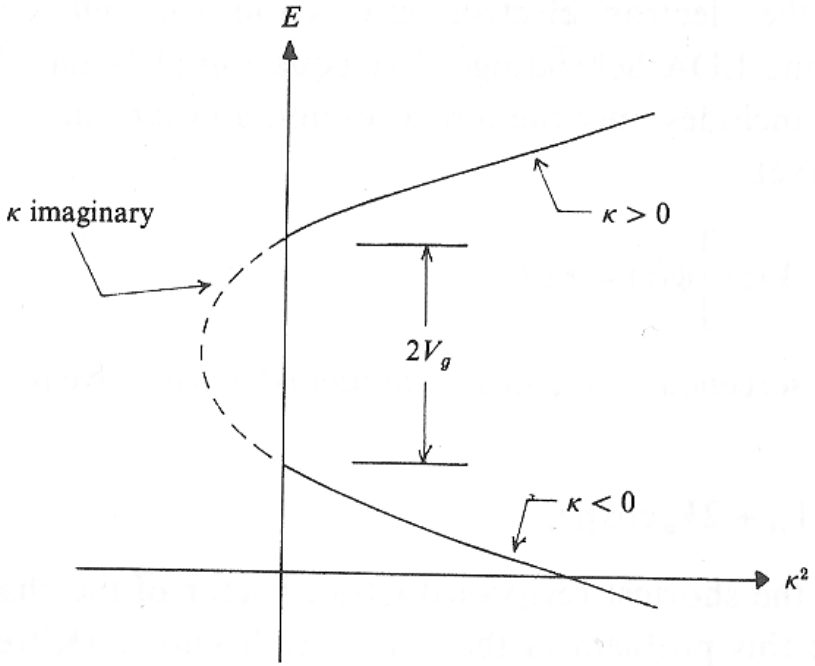
which is readily solved for the wave functions and their energy eigenvalues:

$$E = -V_0 + (g/2)^2 + \kappa^2 \pm (g^2\kappa^2 + V_g^2)^{1/2}$$

$$\Psi_k = \mathrm{e}^{\mathrm{i}kz} \cos(gz/2 + \delta)$$

where $\mathrm{e}^{\mathrm{i}2\delta} = (E - k^2)/V_g$ and the wave vector was written in term of its deviation from the Brillouin zone boundary $k = g/2 + \kappa$.

The familiar energy gap appears at the Brillouin zone boundary $\kappa = 0$.



Nearly-Free Electron Model - Shockley Surface States

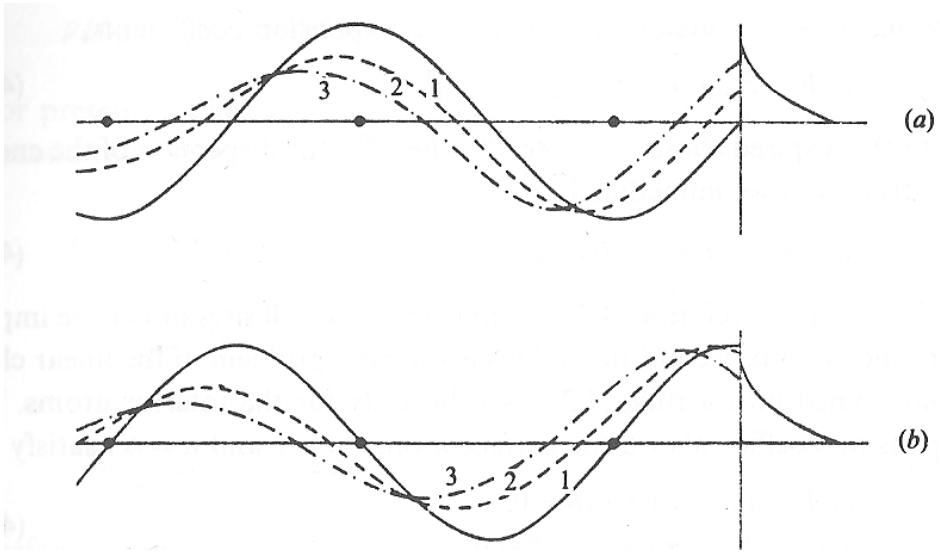
- **In bulk**, the solutions with imaginary κ are discarded because of exponential growth at $|z| \to \infty$ - do not satisfy the usual periodic boundary conditions
- **For the semi-infinite problem**, the solution that grows for positive z is acceptable since it will be matched at $z = a/2$ onto a function that describes the decay of the wave function in the vacuum:

$$\Psi(z) = \mathrm{e}^{\kappa z} \cos(gz/2 + \delta) \quad z < a/2$$

$$\Psi(z) = \mathrm{e}^{-qz} \quad z > a/2$$

where $q^2 = V_0 - E$.

If the logarithmic derivative of $\Psi(z)$ is continuous at $z = a/2$
$\Rightarrow$ existence of electronic state localized at the surface of the lattice chain. The energy of this **surface state** lies in the bulk energy gap.



. . . here, bottom figure (for $V_g > 0$), curve 2

This solution is often called a **Shockley state**.

Tight-Binding Model

1D tight-binding model - wave functions are constructed from atomic-like orbitals (appropriate for **semiconductor surface**). The lattice potential is constructed from a superposition of N free atom potentials, $V_a(\vec{r})$, arranged on a chain with lattice constant a:

$$V_{\mathrm{L}}(\vec{r}) = \sum_{n=1}^{N} V_a(\vec{r} - n\vec{a})$$

where

$$[-\nabla^2 + V_a(\vec{r}) - E_a]\phi(\vec{r}) = 0$$

The non-self-consistent Schrödinger equation for the bands is

$$\{-\nabla^2 + V_a(\vec{r}) + [V_{\mathrm{L}}(\vec{r}) - V_a(\vec{r})]\}\Psi(\vec{r}) = E\Psi(\vec{r})$$

The simplest trial function is a superposition of s-like Wannier functions - one on each site:

$$\Psi(\vec{r}) = \sum_{n=1}^{N} c_n \phi(\vec{r} - n\vec{a})$$

$\Rightarrow$ **Tamm surface states**

Surface States - fast, slow

Surface states can be

- **fast** - Equilibrium between surface and volume is established during relaxation time of $\approx 10^{-8}$ s; density depends on the method of surface treatment, 10^{11}–10^{12} cm^{-2} for well-etched semiconductors.

  Example of fast states that can be found at clean ideal surfaces:
  - **Shockley surface states** - periodic potential is symmetrical terminated at the surface and atoms are sufficiently close and interact strongly $\Rightarrow$ appropriate calculation method is NFE (nearly-free electrons)
  - **Tamm surface states** - change in the potential in the outermost cell of crystall whose atoms are far appart (weak interaction between states) $\Rightarrow$ tight-binding model

  Demonstration for transition metals: nearly-free *s* and *p* electrons form Shockley surface states extending several layers into the solid; *d* electrons forming state with atomic-like wave functions localized on surface atoms.

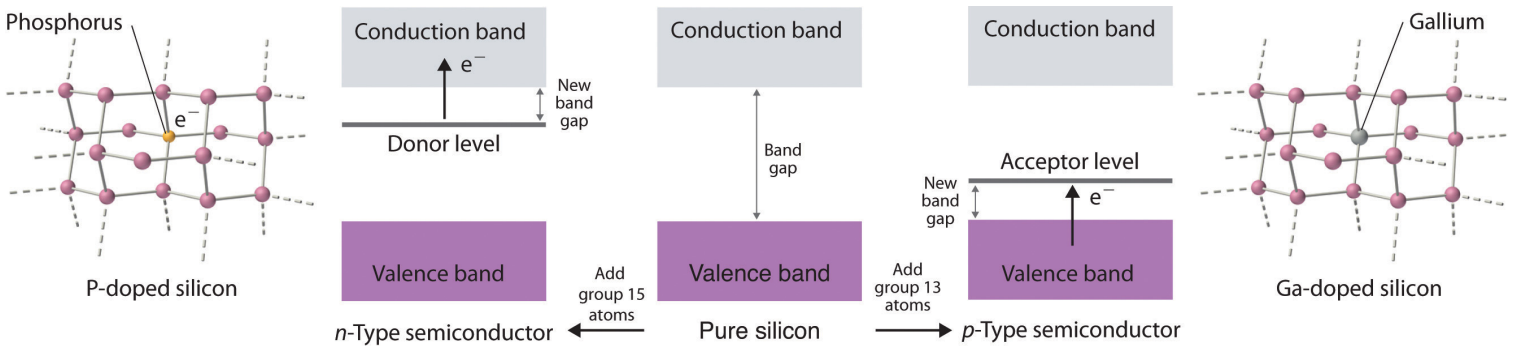
  Example of fast **states related to adsorb gases and surface deffects of crystal lattice.**
- **slow** - Relaxation time ms till hours, density 10^{14}–10^{15} cm^{-2}
  States related to thin oxide layers and presence of charges at its surface as well as its volume.

Surface States - donors, acceptors

Surface states can be

- **donors** - they are occupied (neutral) for $E_{\mathrm{Ds}} < E_{\mathrm{F}}$ and unoccupied (positive) for $E_{\mathrm{Ds}} > E_{\mathrm{F}}$
- **acceptor** - they are occupied (negative) for $E_{\mathrm{As}} < E_{\mathrm{F}}$ and unoccupied (neutral) for $E_{\mathrm{As}} > E_{\mathrm{F}}$

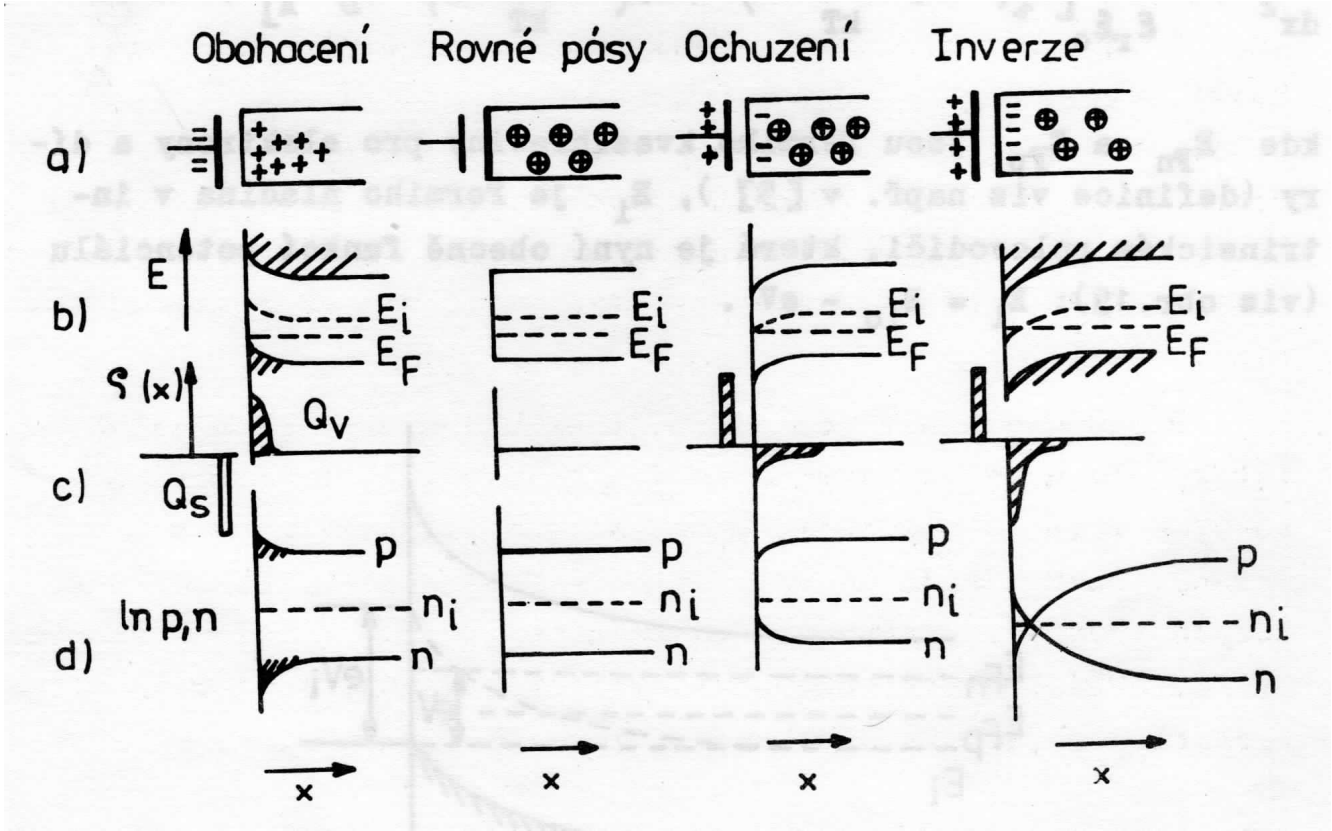
Repetition of terms donor (donating electrons)/acceptor (accepting electrons) from doping of semiconductors:



(a) Doping with a group 15 element (b) Doping with a group 13 element

Surface States - band bending

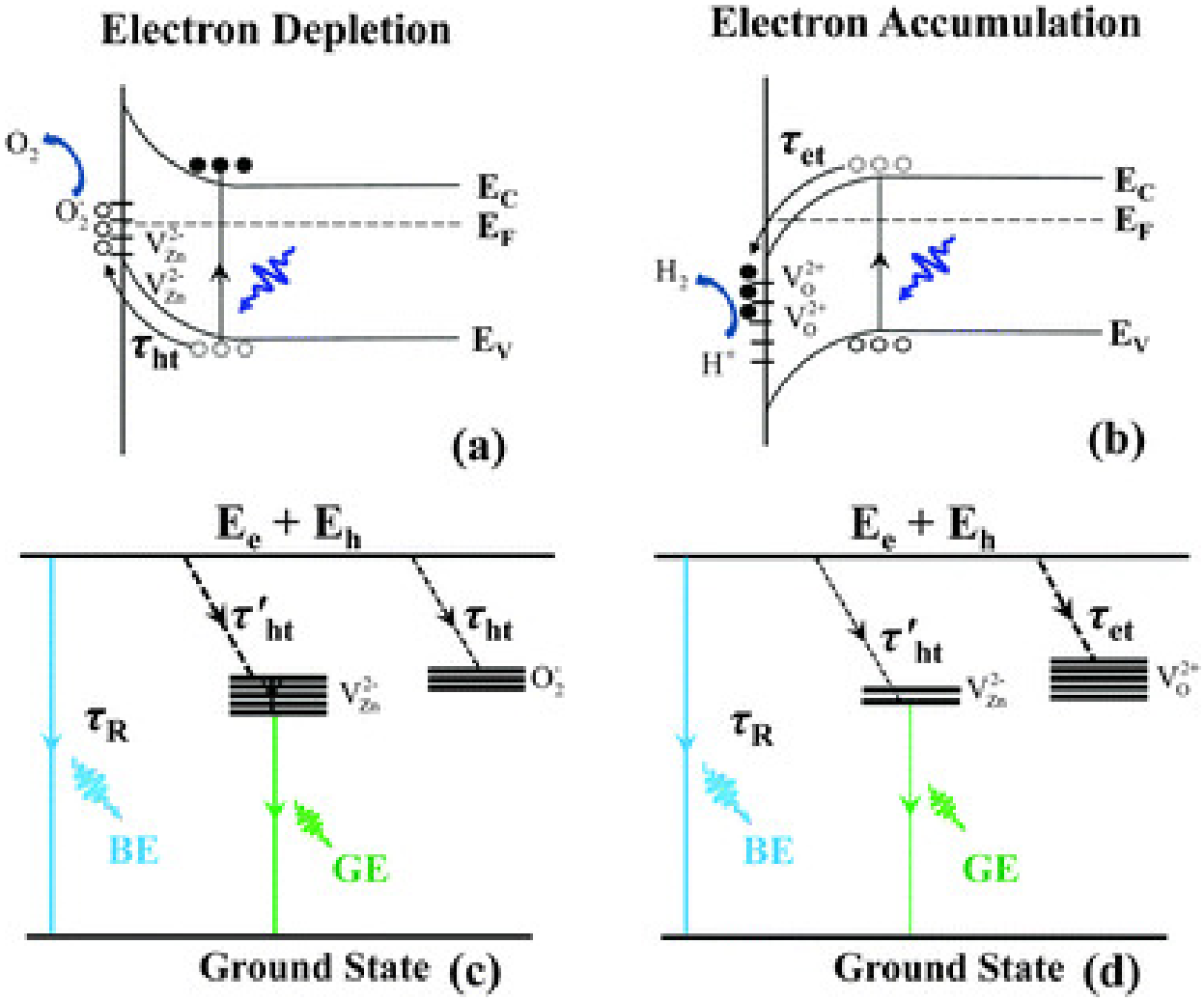
- Energy levels are straight up to the surface in case of no electrical field and no surface states.
- Appearance of **acceptor surface state below E_F** $\Rightarrow$ electrons from valence band will occupy it $\Rightarrow$ **surface will be negatively charged** and positive space-charge sublayer occurs $\Rightarrow$ upwards bending of energy bands



Example for p-type semiconductor

Surface States - example of ZnO nanowires

ZnO is wide bandgap semiconductor. Nanowires have large surface - surface defects, near surface traps and surface adsorbed species play important role.



Work Function, Electron Affinity

Difference between Fermi level and chemical potential is neglected (temperature below 1000 K)

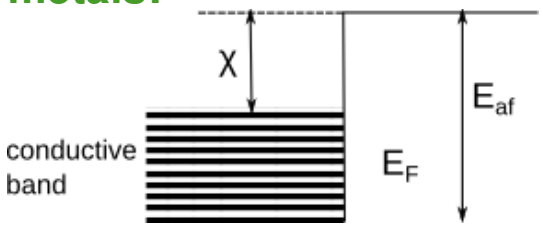
- **work function** for metals:

$$\chi = E_{\mathrm{af}} - E_{\mathrm{F}}$$

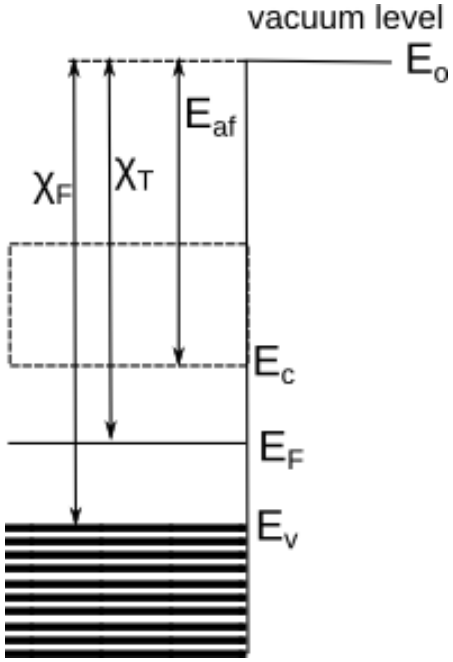
  where **electron affinity** E_{af} is the difference between the vacuum level E_0, and the bottom of the conduction band E_{C}.

- for semiconductors:
  thermoelectric work function χ_{T} - difference between E_0 and E_{F}
  photoelectric work function χ_{F} (ionization potential) - difference between E_0 and E_{v}

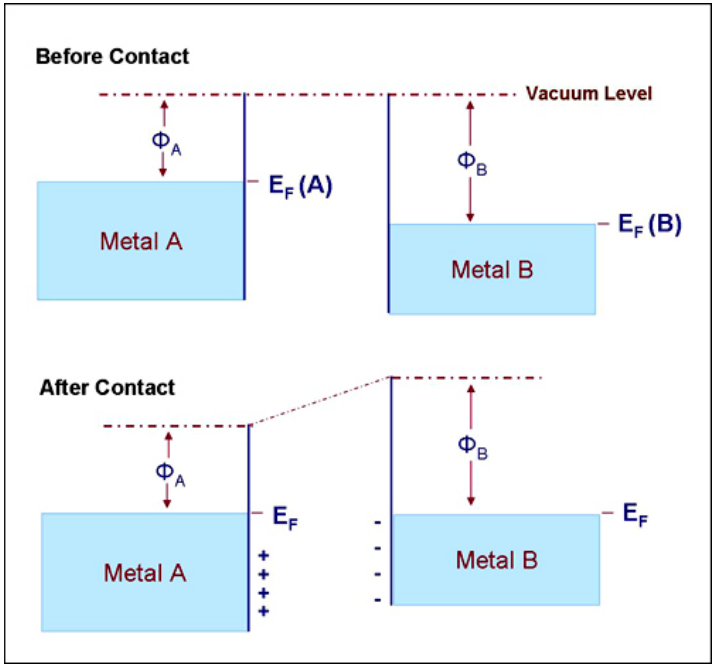
metals:



semiconductors:



Contact Potential - Metal/Metal

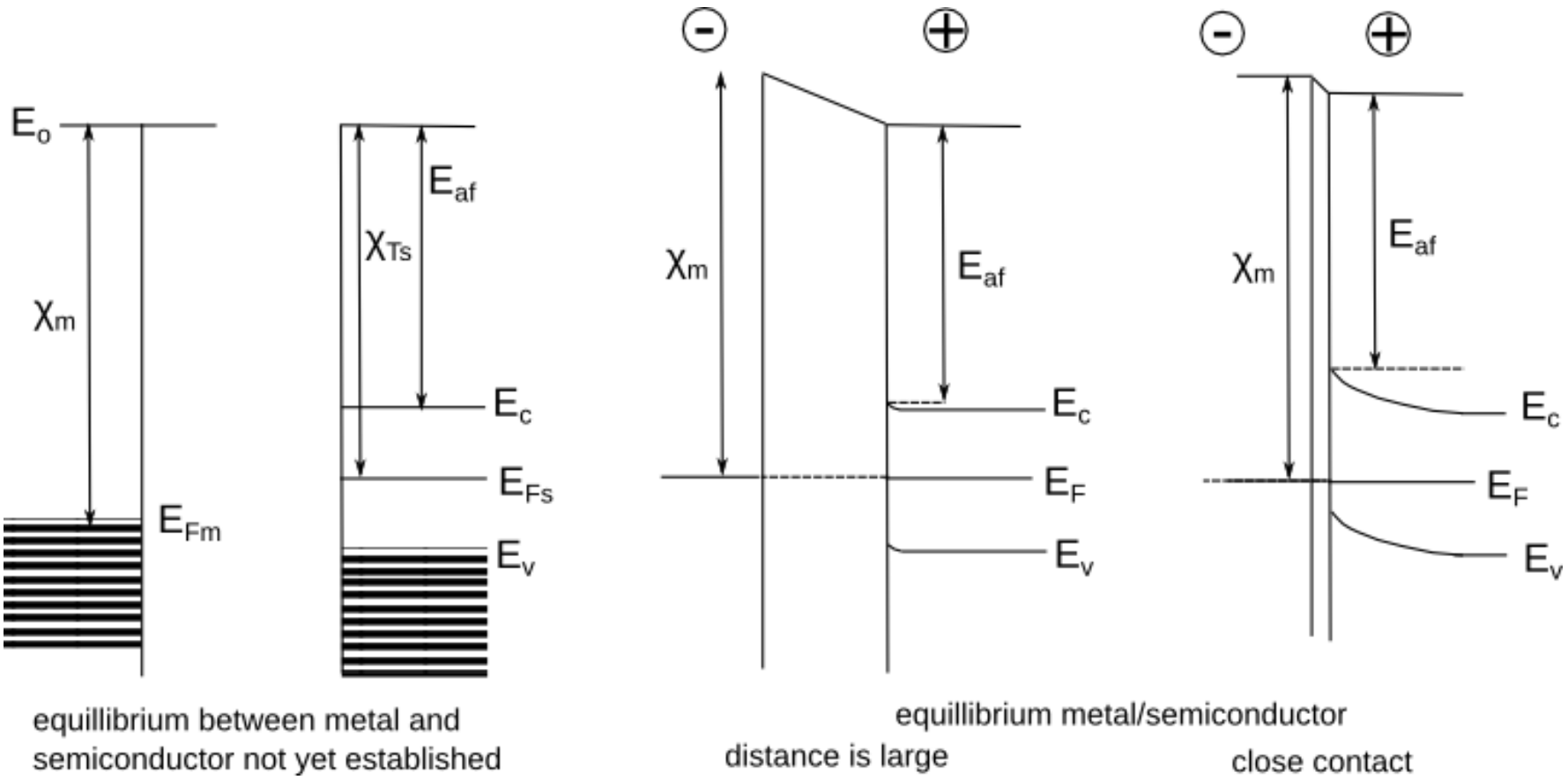


- metals A and B are electrically isolated ($\chi_A < \chi_B$) $\Rightarrow$ an arbitrary potential difference may exist
- metals A and B are brought into contact $\Rightarrow$ electrons flow from the metal B to the metal A until the electrochemical potentials (Fermi energies) are equal. The actual numbers of electrons that passes between the two phases is small.

Metal A is charged positively and metal B negatively, i. e. work functions does not change but **contact potential** appears.

$$eV_{\mathrm{cont.}} = \chi_B - \chi_A$$

Contact Potential - Semiconductor/Metal



contact potential:

$$eV_{\mathrm{cont.}} = \chi_{\mathrm{m}} - \chi_{\mathrm{Ts}}$$

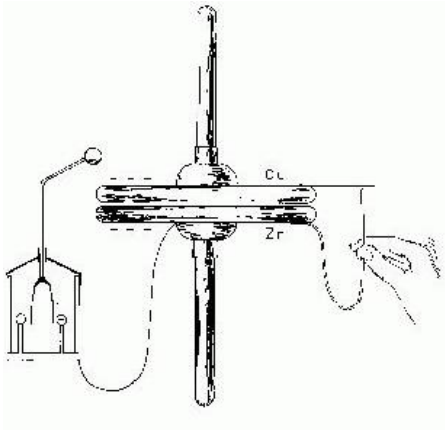
Development of space-charge region in the semiconductor in case of close contact
$\Rightarrow$ band bending

Measurement of Work Function from Contact Potential

Experimental methods for determination of work function

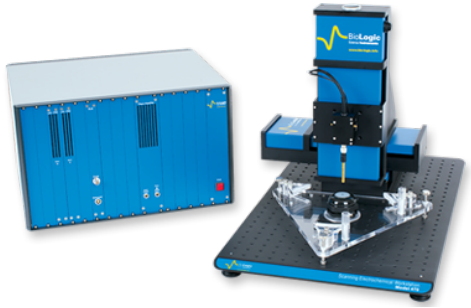
- measurement of contact potential difference $eV_{\mathrm{cont.}} = \chi_B - \chi_A$ in which the work function of one material has to be known;
- measurement of characteristics of various electron emission processes

Measurement of contact potential difference (CPD) by the condensator method (**Kelvin probe**): between two surfaces creating a condensator with capacity C.



If we **apply external voltage compensating the contact potential** the field between the plates can be **reduced to zero** $\Rightarrow$ external voltage is equal to the contact potential difference.

If C is changed, a current I will flow $I = U\frac{\mathrm{d}C}{\mathrm{d}t}$ where U is the voltage difference between the condensator plates. This voltage is equal to the contact potential difference if there is no external voltage applied. The changes of capacity are realized by vibration of one electrode **vibrating capacitor method**. Using a lock-in amplifier, the AC current generated by the oscillation is monitored. Gradual ramping of the potential and finding zero AC current yields CPD.



SKP470 Scanning Kelvin Probe

http://www.bio-logic.info/instruments/skp470-2/

Change of Work Function with Temperature

- For metals the work function has a linear relation with the temperature change:

$$\chi(T) = \chi(T_0) + \alpha(T - T_0),$$

where $-\alpha$ has values between 10^{-4}–10^{-5} eV/K.

- For intrinsic semiconductors and insulators the chemical potential varies strongly with temperature:

$$\chi(T) = E_{\mathrm{af}} + \frac{E_{\mathrm{g}}}{2} + \frac{kT}{2} \ln \frac{N_{\mathrm{c}}}{N_{\mathrm{v}}},$$

E_{g} - band gap, E_{af} - electron affinity, N_{c} and N_{v} - densities of the conduction and valence bands.

- For n-type semiconductors at low ionization of donor states:

$$\chi(T) = E_{\mathrm{af}} + \frac{\Delta E_{\mathrm{D}}}{2} + \frac{kT}{2} \ln \frac{N_{\mathrm{c}}}{N_{\mathrm{D}}},$$

ΔE_{D} - activation energy, N_{D} - density of the donor states.

At high temperatures it is change to:

$$\chi(T) = E_{\mathrm{af}} + \frac{kT}{2} \ln \frac{N_{\mathrm{c}}}{N_{\mathrm{D}}}.$$

- In case of p-type semiconductors:

$$\chi(T) = E_{\mathrm{af}} + E_{\mathrm{g}} - \frac{\Delta E_{\mathrm{A}}}{2} - \frac{kT}{2} \ln \frac{N_{\mathrm{v}}}{N_{\mathrm{A}}}$$

and for high T

$$\chi(T) = E_{\mathrm{af}} + E_{\mathrm{g}} - \frac{kT}{2} \ln \frac{N_{\mathrm{v}}}{N_{\mathrm{A}}}.$$

Change of Work Function in Electrical Field

If we apply el. field E close to the surface of metal there will be two types of forces exerting to the electrons

- attractive image force (between the electron and its mirror image inside metal)

$$F_0 = \frac{e^2}{16\pi\varepsilon_0 x^2}$$

- el. force accelerating electrons out of the metal

$$F(x) = F_0(x) - eE.$$

In certain distance x_k from the surface, the final force $F(x)$ will be equal to zero and for $x > x_k$ the electron will be accelerated from the surface. Work function will be then equal

$$\chi = \int_0^{x_k} (F_0(x) - eE)dx = \int_0^{\infty} F_0 dx - \int_{x_k}^{\infty} F_0 dx - \int_0^{x_k} eEdx$$

$$= \chi_0 - \frac{e^2}{16\pi\varepsilon_0 x_k} - eEx_k = \chi_0 - e\sqrt{\frac{eE}{4\pi\varepsilon_0}}.$$

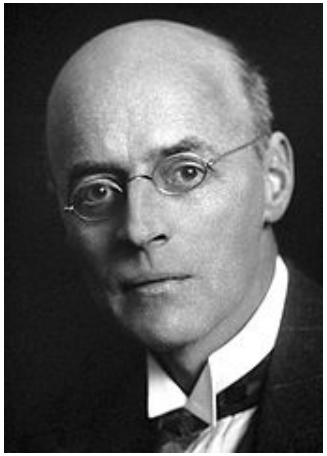
This dependence of work function on external el. field is called **Schottky effect**.

Thermoemission

Addition of heat ⇒ increased energy of lattice vibration and energy of electrons ⇒ some electrons obtain **energy** required to **pass surface potential barrier** and are **emitted from the surface**

Process of **thermoemission** can be described

1. by **thermodynamics** - electrons are the evaporated material, terms like heat of evaporation, Clausius-Clapeyron equation, equation of state
2. by **statistical physics** - known statistical distribution of electron velocities is taken to calculate those electrons that have enough energy to overcome work function. This approach was originally suggested by Richardson for metals (1901) but using classical statistics.



Statistical description of thermoemission using Fermi-Dirac statistics
For a system of identical fermions, the average number of fermions in a single-particle state i, is given by the Fermi–Dirac (F–D) distribution

$$\langle n_i \rangle = \frac{g_i}{\exp \frac{\epsilon_i - \mu}{kT} + 1}$$

where g_i is the state degeneracy (the number of states with energy ϵ_i)

Distribution of Energies Perpendicular to Surface

In solids, the states are characterized by a **quasi-continuum energies** with defined **density of states** $g(\epsilon)$ (the number of states per unit energy range per unit volume) and the average number of electrons per unit energy range per unit volume is for metals

$$\langle n(\epsilon)\rangle = \frac{g(\epsilon)}{\exp\frac{\epsilon-\mu}{kT}+1}$$

where from Heisenberg principle of uncertainity $g(\epsilon) = g_0/h^3$ ($g_0 = 2$) and for reasonable T we assume $\mu = E_{\mathrm{F}}$

Number of electrons having momentum in the range from (p_x, p_y, p_z) to $(p_x + dp_x, p_y + dp_y, p_z + dp_z)$:

$$N(\vec{p})dp_x dp_y dp_z = \frac{g_0}{h^3}\,\frac{dp_x dp_y dp_z}{\exp(\frac{p^2/2m-\mu}{kT})+1},$$

The axis z will be perpendicular to the surface and we look for the number of electrons with the energy from $\langle p_z, p_z + dp_z\rangle$. After integration in polar coordinates ($\int \frac{1}{e^x+1}dx = x - ln(1+e^x)$) and substitution $\epsilon = p_z^2/2m$ we have

$$N(\epsilon)d\epsilon = \frac{\pi g_0 m}{h^3}\sqrt{\frac{2m}{\epsilon}}kT\,\ln\left(1+e^{-\frac{\epsilon-\mu}{kT}}\right)d\epsilon.$$

Density of Thermoemission Current

Number of electrons impinging on unit surface area per unit time with energy $\langle \epsilon, \epsilon + \mathrm{d}\epsilon \rangle$ is obtained by multiplication with $v_z = \sqrt{2\epsilon/m}$

$$\nu(\epsilon)d\epsilon = \frac{2\pi g_0 m}{h^3} kT \ln\left(1 + e^{-\frac{\epsilon-\mu}{kT}}\right) d\epsilon.$$

Emitted electron have to fulfil the condition $\epsilon \geq E_{\mathrm{af}}$ but integration of the flux term is not possible in general.

Assuming $(\epsilon - E_{\mathrm{F}})/kT \gg 1$ (electrons just below Fermi level) the flux can be simplified as

$$\nu(\epsilon)d\epsilon = \frac{2\pi g_0 mkT}{h^3} e^{-\frac{\epsilon-\mu}{kT}}$$

and density of emission current i is obtained by integration considering a certain **probability of electron reflection at the surface barrier $R(\epsilon)$**

$$i = e \int_{E_{\mathrm{af}}}^{\infty} [1 - R(\epsilon)]\nu(\epsilon)d\epsilon.$$

$R(\epsilon)$ is for simplicity approximated by an averaged value $\bar{R} = 1 - \bar{D}$ and then

$$i = \bar{D}\frac{4\pi mek^2}{h^3} T^2 e^{-\frac{E_{\mathrm{af}}-\mu}{kT}} = \bar{D}A_0 T^2 e^{-\chi/kT}.$$

Richardson-Dushman equation

From previous slide we have

$$i = \bar{D} A_0 T^2 \exp\left(-\frac{\chi}{kT}\right)$$

in which the constant $\bar{D}$ should not differ for different metals but it was found out that $\bar{D}A_0$ is quite different for different metals $\Rightarrow$ we need to consider temperature dependece of work function $\chi(T) = \chi(T_0) + \alpha(T - T_0)$ and obtain **Richardson-Dushman equation**

$$i = \bar{D} A_0 T^2 \exp(-\alpha/k) \exp(-\frac{\chi(T_0) - \alpha T_0}{kT}) = AT^2 \exp(-\frac{e\psi}{kT}),$$

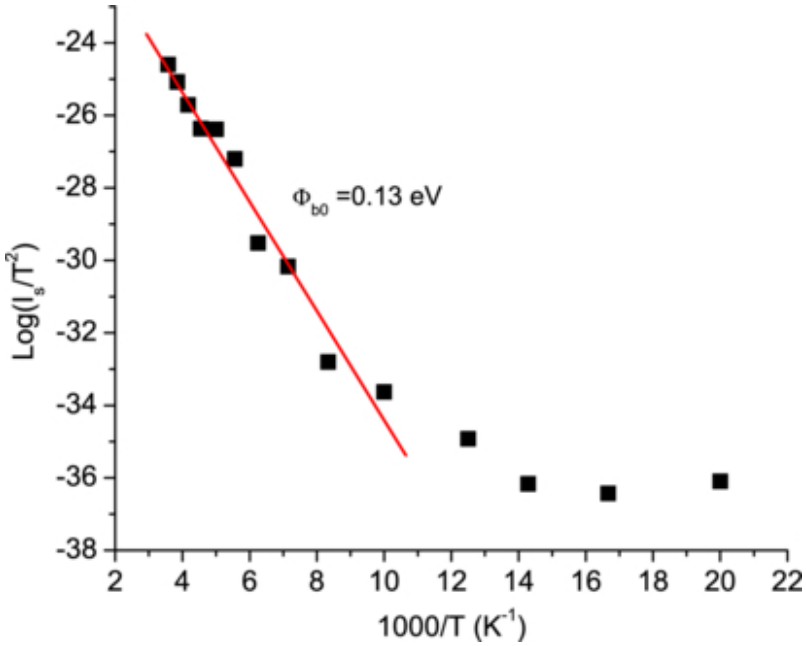
where **Richardson constant** A is not an universal constant but it is characteristics for given material and $e\psi$ is **reduced** or **Richardson work function**.

metal	melting point (K)	A (Acm^{-2}K^2)	χ (eV)
W	3640	80	4.6
Ta	3270	60	4.1
Pt	2050	170	5.6

$\mathrm{d}\psi/\mathrm{d}T$ is of the order of 10^{-4} to 10^{-3} eV/K, with both positive and negative signs.

When data is taken over a limited range of T, this temperature dependence will not show up on such a plot, but will modify the pre-exponential constant.

Measurement of Work Function Using Thermoelectric Methods



Using Richardson line: a plot of $\log(i/T^2)$ versus $1/T$ yields a straight line whose negative slope gives the work function ϕ.

The constant, A, can be measured in principle, but is complicated in practice because we need to know the emitting area independently, since what is usually measured is the emission current I rather than the current density, i.

Je třeba zajistit, aby se měření proudu uskutečňovalo v režimu nasyceného proudu, tj. aby v měřícím systému nehráli roli prostorové náboje. To znamená, že mezi emitující katodu a anodu musí být vloženo dostatečně velké napětí. Při větších napětích se pak ovšem uplatňuje Schottkyho jev, takže naměřené hodnoty by měly být správně extrapolovány na nulové vnější pole:

$$i = AT^2 \exp(-\frac{\chi}{kT}) = AT^2 \exp(-\frac{\chi_0}{kT}) \exp\left(\frac{e}{kT}\sqrt{\frac{eE}{4\pi\varepsilon_0}}\right)$$

Musíme měřit dostatečně přesně teplotu katody (pyrometrická metoda nebo pomocí změn odporu žhaveného vlákna).

Measurement of Work Function Using Thermoelectric Methods

Metoda kalorimetrická: emitované elektrony s sebou odnášejí určitou energii, tj. katoda se ochlazuje a chceme-li, aby její teplota zůstala konstantní, musíme zvětšit příkon. Energie spotřebovaná na jeden elektron je $\epsilon = \chi + 2kT = e\phi + 2kT$ a spotřebovaný výkon pro N elektronů za čas t je

$$w = \frac{Ne}{t}\left[\phi + \frac{2kT}{e}\right] = J_{\mathrm{emis.}}\left[\phi + \frac{2kT}{e}\right].$$

O tuto hodnotu musíme zvětšit příkon, chceme-li aby teplota katody zůstala konstantní.

$$w_z = R[(I_z + \Delta I_z)^2 - I_z^2] \approx 2RI_z\Delta I_z.$$

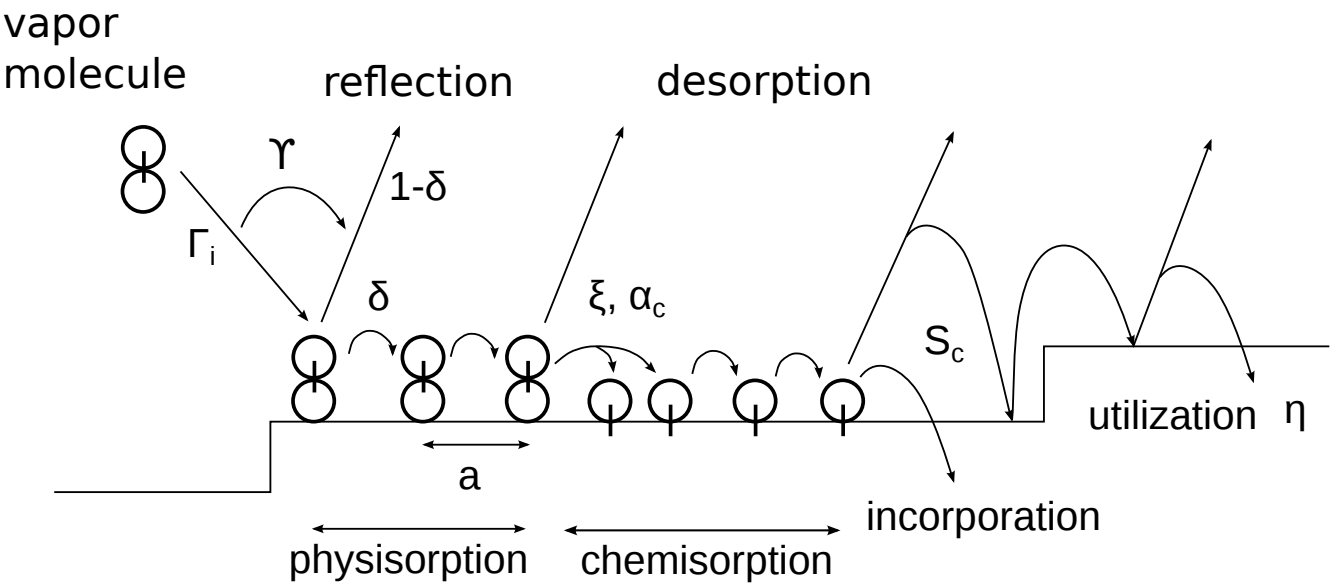
Známe-li odpor katody a změříme příslušné proudy můžeme spočítat výstupní potenciál (práci)

$$\phi = \frac{2RI_z\Delta I_z}{J_{\mathrm{emis}}} - \frac{2kT}{e}.$$

Physisorption

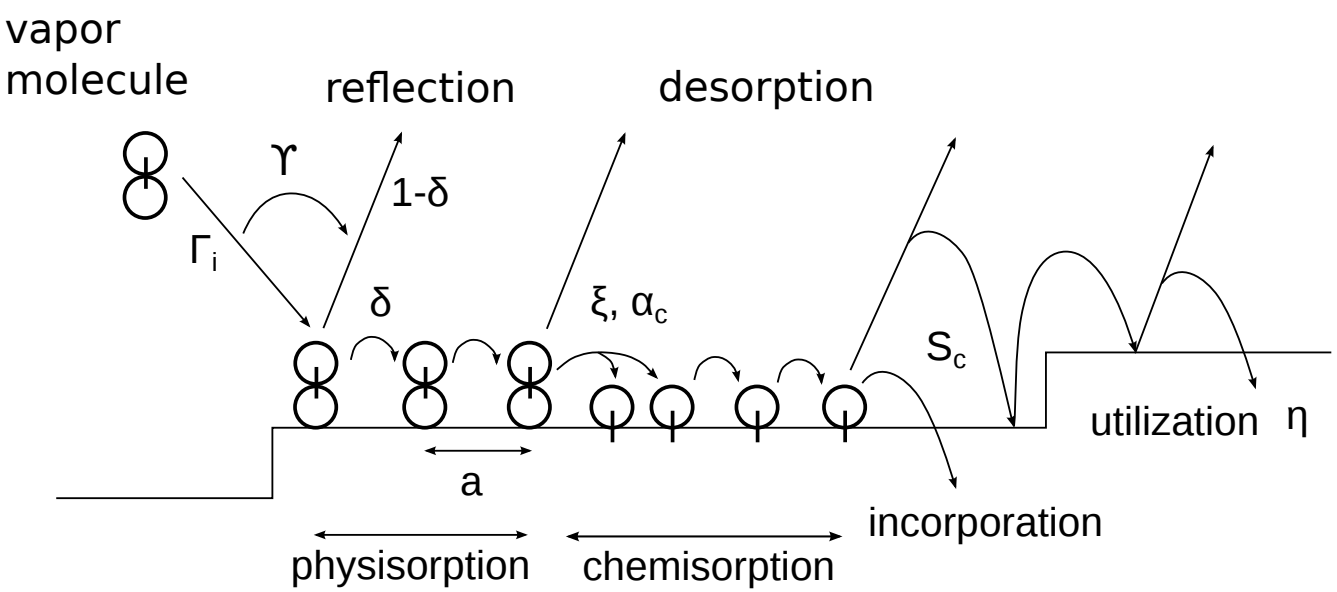
Consider a molecule approaching a surface from the vapor phase:

- **a few atomic distances from the surface** molecule begins to feel an attraction - interaction with the surface molecules by **van der Waals forces** (interaction of permanent or induced dipoles) ⇒ approaching molecule is being attracted to the potential well (like for condensation that is a special case of adsorption in which the substrate composition is the same as that of adsorbant)
- molecule **physisorption** - trapping in the potential well because enough of the molecule perpendicular momentum was dissipated ⇒ **trapping probability** δ
  δ is different from **thermal accomodation coefficient** γ introduced previously, molecule is at least partially accomodated thermally to the surface temperature T_s even when it is reflected



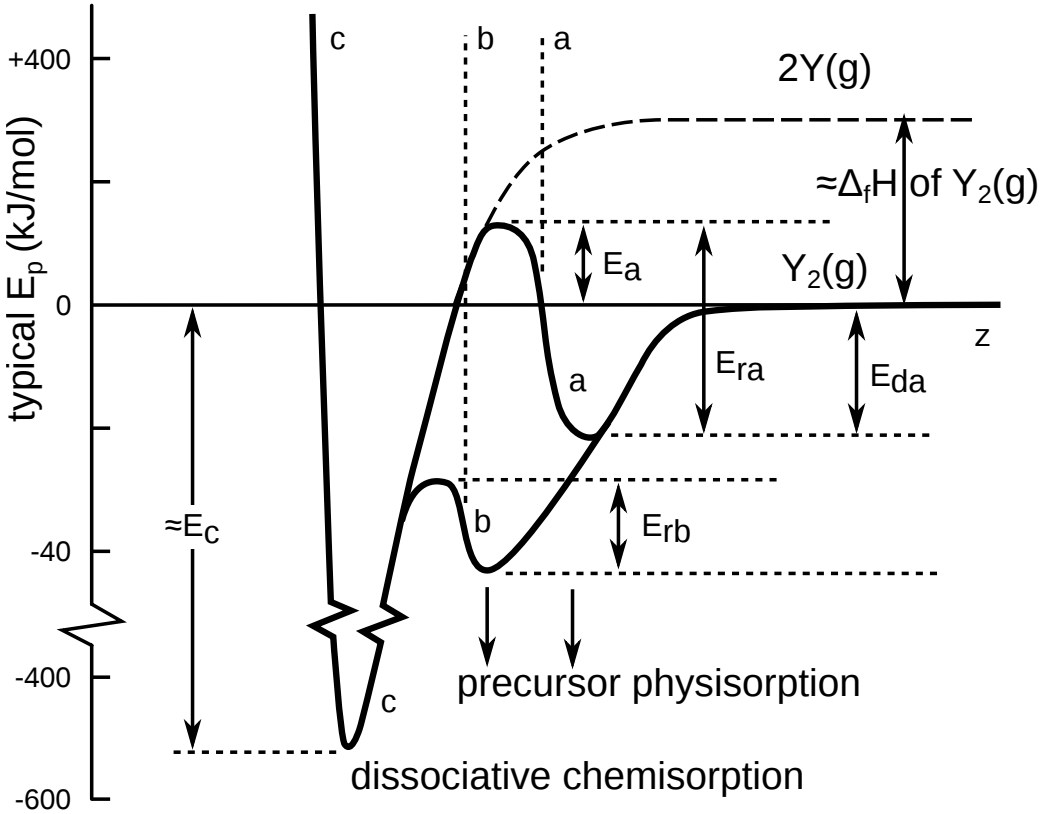
Chemisorption

- The physisorbed molecule is mobile on the surface except at cryogenic T - **hopping** (diffusing) between surface atomic sites.
  - It may **desorb** after a while by gaining enough energy in the tail of the thermal energy distribution.
  - It may undergo a further interaction consisting of the formation of chemical bonds with the surface atoms, i. e. **chemisorption**. The **condensation coefficient** α_c is not used in the case of chemisorption on a foreign substrate, use **chemisorption reaction probability** ξ.
  - Some of adsorbed species eventually escape back into the vapor phase $\Rightarrow$ **sticking coefficient** S_c - fraction of the arriving vapor that remains adsorbed for the duration of the experiment.



Energetics of Precursor Adsorption Model

Consider hypothetical diatomic gas-phase molecules Y_2(g) adsorbing and then dissociative chemisorbing as two Y atoms:



Lifting **atomic Y** out of its potential well along curve *c* results in much higher molar potential energy E_p in the gas phase - roughly the **heat of formation,** $\Delta_f H$, of $2Y$(g) from Y_2(g).

The curve *b* represents **activated chemisorption** - there is an activation energy E_a to be overcome for Y_2(g) to become dissociatively chemisorbed.

For deeper precursor well, *b* chemisorption is not activated though there is still a barrier.

Uspořádané povrchy lze rozdělit do dvou skupin

- povrchy, které mají jednotkovou buňku mřížky stejnou jako průmět objemové jednotkové buňky do roviny povrchu
- povrchy, které jsou charakterizované jednotkovými buňkami, jejichž rozměry jsou celistvým násobkem rozměrů objemové jednotkové buňky
- povrchy, které vykazují jiné pravidelné uspořádání

Povrchové struktury patřící do druhé a třetí skupiny se vytvářejí buď při adsorpci cizích atomů na povrchu, nebo v důsledku rekonstrukce povrchu.
`http://www.chem.qmul.ac.uk/surfaces/scc/scat1_6.htm`

Tepelná desorpce

Dodáme-li adsorbované látce dostatečnou energii ve formě tepla, neudrží se adsorbované částice na povrchu a dojde k desorpci. Rychlost desorpce, tj. počet částic opouštějící jednotku povrchu za jednu sekundu je

$$v_{\mathrm{des}} = n_{\mathrm{s}} \frac{1}{\tau_0} exp(-\frac{Q_{\mathrm{ads}}}{kT}), \tag{1}$$

kde n_{s} je povrchová koncentrace adsorbovaných částic,τ_0 je doba kmitu oscilací částic vázaných na povrchu,Q_{ads} je adsorpční energie, T je teplota. Pro každý systém je možné stanovit teplotu nutnou pro dokonalé vyčištění povrchu (vakuum!) od dané adsorbované látky. Žhavení se provádí

1. přímým průchodem proudu
2. radiací
3. bombardováním elektrony (z opačné strany, jinak změny na povrchu)

Výhody: experimentální jednoduchost;
Nevýhody:

- Protože teploty, které musíme použít, jsou většinou dost vysoké ($\geq$ 1000 K), hodí se tato metoda pouze pro látky s dostatečně vysokým bodem tání a pro látky, které při použitých teplotách nedissociují.
- Při pomalém zahřívání a udržování vzorku na vysoké teplotě nastává difuze nečistot z objemu.
- Díky tepelné desorpci může dojít k porušení stechiometrie a naleptávání povrchu krystalu.
- Nelze odstranit libovolnou nečistotu.

Desorpce v silném el. poli

Kov je kladným pólem. Je-li el. pole dost silné (řádově 10^8 V/cm), může se hladina valenčního elektronu adsorbované látky vyrovnat s Fermiho hladinou kovu, resp. se dostat těsně nad ni. V tomto případě je umožněno protunelování elektronu do kovu. Z atomu se stává kladný iont, který je elektrostatickými silami odmrštěn od kladného povrchu kovu. Nejsnadněji lze realizovat desorpci elektropozitivnívh adsorbátů, je však možné desorbovat i látky elektronegativní, ovšem potřebná pole jsou větší a může dojít i k vytrhávání vlastních atomů (tzv. vypařování v poli). Tento způsob čištění je usnadněn při zahřátí (větší migrace). Nevýhody: omezeno na materiály, ze kterých umíme a chceme vyrobit velmi ostrý hrot (pod 1 μm), a na kovy.

Desorpce elektronovým bombardováním

Přímé ostřelování zkoumaného povrchu elektrony relativně nízkých energií (50–200 eV), takže zahřátí je nepatrné. Jedná se pravděpodobně o přechod adsorbované částice do excitovaného stavu, který může být k povrchu vázán slaběji nebo vůbec.

Iontové bombardování

Používají se těžší ionty, většinou Ar nebo Xe. Díky své hmotnosti předávají ionty účinně energii povrchové částici. Je důležitá čistota pracovního plynu a správné soustředění svazku (pozor na rozprašování okolních materiálů!).
Výhody:

- univerzální metoda pro libovolnou látku
- umožňuje postupné odprašování.

Nevýhody:

- u dielektrika se musí neutralizovat náboj iontů,
- jsou vytvářeny poruchy v bombardovaném materiálu $\Rightarrow$ kombinace bombardu a vyhřátí,

Čištění pomocí laserového paprsku

Moderní modifikace čištění tepelnou desorpcí. Laserový svazek dopadá na čištěný povrch skrz okénko.
Výhody:

- vakuum, žádné cizí částice
- pro krátké pulzy dojde k ohřevu jen povrchu a nikoliv objemu

Nevýhody:

- lokální tavení materiálu
- (jako pro ostatní tepelné metody) nelze odstranit libovolnou nečistotu
- vysoká cena a prostorové nároky vhodných laserů

Štípání nebo lámání v ultravysokém vakuu

Vhodné pro některé monokrystaly. Čistota povrchu je dokonalá.

- štípání břitem zatlačovaným do vrypu na povrchu krystalu $\Rightarrow$ povrch má většinou hodně nepravidelností
- lámání krystalu ohybem $\Rightarrow$ povrch lepší

Využití povrchových reakcí

Vhodné v určitých speciálních případech. Organické nečistoty lze odoxidovat v kyslíku, některé nečistoty lze převést na plynné sloučeniny zahřátím ve vodíku atd. Většinou se vzorek v dané atmosféře žíhá.