

Chapter 9

Work Function, Contact Potential, and Kelvin Probe Scanning Force Microscopy

We already used the term work function when we introduced the tunneling barrier height in STM. The work function can be considered as the energy difference between the vacuum level and the Fermi level of a metal. Here we will see that also a surface term contributes to the work function. The work function is a measurable quantity and the operative definition of the work function is that it is the energy required to remove an electron from the bulk Fermi level of a metal to a certain distance from the solid.¹

Subsequently, we introduce the contact potential between two metals with different work function, which is used by the Kelvin method for the measurement of work function differences. In spite of the fact that we have not yet introduced scanning force microscopy in depth, in this chapter we already present the principles of Kelvin probe scanning force microscopy (KFM), which is the nanoscale variant of the Kelvin method.

9.1 Work Function

The work function Φ of a metal can be defined as the difference between the energy of an electron at some distance d outside of a solid E_{out} and the energy of the highest occupied electron level (at zero temperature), i.e. the Fermi energy, thus

$$\Phi(d) = E_{\text{out}}(d) - E_{\text{F}}. \quad (9.1)$$

This corresponds to an operative definition of the work function as the minimum energy to bring an electron from the solid to some distance d outside the solid. The kinetic energy of the electron outside the solid is considered as zero. Note that with this definition the work function depends on how far the electron is removed from the surface.

¹ This distance is specific to the actual type of measurement performed.

As a limiting case, the energy to bring the electron from inside the solid to infinity can be considered. Let us consider an infinite crystal filling a half space and being terminated by an infinite surface of specific orientation. If the position of the electron outside of the solid is infinitely far from the solid E_{out} will be the vacuum energy at infinite distance from the surface E_{vac}^{∞} and the work function results as

$$\Phi = E_{\text{vac}}^{\infty} - E_{\text{F}}. \quad (9.2)$$

The usual definition of the work function as difference between vacuum energy and Fermi energy hides the fact that the vacuum energy depends on the distance of the electron from the surface.

The work function has two main contributions; one is due to the binding of the electrons inside a solid. Theoretically, one can consider the binding of the electrons inside a solid with different levels of sophistication, from the simple nearly free electron model, the tight binding model, up to ab initio calculations. The essence is always the same: The electrons are bound to the nuclei and this bonding corresponds to a lower energy of the electrons in the solid compared to free electrons. A second contribution to the work function arises due to the passage of the electron through the surface layer, which we will discuss in the following.

9.2 Effect of a Surface on the Work Function

Before we consider the effect of the surface on the work function, we note that the effect of the presence of a surface has a negligible effect on the bulk states. Inside the solid the potential of the positive charges of the nuclei is screened very effectively by the electrons at distances larger than the Thomas-Fermi screening length [14]. The Thomas-Fermi screening length is usually very small in metals. For instance, in copper the screening length is only about 0.5 Å. Thus inside the crystal everything will remain as it was in the infinite bulk crystal since the contribution of the “missing” atoms at the surface is vanishingly small due to the effective screening inside the metal. The energy of the highest occupied electronic level in a metal terminated by a surface will still be E_{F} , as for the infinite crystal.

Now we consider how the changes of the electronic structure at the surface give rise to an additional contribution to the work function, i.e. we consider the work needed to bring an electron through the surface layer. Even if we consider a bulk termination of the surface, which means that the positions of the atom nuclei remain as in the bulk, i.e. undistorted up to the last atom at the surface, as shown for the 1D crystal in Fig. 9.1a, the electron charge distribution near the surface deviates from that in the bulk. Some charge will “spill out” into the vacuum as indicated qualitatively in Fig. 9.1a. This “spill out” of charge is a quantum mechanical effect, as an electron

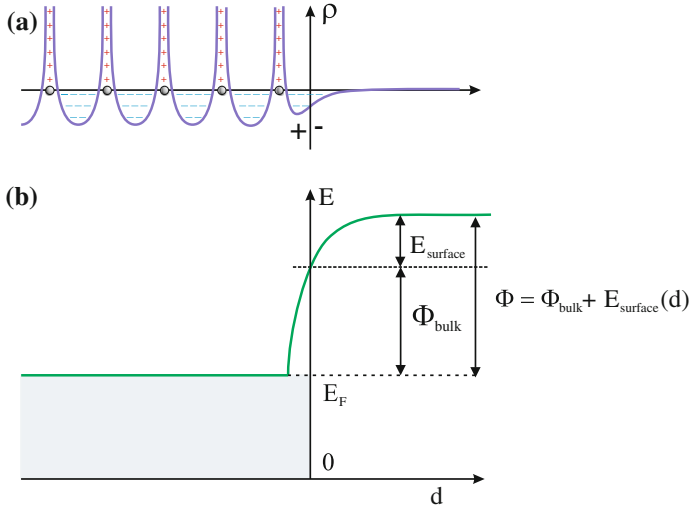


Fig. 9.1 **a** Charge density in a metal crystal which is modified close to the surface and spills out towards the vacuum. This behavior can be described qualitatively by a dipole layer of excess charge density close to the surface. **b** Energy of an electron as function of the distance d from the surface resulting from the charge density given in **(a)**. The passage of an electron through the dipole layer leads to additional work E_{surface} which has to be done in order to remove an electron from the solid

can reduce its energy when it spreads out over a larger region.² The “spill out” of charge at the surface leads to the formation of a charge dipole at the surface with negative charge “spilling out” towards the vacuum and less negative charge (i.e. a positive excess charge) inside the crystal close to the surface as indicated in Fig. 9.1a. The particular way in which the charge distribution at the surface deviates from the bulk structure depends on the crystal structure at the surface (bulk terminated or modified, i.e. known as reconstructed). When an electron is removed from the solid, a contribution to the work function arises from the transfer of the electron through the dipole layer.

The direction of the field in the dipole layer is (usually) such that an additional amount of work E_{surface} has to be done to move an electron through the dipole layer. The total energy to remove an electron at E_F from the solid to some distance d consists of a bulk contribution (binding energy) plus the work done by the electron when passing through the dipole layer now reads

² This can be seen from a simple 1D particle in a box model, where the energy of an electron state as a function of the quantum number n and size of the box L is

$$E(L) = \frac{\hbar^2 \pi^2 n^2}{2m_e L^2}. \tag{9.3}$$

With increasing L (“spill out” of charge) the energy decreases.

$$\Phi(d) = \Phi_{\text{bulk}} + E_{\text{surface}}(d). \quad (9.4)$$

The corresponding energy diagram is shown in Fig. 9.1b. Inside the solid the free electron approximation is used with the energy levels filled up to the Fermi energy. When passing through the dipole layer the additional contribution to the energy E_{surface} is added. This surface contribution to the work function can be of the order of up to 1 eV.

The splitting of the work function into different contributions arises from the different approaches used for each effect. An ab initio quantum mechanical theory would include all these effects when an electron is moved from inside the crystal to an distance from the crystal. Besides the influence of the surface which is difficult to calculate with ab initio methods, also the electrostatic potential at larger distances from the surface is difficult to calculate quantum mechanically. The correlation and exchange forces outside the surface cannot be calculated quantum mechanically up to large distances of 100 nm. The electrostatic image potential is often used as an approximation of the long-range behavior of the exchange-correlation potential in the vacuum.³ On the other hand, for short distances the unrealistic divergence of the classical image potential at the surface is avoided by a transition to quantum mechanical calculations, which describe the region close to the surface better.

The work due to the electrostatic image charges (occurring when an electron is moved out of the metal) reduces at the distance of 100 nm to 1 % of the value at 1 nm, and can thus be neglected for larger distances.

In conclusion we have identified three contributions to the work function: the bulk contribution (binding energy), the surface contribution, and the image charge contribution. These are the contributions which enter for a distance of the removed electron up to 100 nm. A further contribution occurs if the electron is removed to distances comparable to the size of the sample, and results due to external electric fields, as will be discussed in the next section.

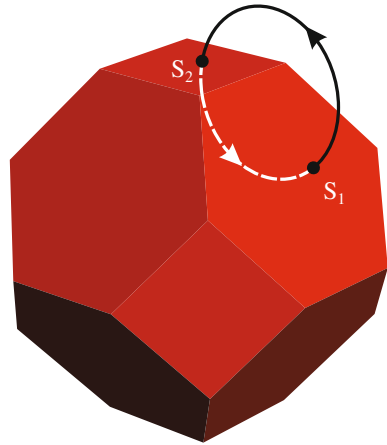
9.3 Surface Charges and External Electric Fields

Now we consider (different from the semi infinite crystal considered so far) a finite crystal which is terminated by different surfaces, as shown in Fig. 9.2. Different surfaces (with different atomic configurations) terminating a crystal, correspond to different “spill out” of charge. This leads to different surface dipoles and therefore

³ In classical electrostatics it is shown that the force between an electron at distance d from a conducting plate is the same as the force between the electron and a positive elementary charge located at a distance $2d$ from the electron (image charge), i.e. $-e^2/(4\pi\epsilon_0 2d)$. Integrating the negative of this force from infinity to d results in the (image) potential of the electron (relative to a position at infinity) as

$$V_{\text{image}}(d) = \int_{\infty}^d \frac{e^2}{4\pi\epsilon_0 2r} dr = \frac{-e^2}{4\pi\epsilon_0} \frac{1}{4d}. \quad (9.5)$$

Fig. 9.2 Due to energy conservation, zero total work has to be done in moving an electron along the closed path from inside the metal crystal through surface S_1 and back through surface S_2 . This argument shows that the two surfaces S_1 and S_2 , which are assumed to have different work functions, have to be at different electrostatic potentials. This different potentials are built up by corresponding surface charges



also to different work functions at different surfaces of a crystal. In the following, we will show that these different work functions at different surfaces of a finite crystal lead to the presence of net surface charges, and corresponding electric fields.

Let us take an electron on a closed loop from a point inside the crystal to a position outside of the crystal through surface S_1 and back through another surface S_2 , as shown in Fig. 9.2. Leaving the crystal through surface S_1 requires work E_1 (surface work to leave the crystal through surface S_1 , plus of course also the bulk contribution to the work function, which we leave out here, since it cancels out later). If there were no net surface charge, the electric field outside the crystal would vanish and there would be no work to transfer the electron outside the crystal from surface S_1 to surface S_2 . When the electron is inserted back into the crystal through S_2 , the work $-E_2$ (negative of the surface work to leave the crystal through surface S_2) is gained. Closing the path inside the metal does not involve energy, since the electric field inside a metal is vanishing. Since the work functions of the two surfaces are different (due to the two different surface contributions to the work function), a perpetuum mobile could be built gaining the energy difference between the two work functions ($E_1 - E_2$) on each cycle. Since this is clearly impossible, there must be an electric field outside the crystal against which a compensating amount of work is done as the electron is carried from S_1 to S_2 . This means the two surfaces must be at two different electrostatic potentials ϕ_1 and ϕ_2 , satisfying the condition

$$e(\phi_1 - \phi_2) = E_1 - E_2 = \Phi_1 - \Phi_2. \tag{9.6}$$

Since dipole layers cannot yield macroscopic fields outside the crystal these fields have to arise from net macroscopic electric charges on the surfaces,⁴ which also lead to an external electric fields with a range corresponding to the size of the crystal. At larger distances from the crystal these fields vanish.

⁴ All net charges are located at the surface of a metal, since the electric field vanishes in the interior of a metal.

In the following, we estimate which surface charge density is necessary to “supply” the necessary energy to compensate for the surface-related work function difference of the order of about 1 eV when an electron is transferred macroscopic distances from one metal surface to the other through the outer electric field. For a rough estimate, we consider a plate capacitor arrangement ($d = 1$ cm). The surface charge per area A can be expressed as

$$\rho_{\text{surface}} = \frac{Q}{A} = \frac{VC}{A} = \frac{V \epsilon_0 A}{A d} = \frac{V \epsilon_0}{d}. \quad (9.7)$$

The resulting surface charge corresponds to $\sim 5 \times 10^{-8}$ electrons per surface atom. This shows that even minute charge densities at the surface lead to considerable work, since the distance over which the electric field extends are on the order of the size of the crystal.

Now we will summarize the results on the work to remove an electron from the solid as a function of the distance d . An electron is considered to be removed from the highest occupied level at E_F . At very short distances from the surface (< 1 nm), the bulk contribution (bonding energy), as well as the surface contribution are the main contributions to the work. (At surfaces with different electronic structure, the different surface contributions lead to different work functions Φ_1 and Φ_2 .) For distances larger than 1 nm from the surface these contributions remain constant. At distances between 1 and 100 nm the work due to the image charge effect is the only distance dependent part of the work function. Between ~ 100 and ~ 1 mm (a distance corresponding to the sample size) there are no further contributions to the work function. When the distance of the electron removed from the solid becomes close to the sample size, the work due to the external electric fields arising from the previously discussed surface charges contribute to the work.

The work to bring an electron to infinity Φ^∞ is independent on the work function of the surface through which it passed.⁵ Any differences due to the surface work are compensated by macroscopic electric fields created by the surface charges at the different surfaces.

Experimental measurements of the work function are performed at a certain distance. Since most of the experiments are performed in a distance range between 100 and 1 mm, in which the work function is independent of the distance, usually work functions are considered as independent of the distance. An exception is scanning probe microscopy. In scanning tunneling microscopy the distance to which the electron is transferred out of the solid is very small (< 1 nm). Thus the image potential and even the surface and bulk contributions can be distance dependent at such small distances. The apparent barrier height Φ in STM is more a parameter than directly corresponding to the work function. Nevertheless, the apparent tunneling barrier height is usually referred as “the work function” and also we will use this not correct wording sometimes.

⁵ It is always assumed that the electron is at rest, i.e. there is no kinetic energy contribution to the work.

9.4 Contact Potential

Now we assume two (different) metals with different work functions which are initially not connected to each other Fig. 9.3a.⁶ In this case, both metals share a common vacuum level, but their Fermi levels are not aligned, due to the different work functions assumed. Suppose now that these two metals are connected (e.g. by a wire) in such a way that electrons can flow freely from one metal to the other, as shown in Fig. 9.3b. In this case, both metals share a common Fermi level. Since initially the two Fermi levels were not yet aligned, electrons flow through the wire from the metal with the higher Fermi level until equilibrium is reached. However, the charge transfer in order to align the two Fermi levels does *not* occur in such a way that half of the electrons between energy $E_{F,1}$ and $E_{F,2}$ flow from metal 2 to metal 1. A very small transfer of charge builds up a surface charge at the metals and a corresponding electric field \mathcal{E} between them. According to (9.7), over the (macroscopic) distance d these surface charges induce a potential drop V_{contact} , which aligns the Fermi levels of the metals. Due to the macroscopic distance only minute surface charges are needed to build up a voltage on the order of the work function difference.

In equilibrium the condition

$$eV_{\text{contact}} = \Delta\Phi \quad (9.8)$$

holds. The voltage V_{contact} is called contact potential, because it occurs if a contact between the metals is established, for instance by a connecting wire.

9.5 Measurement of Work Function by the Kelvin Method

Equation (9.8) suggests that a simple way to measure the (relative) work function of a metal is to measure the contact potential (relative to a metal with known work function) by connecting a voltmeter between the metals. However, this is not possible since a continuous flow of current (through the voltmeter) would have been produced without a sustaining source of energy. Lord Kelvin proposed a simple way to measure contact potentials by a capacitive method which is described in the following. The two samples are arranged in such a way that the two surfaces form a plate capacitor and an outer voltage called the compensation voltage V_{comp} is applied between the surfaces (Fig. 9.4). The total potential difference V can be written as

$$V = V_{\text{contact}} - V_{\text{comp}}. \quad (9.9)$$

⁶ We assume semi infinite crystals so that no surface charges are present and thus no electric fields occur outside the crystals. Since in Fig. 9.3a macroscopic distance between both metals is assumed, the work function rises within 100 nm quasi vertically to $E_{\text{vac}} = E_{\text{vac}}^{\infty}$.

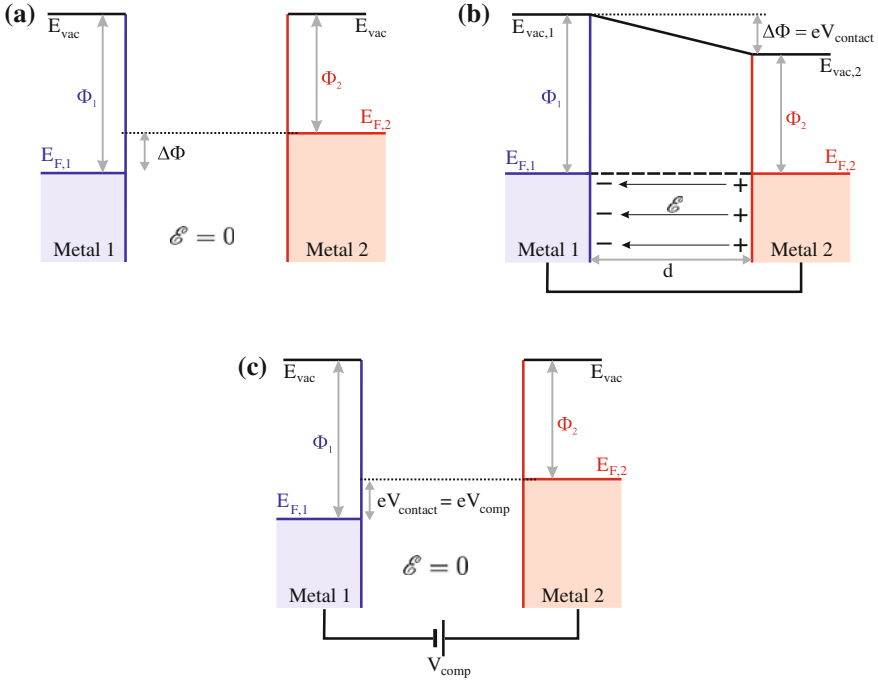


Fig. 9.3 **a** Potential energy diagram for two metals with work functions Φ_1 and Φ_2 , which are initially not connected and share thus a common vacuum level. **b** If the two metals are connected by a conducting wire, the Fermi levels of the two metals align. A buildup of surface charge leads to a macroscopic potential gradient compensating the difference between the work functions of the two metals. **c** The surface charges and the corresponding electric field \mathcal{E} vanish if a voltage $V_{\text{comp}} = V_{\text{contact}} = \frac{1}{e}\Delta\Phi$ is applied between the metals

The charge on the capacitor is accordingly

$$Q = CV = C(V_{\text{contact}} - V_{\text{comp}}). \quad (9.10)$$

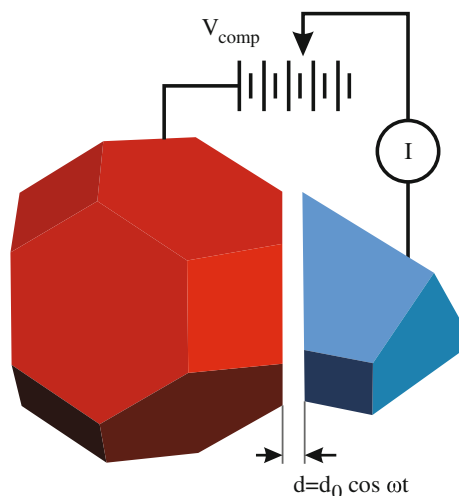
If the distance between the capacitor plates d is now modulated sinusoidally (for instance by a piezoelectric actuator) with a small modulation amplitude a current results as

$$I = \frac{dQ}{dt} = \frac{dC}{dt}(V_{\text{contact}} - V_{\text{comp}}), \quad (9.11)$$

since V_{contact} is constant and V_{comp} varies slowly compared to the modulation voltage. Therefore, a capacitive current is only induced by a change in the capacitance of the plate capacitor ($C = \epsilon_0 A/d$). The measured current has linear behavior as function of $V_{\text{contact}} - V_{\text{comp}}$. The current will vanish if V_{contact} or equivalently the work function difference is compensated by the compensation voltage, i.e. if

$$V_{\text{comp}} = V_{\text{contact}} = \frac{1}{e}\Delta\Phi. \quad (9.12)$$

Fig. 9.4 The surfaces of two metals are brought together in a plate capacitor configuration. When the distance d between the plates is modulated a charge flow (capacitive current) can be measured. When an external bias potential just compensates the work function no current flows anymore



No current flows if this condition is fulfilled and also the electric field between the metals vanishes as shown in Fig. 9.3c. The amplitude of the (capacitive) current can be measured sensitively using the lock-in detection method as a function of the compensation voltage. Using this method, the (macroscopic) contact potential difference between two metals can be measured.

9.6 Kelvin Probe Scanning Force Microscopy (KFM)

While Kelvin probe scanning force microscopy is the microscopic variant of the Kelvin method, there are also some differences. In the macroscopic Kelvin method the distance between the two metals is modulated and the resulting capacitive current is measured, whereas in Kelvin probe scanning force microscopy the voltage between tip and sample is modulated and the corresponding electric (capacitive) force is measured.⁷ For conceptual simplicity we consider a flat surface and the tip is moved at a constant topographic distance over this surface. However, we consider that the surface consists of areas with different work functions which we would like to detect. Our configuration consists of a surface and a tip with a voltage V between them, and a capacitance $C(z)$ for the tip-sample system. Apart from other forces, there is an electrical force between the tip and the sample. If we consider the tip-sample system as a capacitor, the electrical (capacitive) force between tip and sample is the gradient of the potential energy of the capacitor as

$$F_{\text{el}}(z, V) = -\frac{\partial E}{\partial z} = -\frac{1}{2} \frac{\partial C}{\partial z} V^2(t). \quad (9.13)$$

⁷ This is done since the force (not the current) is measured in a scanning force microscopy setup.

Since we assume a scan at constant tip-sample distance, $\partial C/\partial z$ is a constant. The voltage between tip and sample consists of different contributions: the constant contribution $V_{\text{contact}} - V_{\text{comp}}$, and additionally a voltage component which is modulated at the modulation frequency ω_{mod} resulting in a total voltage between tip and sample as

$$V(t) = V_{\text{contact}} - V_{\text{comp}} + V_{\text{mod}} \cos(\omega_{\text{mod}}t) \quad (9.14)$$

Thus the tip-sample force which is proportional to the square of the tip-sample voltage $V(t)$ results as

$$\begin{aligned} F_{\text{el}}(V) &= -\frac{1}{2} \frac{\partial C}{\partial z} [V_{\text{contact}} - V_{\text{comp}} + V_{\text{mod}} \cos(\omega_{\text{mod}}t)]^2 \\ &= -\frac{1}{2} \frac{\partial C}{\partial z} \left[(V_{\text{contact}} - V_{\text{comp}})^2 + 2(V_{\text{contact}} - V_{\text{comp}}) V_{\text{mod}} \cos(\omega_{\text{mod}}t) \right. \\ &\quad \left. + V_{\text{mod}}^2 \cos^2(\omega_{\text{mod}}t) \right]. \end{aligned} \quad (9.15)$$

The first term in the square bracket is time independent (constant), the second term is a modulation with the frequency ω_{mod} , while the third term consists (after using a mathematical identity) of a constant term plus a component at twice the frequency ω_{mod} . Using the lock-in technique, which we introduced in Chap. 6, the amplitude of the term at the frequency ω_{mod} can be selectively measured. This component vanishes if $V_{\text{contact}} - V_{\text{comp}} = 0$. In the practical implementation, a feedback control of V_{comp} keeps the ω_{mod} component of the force at zero. Thus by recording the voltage V_{comp} , which nulls the ω_{mod} component of the force signal $\propto \frac{1}{e} \Delta \Phi - V_{\text{comp}}$, the work function difference is measured locally on the nanoscale while scanning over the surface. Due to the modulation of the voltage V , a modulated force is exerted on the cantilever, which induces a cantilever oscillation at the modulation frequency.

So far we have left out the complication that in a practical implementation of an SPM setup the tip-sample distance also has to be measured, and to adapt the setpoint value. In dynamic atomic force microscopy this can be done using a (second) modulation of the cantilever close to its resonance frequency (as we discuss in detail in Chap. 14). Thus the cantilever is modulated at two (different) frequencies and two lock-in detection units detect the oscillation amplitudes at the respective modulation frequency.

9.7 Summary

- The definition of the work function as the difference between the vacuum level and the Fermi level, includes also a surface contribution to the work function.
- Due to a “spill out” of charge to the vacuum, a charge dipole occurs at the surface. A certain amount of work has to be done to move an electron through this dipole layer. This is the surface contribution to the work function.

- Also a net charge can accumulate at the surface giving rise to a contact potential between metals with different work functions. The contact potential is the difference between the work functions.
- The contact potential can be measured using the Kelvin method by modulating the distance between the surfaces of the metals and measuring the induced capacitive current.
- In Kelvin probe scanning force microscopy (KFM) the work function can be measured locally by modulating the tip-sample voltage.