V. Electrical Properties at Surfaces

Interface: two different bulk materials are brought together to form an interface
The abrupt change of electronic structure from one material to another induces the structural rearrangement of nuclei and electrons in the interface region in order to reduce the total energy of the system.

The overall result is forming an interface dipole.

Roughness reduces the interface dipole
Adsorption of atoms or molecules perturbs the electronic structure, thus the interface dipole.

Jellium model

If we consider atomically-smooth slab of solid in UHV.
The ion cores of atoms can be viewed as being smeared out to produce a uniform density of positive charge.

Electrons are bound to this uniform charge by electrostatic forces.
In jellium model, the Fermi energy, the energy of the highest occupied state by conduction electrons

$$E_F = \frac{h^2}{8m}\left(\frac{3}{\pi}\right)^{2/3} \bar{n}^{2/3}$$

Where, is the average conduction electron density in the bulk, E_F and n are in the unit of eV and nm^{-3}
Then, $E_F = 36.46 \times 10^{-2} n^{2/3}$
$r_s = (3/4\ \pi n)^{-1/3}$, that is the radius of a sphere whose volume is equal to the volume per conduction electron.

Fermi wavelength – defined as the de Broglie wavelength of the conduction electrons at the Fermi level.

$$\lambda_F = \frac{hc}{(2mE_F)^{1/2}}$$

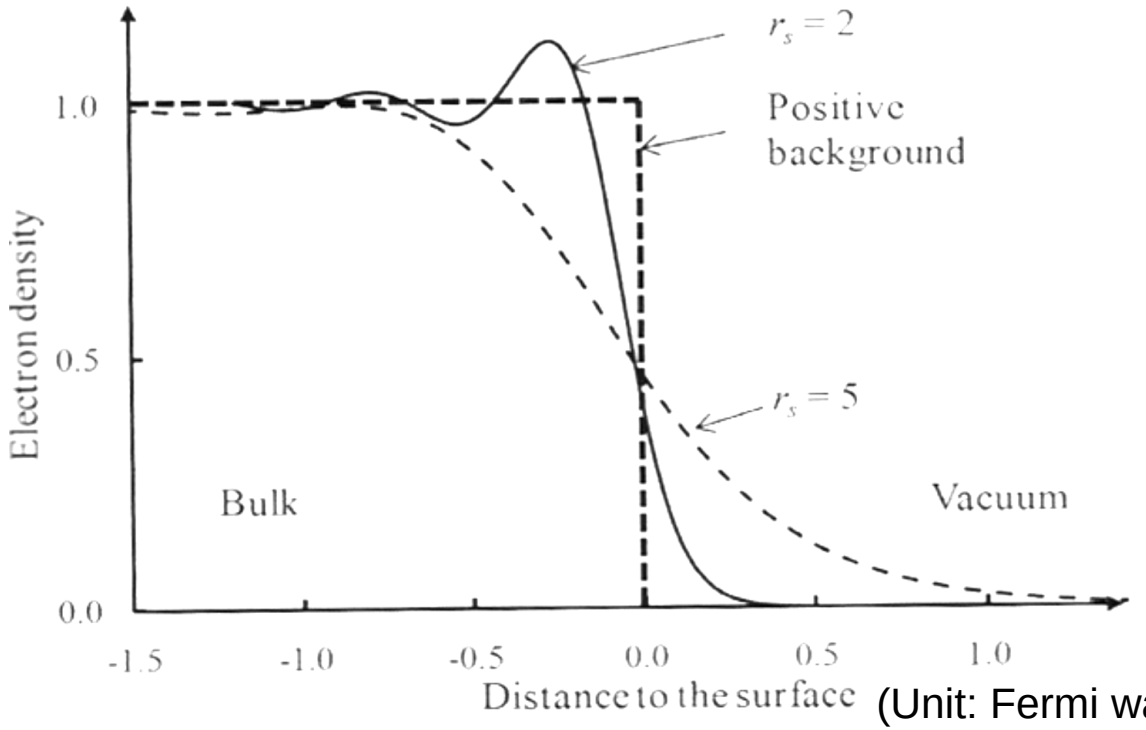
Jellium model

The ion cores are replaced by a uniform sea of positive charge, having the same average charge density.
The crystal surface is the edge of this area of positive charge.

Jellium model

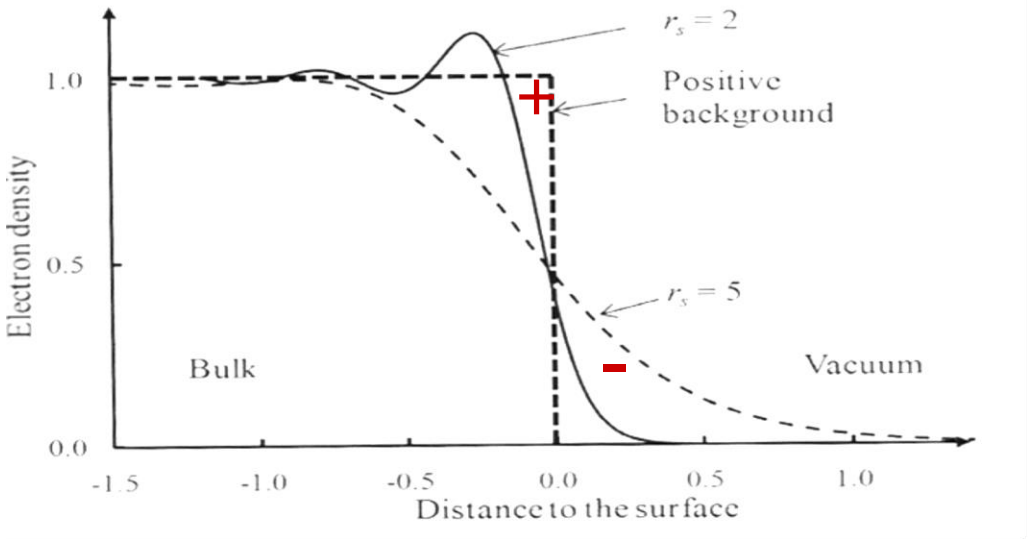
Interface dipole formation

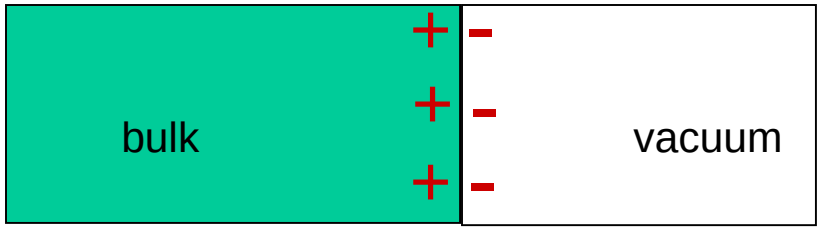
At the surface, the electrons are bound only toward the positive background on the bulk side, and they can spill out by tunneling into the vacuum, resulting in exponential dropping of electron density from the surface. This charge separation leads to the formation of the surface dipole.



(Unit: Fermi wavelength)

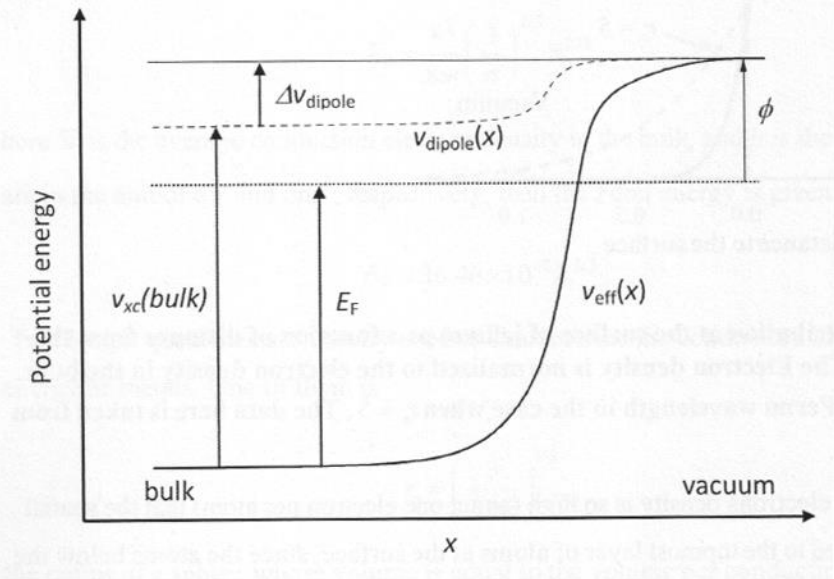
Surface dipole formation





For a metal, the free conduction electron density is high (~ 1 el/atom), and screening of the metal atoms by the large free-electron density is effective.
Spatial extent of the surface dipole decreases as the electron density in the bulk increases.

Energy level diagram



The surface dipole causes an increase of electrostatic energy of electrons when they move across the surface region into vacuum. This electrostatic energy potential $v_{dipole}(x)$ is called as surface dipole potential

The interaction between electrons is taken account by introducing the exchange-correlation energy.

The work function is the minimum potential that the most loosely bound valence electrons (at the Fermi level) in the solid must overcome to be ejected into the vacuum.

$$\phi = v_{xc}(bulk) + \Delta v_{dipole} - E_F$$

Effect of surface structure on work function

Table 5-1 Work Functions Measured from Different Crystal Faces of Tungsten, Molybdenum, and Tantalum

Work Function						
	Tungsten [a]		Molybdenum [b]		Tantalum [b]	
Crystal face	eV	10^{-19} J	eV	10^{-19} J	eV	10^{-19} J
(110)	4.68	7.50	5.00	8.01	4.80	7.69
(112)	4.69	7.51	4.55	7.29	—	—
(111)	4.39	7.03	4.10	6.57	4.00	6.41
(001)	4.56	7.31	4.40	7.05	4.15	6.65
(116)	4.39	7.03	—	—	—	—

$$\phi = v_{xc}(bulk) + \Delta v_{dipole} - E_F$$

The surface structure sensitivity of work function mainly comes from the surface dipole potential since other two terms are basically bulk properties.

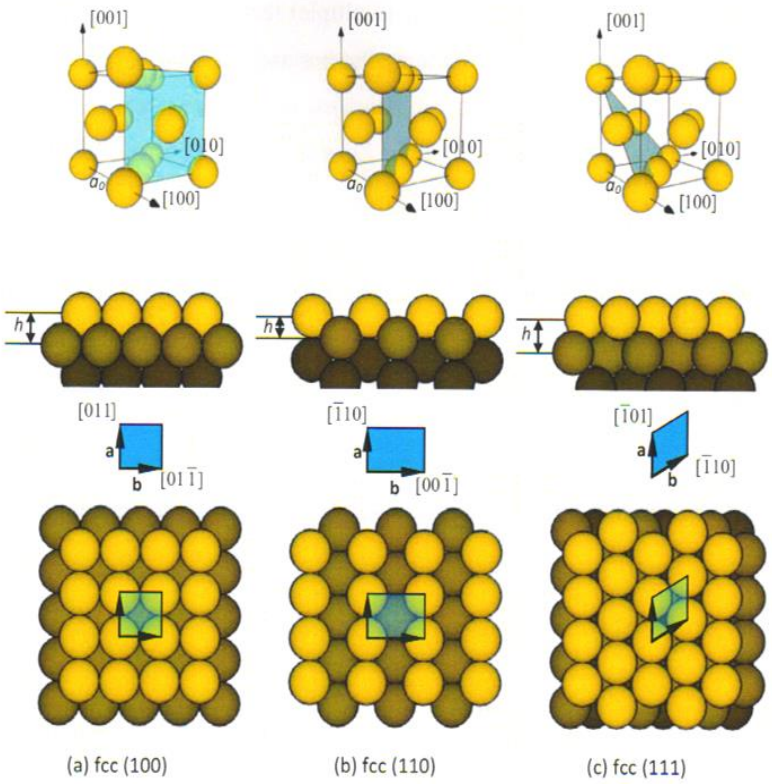
The surface with higher roughness exhibits low work function

Effect of surface structure on work function

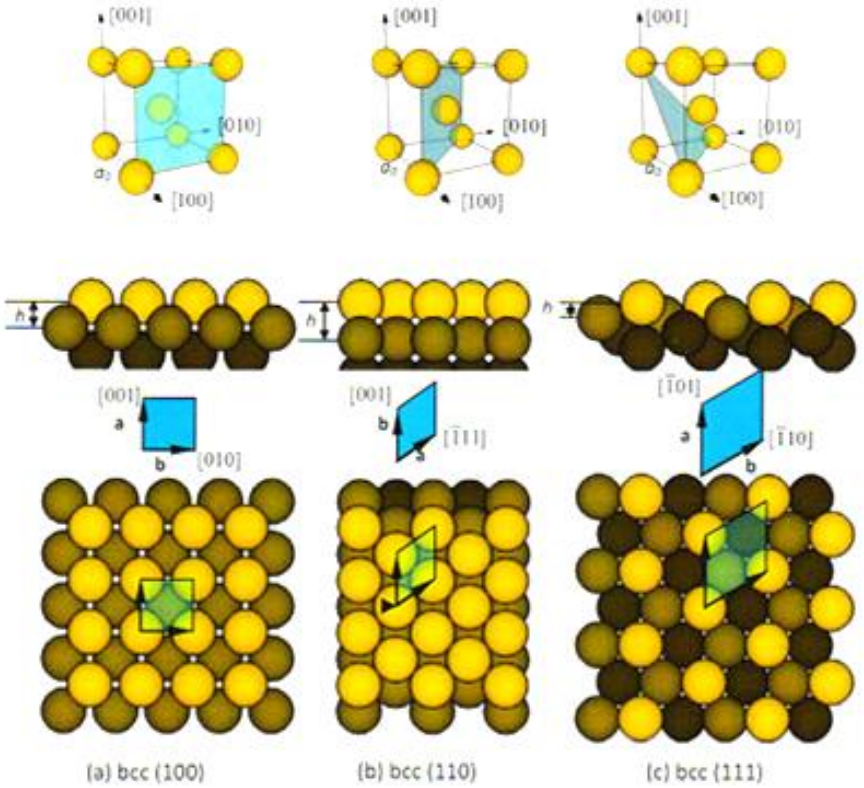
Table 1. The work function of single-crystal surfaces of silver.

	φ (eV)		
Author	Ag(110)	Ag(100)	Ag(111)
Farnsworth and Winch (1940)		4.81	4.75
		4.72	4.66
Anderson (1941)		4.62	
Clarke and Farnsworth (1952)		4.76	
Dweydari and Mee (1973, 1975)	4.52	4.64	4.74
Present work	4.14	4.22	4.46
Steiner and Gyftopoulos (1967)	4.17	4.45	4.74
Lang and Kohn (1970, 1971)	3.35	3.55	3.70

J. Phys. C:Solid State Phys. 15, 2305 (1982)



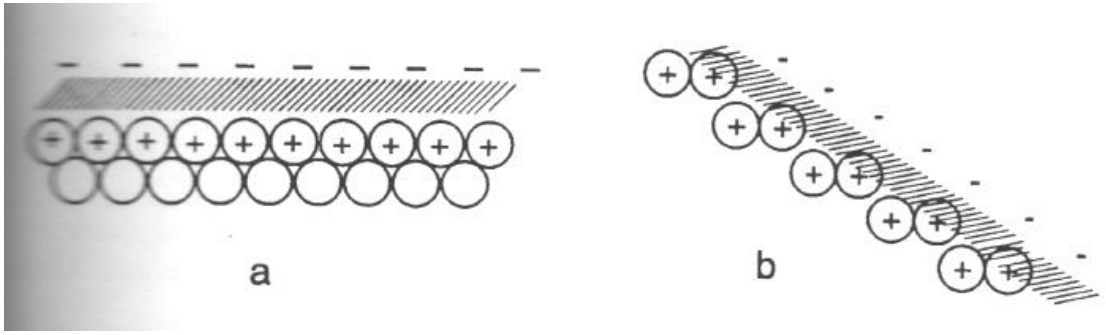
(a) fcc (100) (b) fcc (110) (c) fcc (111)



(a) bcc (100) (b) bcc (110) (c) bcc (111)

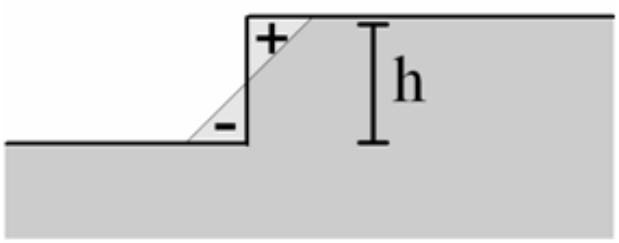
Effect of surface roughness on work function

The valence electron in the rough surface smooth out the roughness in the positive charge distribution. The result is an electrostatic dipole orientated opposite to the spill-out dipole. As a result, the net dipole is reduced relative to its value at the higher-atomic-density, smoother surface, yielding a lower work function.

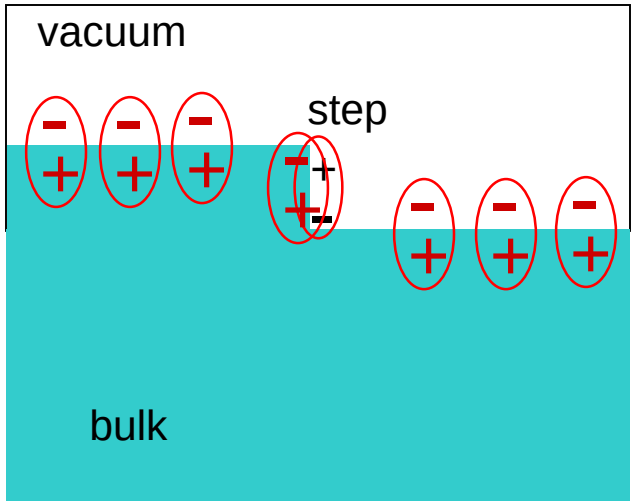


Schematic picture of surface electron charge density for (a) flat and (b) rough surfaces. (a) shows the large surface dipole and high work function, and (b) small surface dipole and low work function

Effect of surface steps on work function



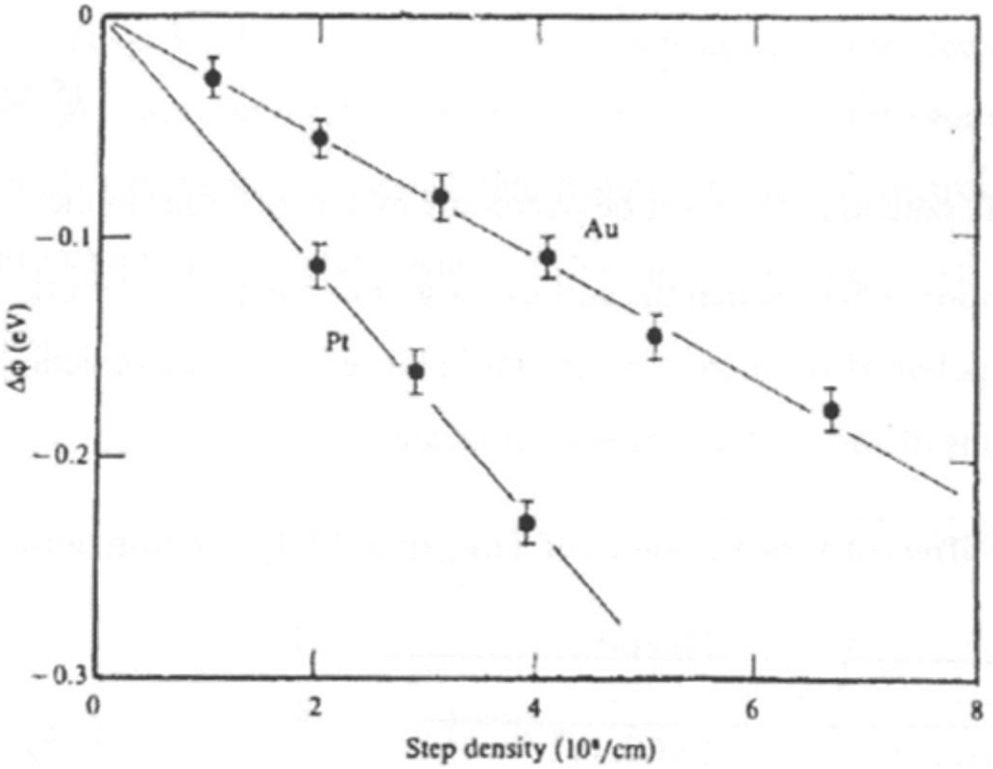
The Smoluchowski effect:
the formation of electrostatic dipoles at atomic steps



The net dipole at the atomic steps is reduced relative to its value at the higher-atomic-density, smoother surface

This indicates that atomic steps modify the electronic structure of flat surfaces. Steps on conducting surfaces can have a dipole moment arising from the incomplete screening of the positive ion cores by conduction electrons.

Effect of surface steps on work function



The work function decreases linearly with increasing step density.

The induced dipole moment μ due to steps can be calculated from the work-function change because

$\Delta\phi = 4\pi N_s \mu$ where N_s is the step density

Adsorption induced charge transfer at surfaces

Table 5-3 Sign of Work-Function Change, $\Delta\phi$, Upon Adsorption at 300 K

System	Sign of Work-Function Change, $\Delta\phi$	Reference
O/Ag(111)	Positive	1
O/Cu(100)	Positive	2
O/Cu(110)	Positive	2
O/Cu(111)	Positive	2
O/Ni(110)	Positive	3
CO/Cu(100)	Negative	4
CO/Mn	Positive	5
CO/Ni(111)	Positive	6
H/Mo(001)	Positive	7
H/Mo(011)	Positive	7
H/Mo(111)	Positive	7
H/Ni(110)	Positive	8
H/W(100)	Positive	9
Cs/Ni(100)	Negative	10
Cs/W(100)	Negative	11
K/Ni(110)	Negative	12
Xe/Pd(100)	Negative	13
Substitute /Pt(111)	Negative	14
Aromatic molecules / Pt(1 00)	Negative	12
C1/W(100)	Positive	15
$Cl/_0Ti$	Positive	16
Ba/W(100)	Negative	17
CH_4/W(110)	Positive	18
Na/W(110)	Negative	19
Li/W(110)	Negative	20

Work function of various elements

Element	eV	Element	eV	Element	eV	Element	eV	Element	eV
Ag:	4.52-4.74	Al:	4.06-4.26	As:	3.75	Au:	5.1-5.47	B:	~4.45
Ba:	2.52-2.7	Be:	4.98	Bi:	4.34	C:	~5	Ca:	2.87
Cd:	4.08	Ce:	2.9	Co:	5	Cr:	4.5	Cs:	2.14
Cu:	4.53-5.10	Eu:	2.5	Fe:	4.67-4.81	Ga:	4.32	Gd:	2.90
Hf:	3.9	Hg:	4.475	In:	4.09	Ir:	5.00-5.67	K:	2.29
La:	3.5	Li:	2.93	Lu:	~3.3	Mg:	3.66	Mn:	4.1
Mo:	4.36-4.95	Na:	2.36	Nb:	3.95-4.87	Nd:	3.2	Ni:	5.04-5.35
Os:	5.93	Pb:	4.25	Pd:	5.22-5.6	Pt:	5.12-5.93	Rb:	2.261
Re:	4.72	Rh:	4.98	Ru:	4.71	Sb:	4.55-4.7	Sc:	3.5
Se:	5.9	Si:	4.60-4.85	Sm:	2.7	Sn:	4.42	Sr:	~2.59
Ta:	4.00-4.80	Tb:	3.00	Te:	4.95	Th:	3.4	Ti:	4.33
Tl:	~3.84	U:	3.63-3.90	V:	4.3	W:	4.32-5.22	Y:	3.1
Yb:	2.60 [2]	Zn:	3.63-4.9	Zr:	4.05				

Unit of dipole

The debye (symbol: D) is a CGS unit (a non-SI metric unit) of electric dipole moment named in honor of the physicist Peter J. W. Debye

$1D = 10^{-10}$ esu·Å $= 3.33564 \times 10^{-30}$ C·m

Typical dipole moments for simple diatomic molecules are in the range of 0 to 11 D.
Symmetric homoatomic species, e.g. chlorine, Cl_2, have zero dipole moment and highly ionic molecular species have a very large dipole moment, e.g. gas phase potassium bromide, KBr, with a dipole moment of 10.5 D

Surface energy

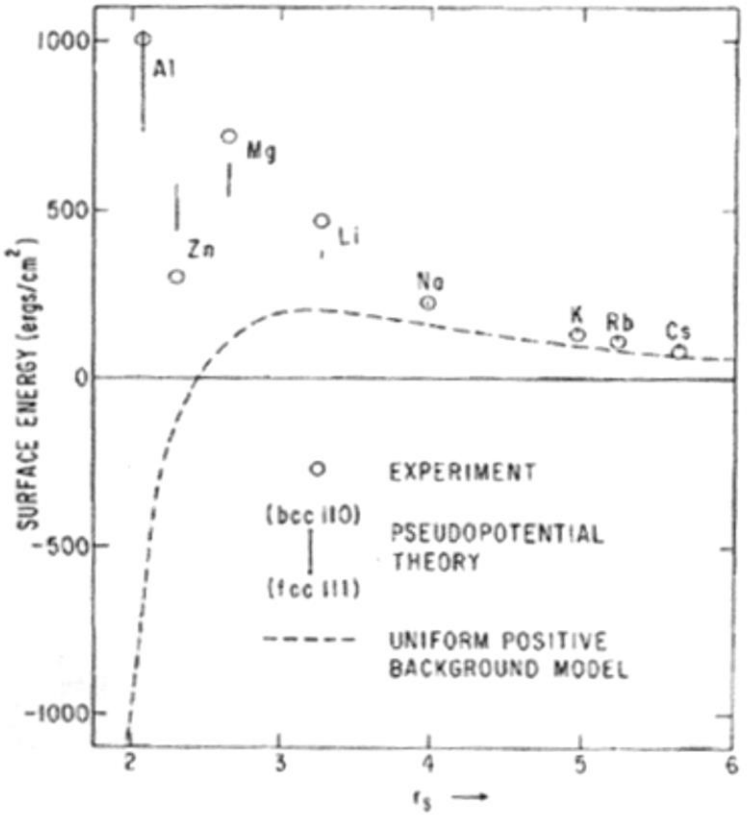
Most experimental work was obtained from surface tension of liquid metals

Theoretical modeling
In the jellium model, taking energy difference between the split and unsplit crystal leads to three terms

$\sigma = \sigma_s + \sigma_{xc} + \sigma_{dipole}$

where σ_s is the kinetic energy change between the split and unsplit crystal, and σ_{xc} is difference of the exchange correlation energy between the split and unsplit crystal, and σ_{dipole} is the surface dipole layer contribution

Another approach is DFT calculation with pseudopotential with exact atomic structure.



Comparison of DFT results of the surface energy with experimental results

Case study -Probing step dipole with scanning probe microscopy

Scanning tunneling microscopy

feedback signal :

tunneling current

Atomic probe with “true atomic resolution”

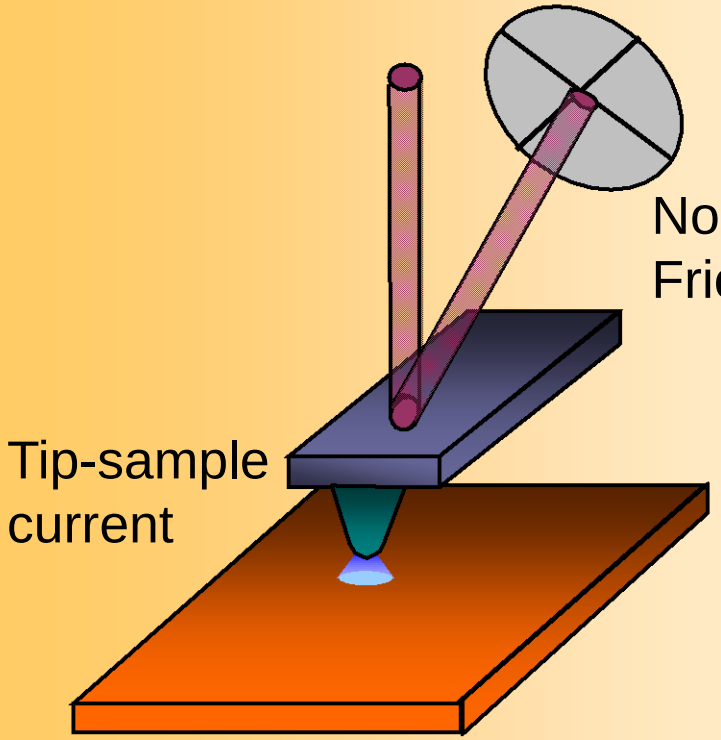
sensitive to the electronic density of state

Atomic force microscopy

Feedback signal: Force

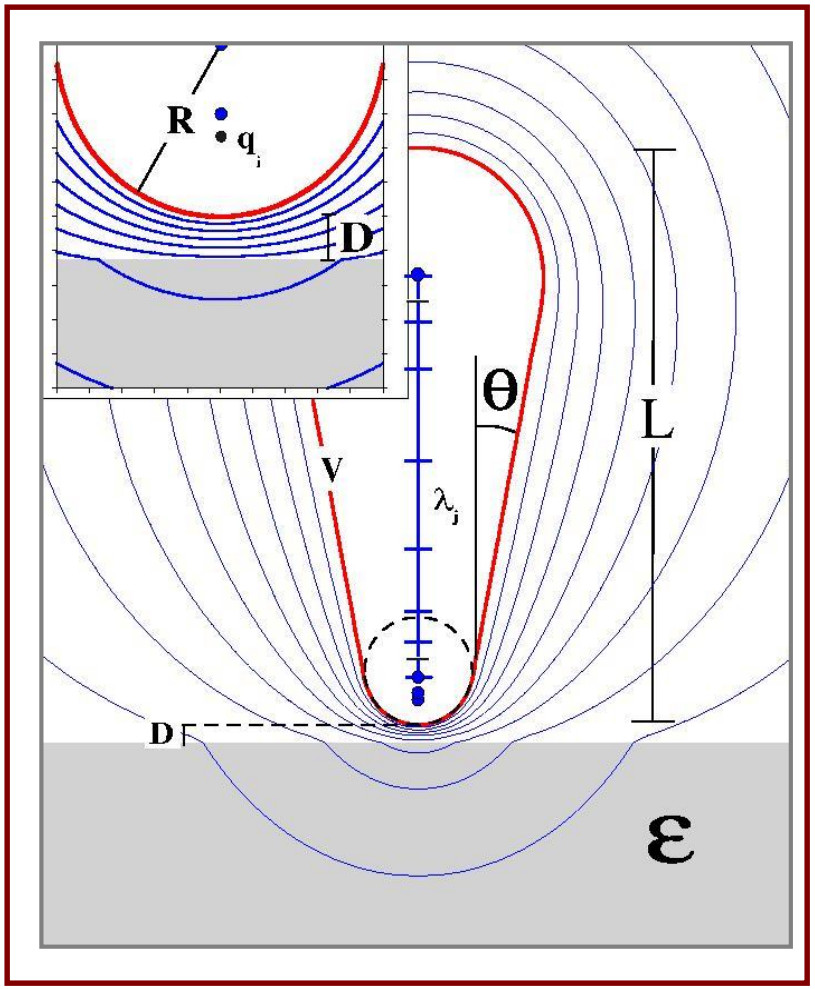
Lattice imaging due to atomic stick-slip process

Be able to measure mechanical properties (adhesion, friction, elasticity,etc)



Schematic of combined apparatus of AFM/STM

Probing step dipole with scanning probe microscopy

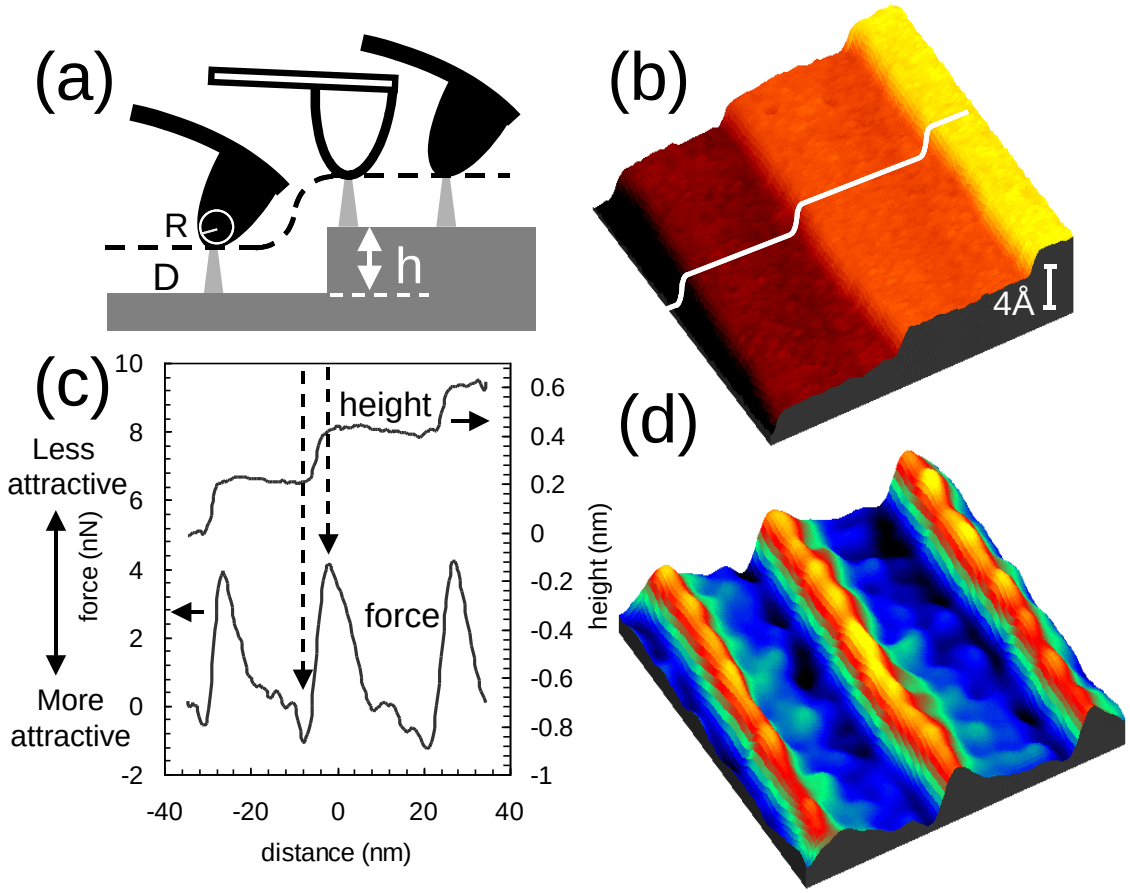


$$F' = \pi \varepsilon_0 V_0^2 \frac{R}{D^2}$$

electrostatic force between a metallic tip and a plane dielectric sample for different tip sample distances varies, but it doesn't have the polarity dependence.

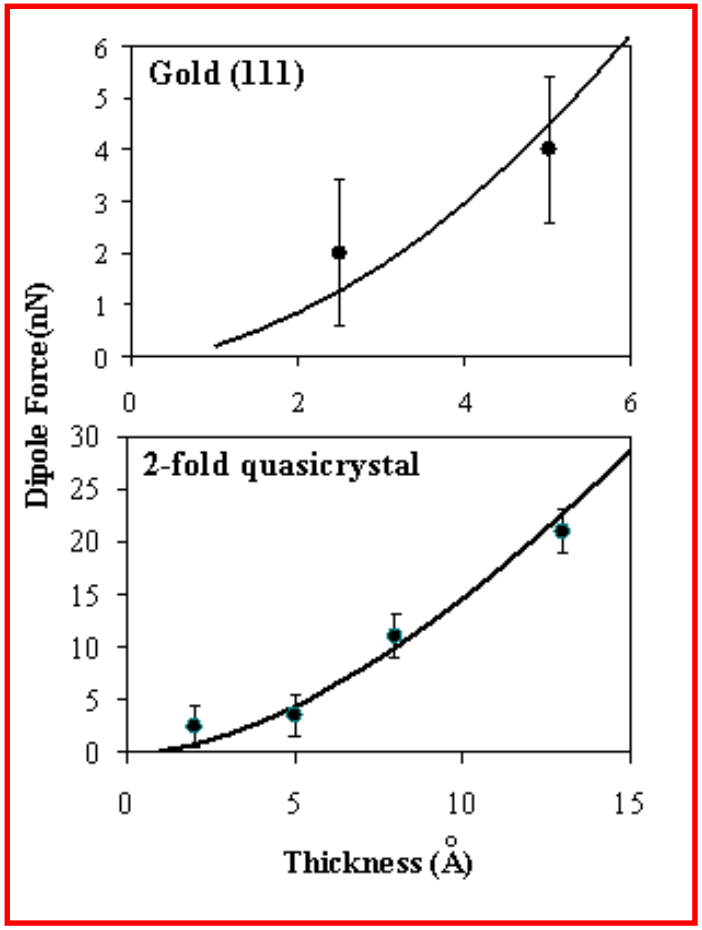
Small atomic package at the steps induces a less attractive force. The polarization of the steps is smaller than the polarization of the terraces.

Sensing dipole fields at atomic steps with combined scanning tunneling and force microscopy



(a) STM-AFM configuration using a conductive cantilever bending in response to forces. (b) 70 nm x 70 nm STM image of a Pt (111) surface (V_t = –0.2V, I=0.16nA). (c) Height and force profile across the steps. The force on the tip is more attractive at the bottom of the steps and less attractive at the top. (d) Force image simultaneously acquired with (b). Yellow and blue colors represent low and high attractive forces, respectively.

A difference between the positive and negative polarization leads to the step dipole moment



Permanent dipole moment per atom:
Gold (111): P=0.3D/step atom

2-fold Quasicrystal: P=1D/step atom

The permanent dipole moment increases when the atomic package at the step decreases

Distance between atoms at the step:
Gold (111): 1.8 A

2-fold Quasicrystal: 4A

J. Y. Park et al. Phys. Rev. Lett 95, 136802 (2005).

Chemisorption-induced changes in work function

Chemisorption of an atom or a molecule leads to charge transfer to or from the metal. This charge transfer results in a large change of work function, with the magnitude of the change depending on the nature of the adsorbate-substrate bond and on the coverage.

If we consider well-separated chemisorbed species with surface concentration σ and, the work function change $\Delta\phi$ is given by the Helmholtz equation

$\Delta\phi = -4\pi e\mu\sigma$

Where μ is the dipole moment induced by the adsorbate.

$\Delta\phi = -3.76 \times 10^{-5}\ \mu\sigma$

Where $\Delta\phi$ is in eV, μ is in Debyes, and σ is the number of adsorbate atoms per cm^2

Dipole-dipole interaction causes depolarization, which shows up at higher coverages that modify the Helmholtz equation according to the point-depolarization model developed by Topping

$\Delta\phi = -4\pi e\mu\sigma/[1+9\ \alpha\ \sigma^{3/2}]$

where α is polarizability

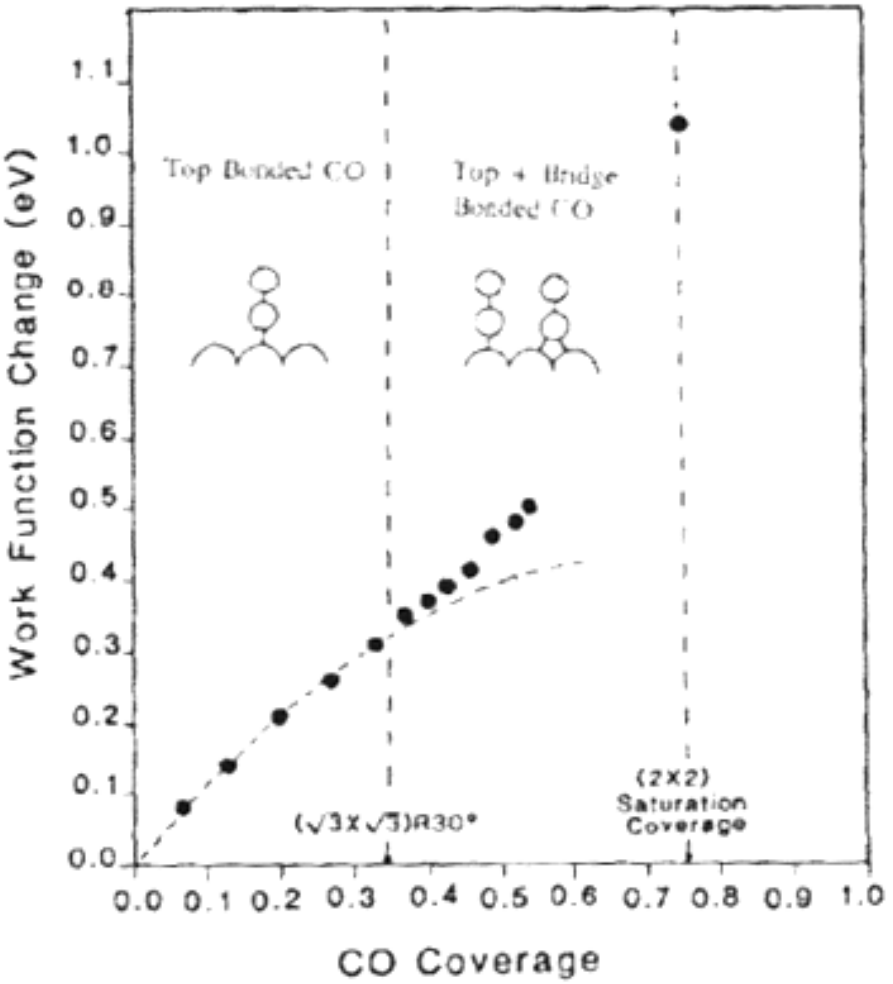
Chemisorption-induced changes in work function

Carbon monoxide increase the work function of Rh(111) upon chemisorption

$\Delta\phi = -4\pi e\mu\sigma/[1+9\ \alpha\ \sigma^{3/2}]$

Good fitting can be obtained for CO coverage(θ) θ <0.33 with μ_{CO} = -0.2 Debye, and α_{CO} = 0.34 x 10^{-28} m^3

For θ >0.33, $\Delta\phi$ increases dramatically until reaching a value of +1.05 eV at θ =0.75



The change of work function of Rh(111) upon CO adsorption

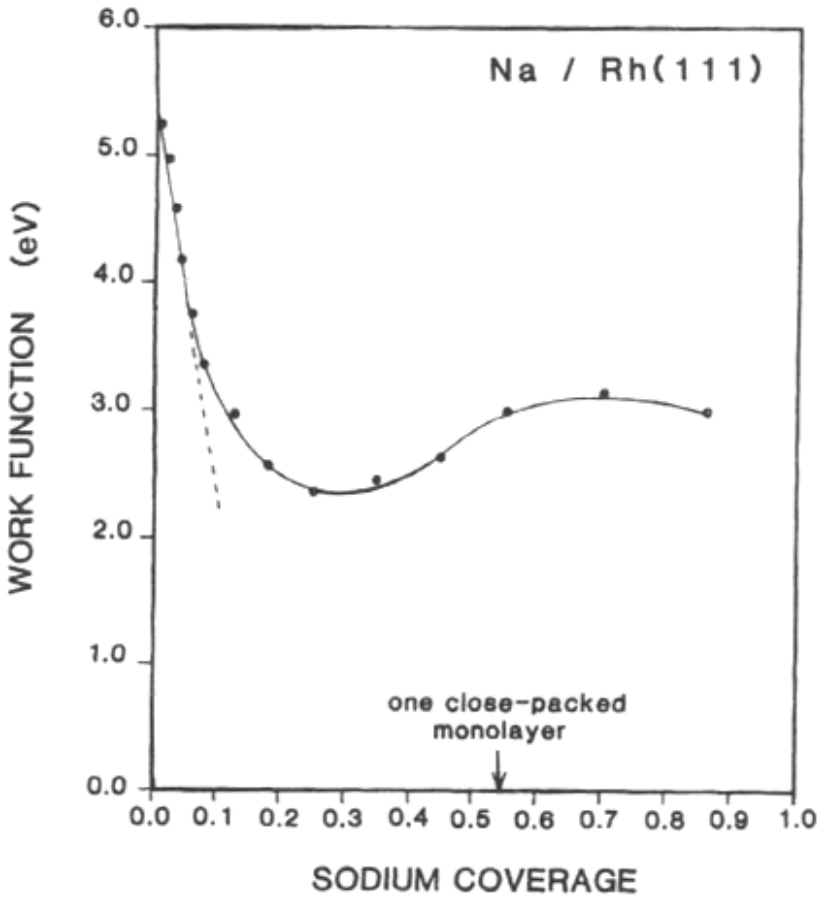
Chemisorption-induced changes in work function

Chemisorption of sodium decreases the work function of Rh(111).

$\Delta\phi = -4\pi e\mu\sigma/[1+9\ \alpha\ \sigma^{3/2}]$

Using the equation above, we can obtain a surface dipole moment of μ_{Na} = +5.1 Debye, and α_{Na} = 2.9 x 10^{-28} m^3 for low sodium coverage.

Similar trend can be observed for chemisorption of alkali adatoms on other transition metals as well.



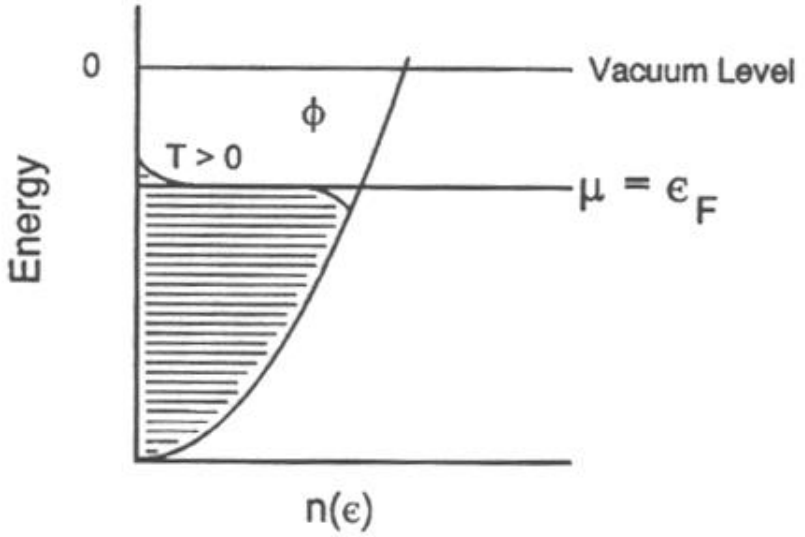
Measurement of work function

The electron in the conduction band follow Fermi-Dirac statistics with the probability of occupancy being given by

$$f(\varepsilon) = \frac{1}{\exp\left[\frac{\varepsilon - \mu}{kT}\right] + 1}$$

At T=0K, all of the states for which $\varepsilon \leq \mu$ will be filled and all states for which $\varepsilon > \mu$ will be empty.
The value of ε corresponding to $\varepsilon = \mu$ is called the Fermi energy.

At temperature above 0 K, the probability of occupancy of states just above ε_F becomes finite.

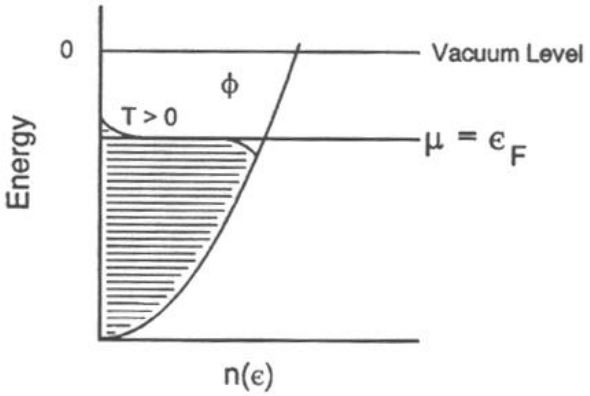


Density of state curve for the conduction band of a free electron metal

Measurement of work function – a. Thermionic emission

At high temperature, states with $\varepsilon - \varepsilon_F > \Phi$ will have a probability of occupancy given by

$$f(\varepsilon) = \exp\left[-\frac{\Phi}{kT}\right]\exp\left[\frac{-(\varepsilon-(\mu+\Phi))}{kT}\right]$$



Where $\varepsilon - (\mu + \Phi)$ represents the energy in excess of that needed to reach the vacuum level. Any electron with $\varepsilon - (\mu + \Phi) > 0$ is essentially outside of the crystal and can be collected as a free electron.

Such electrons are called thermionic electrons and the process by which they are produced is called thermionic emission.

Measurement of work function- a. Thermionic emission

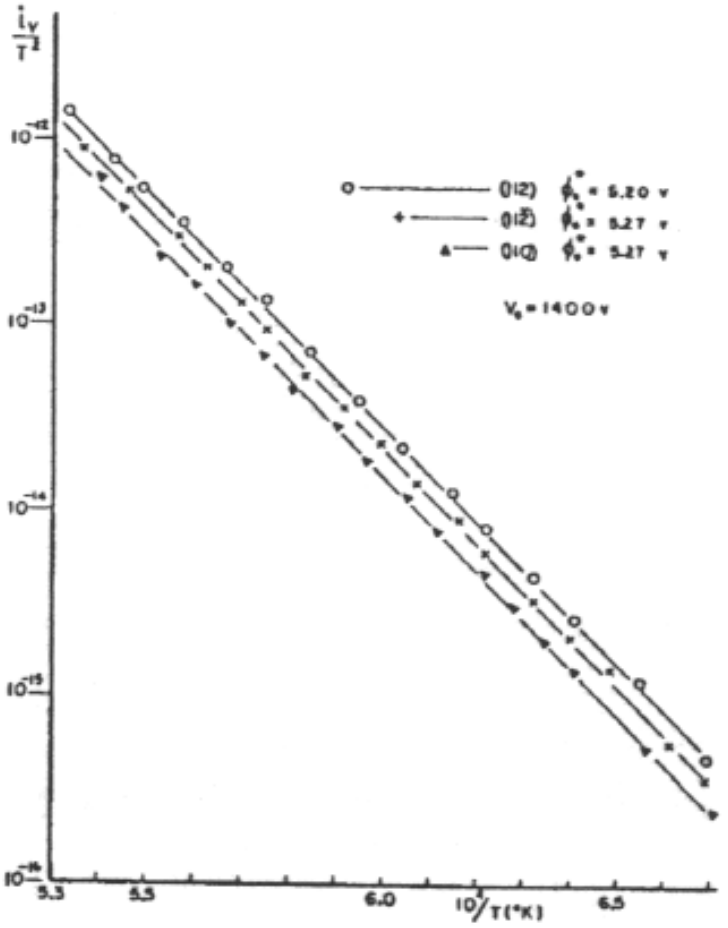
Richardson-Dushman equation

The expression relating thermionic current j to temperature

$$j = AT^2 \exp\left[-\frac{\Phi}{kT}\right]$$

Where A ~ 120 A /cm^2 deg^2

To obtain work function from a thermionic emission measurement, one plots ln (j/T^2) as a function of 1/T



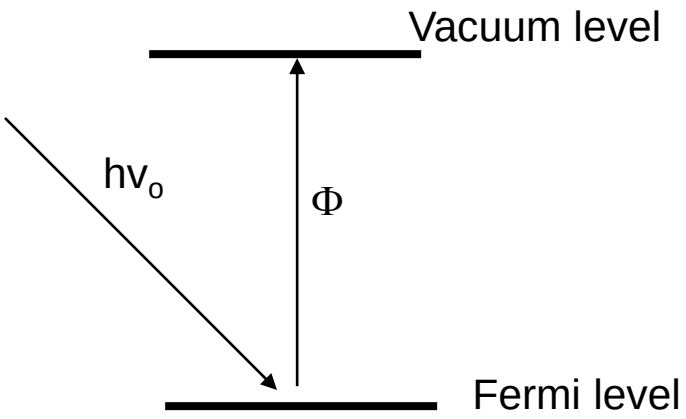
Plot of Richardson-Dushman equation
For different faces of tungsten

Measurement of work function- b. Photoelectron emission

Any photon incident on the sample surface can interact with an electron in the solid to transfer its energy to the electron. If this energy is greater than the difference between the initial energy of the electron and the vacuum energy, then the electron may escape from the solid.

This process is called photoelectron emission. The ejected electrons are called photoelectrons.

If the minimum photon energy, hv_o, can cause electron ejection, the work function (Φ) is the same with hv_o



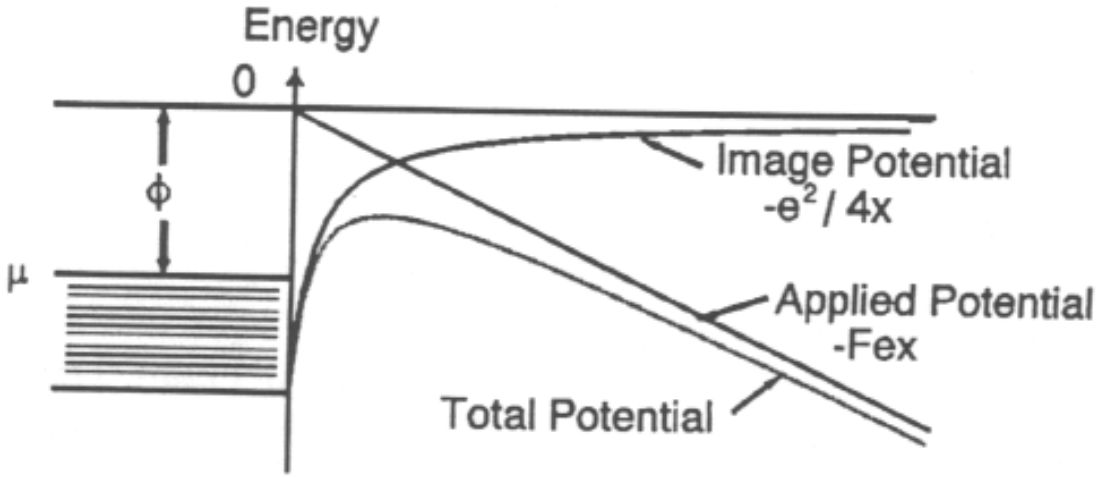
Photoelectron emission- Fowler law

The total electron current generated in this process is given by the Fowler equation

$$j = BT^2 \exp\left[\frac{h(\nu - \nu_o)}{kT}\right]$$

Where B is a parameter that depends on the material involved. If measurements are made of the photoemitted current as a function of photon energy, extrapolation allows the determination of v_o, thus Φ

Measurement of work function- c. Field emission



If a strong electric field is present at the surface with the surface electrically negative wrt the surroundings, the effective surface barrier will be modified with smaller height and width.

In this case, a quantum mechanical calculation indicates that electrons can escape through the barrier by quantum mechanical tunneling and appear in the space outside the metal as field-emitted electrons

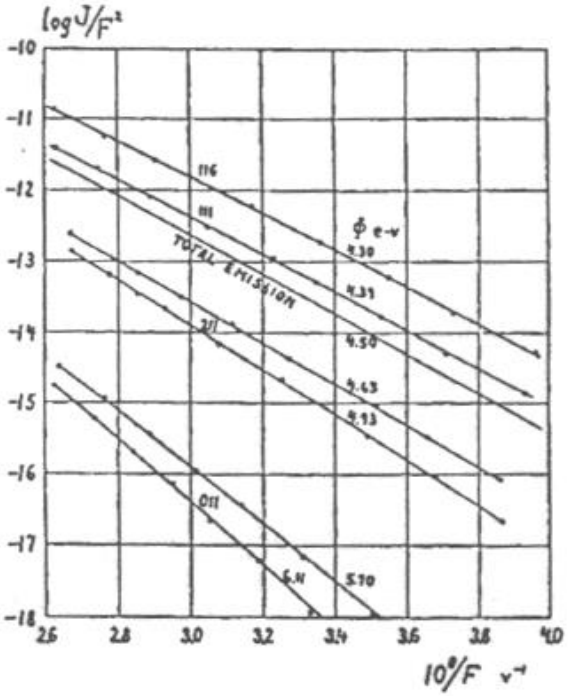
Measurement of work function- c. Field emission Fowler-Nordheim equation

The current arising from this process is given by the Fowler-Nordheim equation as

$$j = (6\times10^{6})(\frac{\mu}{\Phi})(\mu+\Phi)^{-1}(\frac{F}{\alpha})^{2}\exp\left[\frac{-(6.8\times10^{7}\,\alpha\Phi^{3/2})}{F}\right]$$

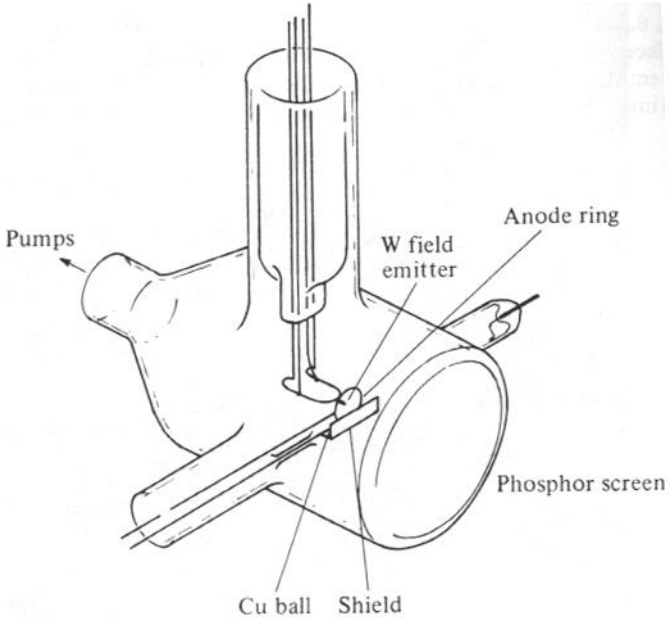
Where F is the electric field strength, and α is a slowly varying function of F, of the order of unity.

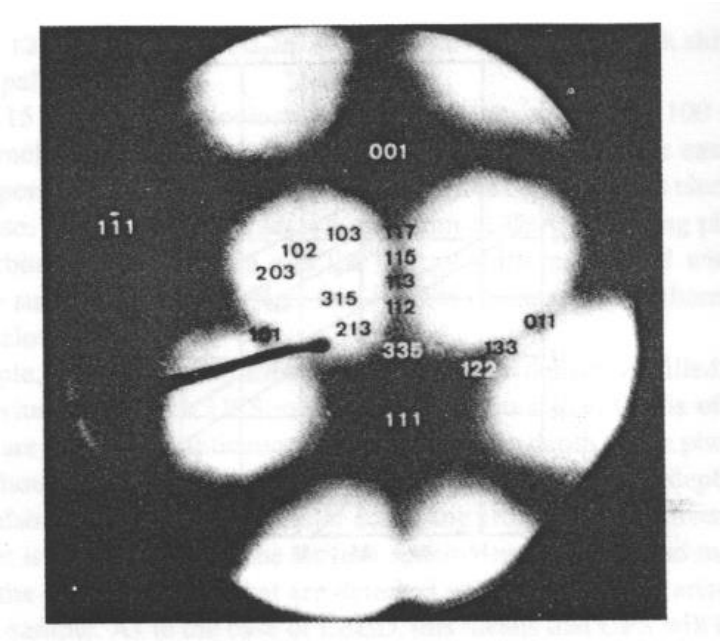
A plot of this relation, ln (j/F^2) vs (1/F) can be used to determine work function



Measurement of work function- c. Field emission
Field emission microscopy

The contrast observed in FEM arises from the variation in work function with crystallographic orientation over the tip.





Field emission microscopy image of a clean Rh(111)

This technique along with F-N plot, allows the measurement of the variation of work function with orientation.
FEM(field emission microscopy) has been used to measure adsorption and surface diffusion processes.