Appendix

**Thermodynamic Equilibrium Hypothesis: Charge Transfer between Metal and Insulator**

(Lowell and Rose-Innes, 1980)

Consider charge transfer across a plane interface between an insulator and a metal. Suppose the interface lie in the yz-plane, so that nothing varies except in the x-direction. Assume that the Fermi level of the metal is initially above that of insulator, so that electrons will transfer from the metal to the insulator when contact is made; in this case, the insulator become negatively charged. Note also that the case of a positively charged insulator can be treated in an analogous way.

The charge in the insulator at thermodynamic equilibrium must be first assumed that the Fermi level of the insulator is everywhere constant and at the same energy as the Fermi level of the metal. Moreover, the charge density in the insulator must satisfy Poisson’s equation:

\[
\frac{\partial^2 V}{\partial x^2} = - \frac{\rho}{\varepsilon \varepsilon_0},
\]

where \( \rho \) is the charge density and \( V \) is the electrostatic potential. If the density of states in the insulator is \( n (E', x) \) at energy \( E' \) and depth \( x \), then

\[
\rho (x) = en (E', x) f (E'),
\]

where \( f (E') \) is the Fermi-Dirac function. The Fermi-Dirac function is

\[
f (E') = \{1 + g \exp[(E' - E_F) / kT] \}.
\]
where \( E_F \) is the Fermi level of the insulator; \( g \) is equal to 1 for Bloch states, \( \frac{1}{2} \) for donor-like states and 2 for acceptor-like states. To simplify the calculations, note that for states more than a few \( kT \) above the Fermi level:

\[
f \to \exp(-E/kT)
\]

(A4)

(where \( E = (E' - E_F) \) is the energy relative to the Fermi level), and for states more than a few \( kT \) below,

\[
f \to 1
\]

(A5)

(the exclusion of \( g \) in (A4) is valid if spin is not included in the density of states).

Suppose now that the insulators contains only acceptors; let there be \( n_A \) acceptors per unit volume, lying at an energy \( E_A \) above the Fermi level. (If the acceptor states are initially above the Fermi level of the metal, they will all lie above the common Fermi level when the metal and insulator are in contact and in equilibrium.) From eqns. (A2) and (A4),

\[
\rho = -n_Ae \exp\{-[E_A - eV(x)]/kT\},
\]

(A6)

where \( eV(x) \) is the depression of the energy of a trap at a distance \( x \) from the surface. Substituting (A6) into (A1) and solving:

\[
(\partial V/\partial x)^2 = (2n_AkT/\varepsilon_r\varepsilon_0) \exp(-E_A/kT)\{\exp(eV/kT) - 1\},
\]

(A7)

where the electric field and \( (\partial V/\partial x) \) is zero at \( x = \infty \) if the condition \( V = 0 \) at \( x = \infty \) is chosen and used.

By Gauss’s theorem \( \sigma = -\varepsilon_0 (\partial V/\partial x)_{x=0} \); with the condition \( V = V_c \) at \( x = 0 \), we find
The charge density predicted by eqn. (A8) is usually very small, because the acceptor states are above the Fermi level and therefore thinly populated. The charge density will be much larger if, before contact, the insulator contains empty states below the Fermi level of the metal. After contact, there will be a layer near to the interface in which all the states are filled. However, this simple model is inadequate because many experimental findings imply that there must be a level which is partly full and partly empty. The Fermi level of the insulator must be very near to any level which is partly full, according to eqn. (A3). \( E_A \) is thus very small that can be taken to be zero. If there are \( n_D \) donors and \( n_A \) acceptors per unit volume, there will be \( n_A \) empty states and \( n_D - n_A \) full states per unit volume near to the Fermi level. When the metal and the insulator are brought into contact, the Fermi level of the insulator must rise in energy by \( eV_c \) in order to become coincident with that of the metal. States near to the insulator surface will at this moment be full and the charge density in this region of full states will be \( -en_A \), since \( n_A \) states per unit volume will have been filled by electrons. If the thickness of the charged layer is \( x_0 \), the charge density will be: \( \rho = -en_A \) for \( x < x_0 \) and \( \rho \equiv 0 \) for \( x > x_0 \). Note that a narrow region around \( x_0 \), spanning \( \sim kT \) in energy, where the charge density lies between these limits, is ignored in this case.

The boundary conditions on eqn. (A1) are that \( V = 0 \) at \( x = x_0 \) (an arbitrary choice) and \( \partial V/\partial x = 0 \) at \( x = x_0 \) since there is no charge and no electric field for \( x > x_0 \). A solution to (A1) is

\[
V = (n_Ae/\varepsilon_0\varepsilon_0)(x - x_0)^2.
\]

Now the potential difference across the charge layer is \( V_c - E_A/e \). If \( E_A \ll eV_c \), then \( V \) is equal to \( V_c \) at \( x = 0 \). The charge density \( \sigma \) is given by \( \sigma = n_Ae\varepsilon_0 \). Hence,

\[
x_0 = (2\varepsilon_0\varepsilon_0V_c/n_Ae)^{1/2}, \quad \text{and} \quad \sigma = -2\varepsilon_0\varepsilon_0n_AkT \left\{ \exp(-E_A/kT) \right\}^{1/2} \left\{ \exp(eV_c/kT) - 1 \right\}^{1/2}, \quad \text{and}
\]

\[
\sigma = -2\varepsilon_0\varepsilon_0n_AkT \exp(-E_A/kT)^{1/2} \exp(eV_c/2kT). \quad \text{[A8]}
\]
\[ \sigma = - (2\varepsilon_r\varepsilon_0 n_A e V_c)^{1/2}. \]  

If the metal Fermi level is initially below the insulator Fermi level, similar evidence leads to equations analogous to (A9) and (A10), but with \((n_D - n_A)\) in place of \(n_A\) (since \(n_D - n_A\) states per unit volume are now emptied).

The insulator states mentioned above have, so far, been considered at a single discrete energy. However, in practice they may be spread over a wide range of energy so that there are \(n_0dE\) states in the energy range \(E\) to \(E + dE\) \((n_0 = \text{constant})\). In that case, if the potential at \(x\) is \(V\), an electron’s energy at \(x\) is shifted by \(-eV\) and there will be an excess \(n_0eV\) of electrons, which in turn results in an excess charge \(n_0e^2V\) per unit volume. Substituting \(\rho = n_0e^2V\) in (A1) will give (because \(V = V_c\) at \(x = 0\))

\[ V = V_c \exp(-x / \lambda), \text{ and} \]

\[ \lambda = (\varepsilon_r\varepsilon_0 / n_0e^2)^{1/2}. \]

The charge density is, therefore, given by

\[ \sigma = \varepsilon\varepsilon_0 \left( \frac{\partial V}{\partial x} \right)_0, \text{ so} \]

\[ \sigma = (\varepsilon_r\varepsilon_0 n_0e^2)^{1/2} V_c. \]