INSULATOR CHARGING BY CONTACT WITH METALS

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SUMMARY

In spite of the fact that charge transfer is one of the oldest physical phenomena known, the basic mechanisms involved are not yet quite understood. For experimental investigations of the charge transfer to insulators it is still informative to scrutinize electrification systems consisting of as simple components as possible. The choice of one metallic component is justified by the well-known electronic properties of metals.

The charge transferred on (100) oriented surfaces of NaCl crystals from a sliding gold electrode has been measured as a function of sliding velocity and normal force between the electrode and the insulator surface. Besides (100) surfaces other crystallographic orientations of NaCl have been investigated with electrodes of different metals. A series of experiments comparing the sliding and the rolling modes of separation has also been carried out on (100) surfaces and it is shown that in broad outline the different modes of separation are consistent. The results from the investigations on metal-NaCl systems suggest that electrons are transferred into trapping levels in the forbidden energy range of the NaCl crystal.

Electrification of insulators by metals is currently explained by uniform carrier injection to a constant depth for each particular material or by the formation of a strictly two-dimensional surface charge. Calculations concerning a more general model are presented, which includes both alternatives as special cases. An expression for the effective surface charge is obtained for the case where an electric field is applied across the insulator. Electrification experiments with polyethylene and various metals have been carried out, and the results are compared with the theoretical predictions. It is found that the assumption of a two-dimensional charge distribution leads to contradiction, and must be rejected. It is shown that the depth of injection in the bulk charge model may be obtained from the experimental data and the formalism developed. The possibility of a non-uniform space charge density is also discussed.

By means of special equipment which permits measurements of charging of capacitors due to a step voltage after the capacitors are classically fully charged, the electron injection has been studied as a function of time. This has been done on commercial polymeric capacitors as well as on gold evaporated foils of Teflon (PTFE) or polyethylene. The findings in the case
of polyethylene are correlated with the results on the field dependence of electrostatic charging and support the model of electron injection to a finite depth.

An appendix will give some brief considerations concerning the release of electrification charge by exposing the insulator surface to light in the UV-range.
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PRELIMINARY NOTES

S.I. units are used in the equations. Equations quoted from other authors are, where necessary, transformed into S.I. units and expressed in the notation used in this thesis.

A large number of equations refer to processes with electrons involved, and it is noted as well that in these equations the electron charge has been written \(-e\), where \(e\) is the modulus of elementary charge.

Symbols used are defined the first time they appear in each chapter. In order to assist the reader, symbols are given in a special "LIST OF SYMBOLS". Subscripts which refer to a co-ordinate or to a special piece of material are not included in the LIST.
LIST OF SYMBOLS

a
A
A_{app}, A_{real}
\alpha
B
C
C_k, C_r
d
D(x)
D_s
D_v
e
E
E_C
E_g
E_V
E_F
E_{FI}, E_{FM}
\Delta E_{FI}
\varepsilon
\varepsilon_0
\varepsilon_1
\Delta \varepsilon(\tau)
f(w)
F
\phi_I
\phi_M
\Delta \phi_I
G
I, I_i, I_k, I_{op}, I_r
k
K_B
L
radius of a sphere
area in chapter 5, a constant in chapter 7
apparent and real area of contact, respectively
defined in equation (7.28)
the Richardson-Dushman constant
capacitance
constants defined in equations (8.14) and (8.15), respectively
distance between metal and insulator charge layer
electric displacement
trap density per energy unit and area unit
trap density per energy unit and volume unit
the modulus of elementary charge
strength of electric field
energy of the lower conduction band edge
band gap of an insulator
energy of the upper valence band edge
Fermi energy
local Fermi energy of an insulator and a metal, respectively
Fermi energy shift of an insulator
dielectric permittivity of an insulator
dielectric permittivity of free space
dielectric permittivity without time dependence
contribution to the permittivity due to interfacial polarization
the Fermi distribution function
force
work function of an insulator
work function of a metal
shift of the work function of an insulator
Gibbs function
currents
a time constant
the Boltzman constant
the symbol of a distance; used at several places
λ  penetration depth of electrons  
M  defined in equation (7.28)  
μ  electrochemical potential  
n  density of electrons  
N  number of particles  
P  a constant  
q  charge  
q_{\text{in}}  induced charge  
q_L  linear charge density  
Q  a constant  
r  a time constant  
R  input resistance  
ρ  volume charge density  
ρ_I  resistivity of an insulator  
s(w)  density of states  
σ  surface charge density  
σ_{\text{real}}  surface charge density based upon the real area of contact  
t  thickness of an insulator  
T  temperature  
τ  time  
U  electrostatic potential  
U_i  input voltage  
w  electron energy  
x  distance from a metal surface to a point in an insulator  
χ  electron affinity
1 GENERAL INTRODUCTION

1.1 Historical survey

Charging of insulating materials by contact is one of the oldest physical phenomenon known to man. At least as early as 600 B.C., but presumably earlier the Greeks had amber at hand which tradesmen had brought from their extensive journeys to the North. Due to its beauty amber was used as a jewel which made it an attractive barterable commodity. Among the Greeks amber was called "electron" (ηλεκτρόν) since the colour of the material reminded them of the pale yellow of sunlight (ηλεκτρόφων = beaming sun).

Certainly people who wore amber jewels could not avoid noticing that dry hair or other light objects were attracted to a rubbed piece of amber. The discovery of this so called "amber effect" has been credited to Thales of Miletus (6th century B.C.). However, this cannot be verified since none of his writings, if he ever left any, has been handed down to posterity. The first written verification that the amber effect was known in ancient Greece is dated to about 400 B.C. in a dialogue by Plato.

Despite the ancient history of electrostatic phenomena little was added to the world knowledge about them during the next two thousand years. The status of the problem until 1600 is illustrated by the philosophic thoughts of the Chinese author Kuo P'o in "Eulogy of the magnet" (A.D. 4th century):

"The magnet draws the iron, and the amber attracts mustard seed. There is a breath which penetrates secretly and with velocity, and which communicates itself imperceptibly to that which corresponds to it in the other object. It is an inexplicable thing."

Some light was thrown on the phenomenon when Gilbert (in 1600) in his book "de Magnete" made apparent the commonness of generation of static charge by rubbing contact. Gilbert named the phenomenon "electric" after the Greek term for amber. More than a century elapsed before du Fay (in 1733) demonstrated the existence of two kinds of electricity, one kind appearing on glass and similar transparent materials and the other kind on amber. Our very terminology - plus and minus, positive and negative -,
however, stems from Franklin in the 1740's.

During the following 50 years knowledge about electricity was accumulated by development of theoretical concepts, for instance the law of conservation of charge (Watson in 1746 and independently Franklin in 1747) and the law of interaction of charge (Coulomb in 1785). These theoretical ideas combined with the invention of experimental tools such as electrometers and multipliers (e.g. Henley in 1772 and Bennet in 1787) opened the way to substantial investigations of the magnitude of charge transferred at contact between solids. It seems, however, that scientists of that age did not realize the field accessible since surprisingly little work on the amount of charge transferred upon contact was reported during the 19th century. The interest in electrostatics in this period can be said to have been mainly of technical nature.

The ideas about charge transfer between materials upon contact (static electrification) put forward by Volta in 1789 are wholly or partly accepted in modern theories. In short, Volta postulated that it is the act of contact, rather than the rubbing which is responsible for charge transfer. Helmholtz in 1879 extended the picture of Volta by suggesting a redistribution of charge at the solid-solid interface to form a double layer. Shaw in 1918 and Freundlich in 1926 thought of such a double layer existing in the materials even before they are brought into contact and the effect of rubbing was a layer break-up and subsequently charge transport between the surfaces. The similarity between the charged layers postulated and contact potential difference between metals was evident and the search for static electrification (triboelectric) series analogous to the electromotive series for metals was a natural consequence. The idea of a triboelectric series, such that contact between any two members of the series left the material higher in the series positively charged was first put forward by Wilcke as early as 1757. Coehn in 1898 tried to predict the triboelectric series by suggesting that a member positioned high in the series had a larger permittivity than a member positioned lower, a hypothesis long since disproved.

Interest in static electrification was rather half-hearted until the late 1940's. New materials such as plastics and synthetic textiles were at that time more and more commonly in use and they were shown to behave undesirably in the electrostatic sense. The effort of the industry to
avoid static electrification initiated a renewal of interest in the problem, which could then be attacked with vigour and tenacity on the basis of improved understanding of the solid state during the 20th century.

1.2 Introduction to the present study

When one tries to clarify the electrification process in solid-solid systems it still seems wise to concentrate on the simplest possible components, and of all the materials available metals are probably best understood from the electronic point of view. It is far more difficult to decide which insulator to choose in order to have a simple and controllable situation. The reason for choosing ionic crystals in the present investigation is that they have a well-known structure and they are susceptible to electron band calculations. It may be debatable whether bands have anything to do with the electrification of insulators, since any excess charge placed in a band would be mobile in the crystal. However, in NaCl the valence band is known to be at a lower energy than any metallic Fermi level, and there is a sufficiently wide gap up to the conduction band to ensure that the relevant traps have no interaction with the bands. In addition, NaCl may be obtained as ultra-pure single crystals.

The electrification charges may be separated by lifting, rolling or sliding the metal on the insulator surface. The sliding mode separates the charges by a motion on the insulator surface. Lifting and rolling involves perpendicular separation, and these processes have been thoroughly investigated (see for instance Davies (1967a, 1969, 1970)). It seems, however, that sliding is still considered to be a fundamentally different mode. It is often referred to as "electrification by friction", although it has never been shown that friction would play a dominant role in this process, except for the case where the thermal conductivity is low for both components in the electrification system, and the friction so violent that appreciable local heating occurs (Henry (1957)). In the present electrification study of NaCl the sliding mode was mainly used. Electrification in the rolling mode was carried out as well in order to compare these modes of separation.

In the last couple of decades some quantitative theories on electron transfer upon metal-insulator contact have been developed (e.g. Rose (1956), Davies (1967a) and Bauser et. al. (1970)). They all have in common
an invocation of trapping sites at energies in the forbidden energy range of the insulator in order to be consistent with experimental results. There are, however, divergences of opinion whether the electrons are transferred only to the surface or if they penetrate into the bulk of the insulator. The surface trap theory (Bauser et. al. (1970)) and the penetration theory (Davies (1967a)) are indistinguishable in the sense that they both correctly predict the qualitative experimental dependence between charge transfer and metal work function. Bauser et. al. (1970) invoked a surface trap density and Davies (1967a) a maximum penetration depth, quantities which have not been independently observed. With the purpose of comparative testing these current theories, calculations were made on a more general model which would yield the theoretical results of Davies (1967a) and Bauser et. al. (1970) as special cases. The model used included the possibility of an applied electric field in the insulator.

Experimental results from electrification of polyethylene in an electric field, interpreted according to the general model suggested, demonstrated that electrons penetrate into the bulk of the insulator, and that the charge transfer is a function of the electric field. It is improbable that the charge redistribution from varying the electric field occurs instantaneously. In order to give support to the model used the electron injection was studied as a function of time on commercial polymeric capacitors as well as on gold evaporated foils of Teflon (PTFE) and polyethylene by means of a special technique as described in chapter 8.
CONTACT CHARGING PROCESSES

One of the principal questions to be answered in order to clarify the phenomenon of charge transfer between metals and insulators is whether the transfer is due to ions, electrons or maybe charged fragments of material. The fact that a well-defined electrification system may show different properties in different ambient atmospheres or for different kinds of contact achievement illustrates the complexity of the charge transfer problem. Consequently, theoretical studies of the charging of insulators in general are at a rather inconclusive stage, effort being concentrated on electron transfer models since results from many electrification experiments can be interpreted in this way (i.e. Arridge (1967), Davies (1967a, 1969, 1970), Bauser (1974)). There is, however, evidence for the existence of other kinds of charging and these will be discussed in some detail before the discussion of the electron transfer mechanism.

2.1 Frictional charging

There is no doubt that in many cases sliding between two surfaces has a large effect on the contact charge transferred (see for example the recent investigation by O'Neill and Foord (1975)). However, the sliding mode of electrification might not always be called "frictional charging" since the effect from sliding can be due simply to an increase of area of contact between the materials. The evidence that friction may give rise to charging comes from experiments on the rubbing of two apparently identical surfaces together which have been performed by various workers including Rudge (1914), Shaw (1927), Gill (1948) and Henry (1953).

The study by Henry (1953) of perpendicular rubbing of crossed rods demonstrated that the asymmetry of the rubbing action played an important part. In these experiments one surface was rubbed over the same small area all the time whilst the other was rubbed over a wider area. There was shown to be reversal of the sign of the charge by reversing the roles of the two surfaces. Henry (1953) concluded that the friction concentrated on a smaller area of one surface than of the other gave rise to a strong temperature gradient across the contact, since the area of one surface heated by friction during rubbing made contact with cold unrubbed areas of the other surface.
The friction charging mechanism is not to be associated to one special kind of carrier. Asymmetric heating of a contact point can favour transfer of charged material particles as well as increase the mobility of ions or electrons. The charge carriers will tend to diffuse to the colder part of the contact so charging this surface negatively if the carriers are electrons and/or negative ions or the charging is positive if there are positive ions mobile. There are experimental results showing both positive and negative charge transfer (i.e. Shaw (1927), Shaw and Hanstock (1930) and Henry (1957)).

A secondary effect of friction is transfer of material from one surface to the other which results in charge transfer if the material particles for some reasons possess excess charge. Kornfel'd (1969) made frictional electrification experiments between insulator surfaces of the same material as well as different materials. He proposed an electrification mechanism based on the assumption that there exists an "intrinsic" charge in solid insulators which is compensated by adsorbed ions from air. The effect of friction would then be a mixing of the contamination surface layers which would result in destroying the charge compensation. Charge would then be unequally distributed on the surfaces. The results of Kornfel'd (1969) agree even quantitatively with his model. However, since it is to be expected that temperature gradients occur in rough sliding of dielectrics, the conclusions of Harper (1953) may be equally likely to be valid. No doubt, transfer of charged material particles makes the interpretation of friction dependent charging particularly difficult. As the above discussion shows, many effects may contribute to frictional charging and this complexity makes clear that there is not much knowledge about the consequences and importance of charging by material transfer.

There are great divergences of opinion as to the extent to which frictional charging plays a significant role in static electrification of insulators. For instance Loeb (1958) stated that it is only in exceptional cases that transfer of charge is due to generation of heat by friction. On the other hand, the frictional electrification study by Cunningham (1964), where a relationship between the charge transferred and work against the force of friction was found, supported the idea of Henry (1957) that frictionally generated charge may dominate in charge transfer. A more recent study by Zimmer (1970) is another example of support for the notion that heat generation is involved in charging by friction. Zimmer (1970)
investigated the charging of plastics by rubbing against a metal brush with different rubbing velocity. The charge acquired by polyethylene terephthalate, for instance, was negative for low velocities and positive for high velocities. There was a similar change in sign at high temperatures in contact electrification experiments without rubbing. Zimmer (1970) concluded that there was a causal connection between these two sets of observations. Although there is strong evidence that friction, possibly together with additional related parameters (mainly temperature), may contribute to the contact charging of insulators in some cases, it is by no means evident that friction always gives rise to frictional charging.

2.2 Ionic transfer

In some cases transfer of ions seems very probably to play a predominant role in contact charging. In particular, this mechanism may be important when the surface of the solid is previously exposed to a treatment causing adsorption of ions or in cases involving ionic "conductors". Some experiments also show fairly clear evidence of electrification due to ion transfer. Knoblauch (1902), for instance, describes a study with powders of varying chemical composition. The powder was allowed to slide from a Pt or other plate. A sulfur-coated plate was usually charged negatively but by a few acid powders it was charged positively. A glass plate, however, was left positively charged except by some alkaline powders. The connection became somewhat clearer in the experiments with paraffin and Pt plates, which nearly always were charged positively with acid substances and negatively with basic substances. Knoblauch (1902) interpreted his results in terms of electrolytic processes in a thin layer of moisture, the carriers being the relatively light $H^+$ and $OH^-$ ions. Since paraffin and Pt are relatively inactive and insoluble materials chemically the charge being left consists of $H^+$ ions after contact with acids and $OH^-$ ions after sliding with alkalines. The basic character of the glass and the acidic properties of sulfur may, however, reverse the ion transport (these findings of Knoblauch (1902) were confirmed by Rudge (1914)).

Further evidence that electrolytic charging exists was presented by Medley (1953). He experimented with acidic and basic ion-exchange resins with the hydroxyl and hydrogen ions mobile and the heavier ions bound to the polymer chain. When the resins were shaken from a filter paper, the acidic resin acquired a negative charge and the basic resin a positive
one. Medley interpreted this as retention of the mobile ions in the resin by the filter paper.

More recently Robins et. al. (1975) clearly showed that surface ions have a dominant effect on the contact charging of pyroelectric samples of polyvinylfluoride and triglycine sulfate even if it may be debatable whether the charge transfer is ionic. They polarized the samples and allowed ion layers of a certain sign to be adsorbed. Their measurements resulted in a negatively charged insulator after contact with a metal sphere if the insulator surface was coated initially with positive ions, whereas a surface coated with negative ions acquired a positive charge. They explained their experimental observations with two alternative hypotheses which are electrically equivalent. These hypotheses are that either there was ion transfer from the insulator sample to the metal or there was neutralization of ions on the surface by charge exchange with the metal. However, the latter transfer mechanism was considered physically more plausible.

Bauzer (1974) reported a contact charging study on a pyrene organic crystal, which was grown by sublimation from the gas phase. The charge transferred was shown to be linearly dependent on the work function of the metal in contact, which is taken as evidence for electron transfer (Davies (1969)). By treating the pyrene in a corona discharge, ions were adsorbed on the surface. But even with this increased density of ions the charge transfer seemed to be electronic. The measurements were also taken at various values of relative humidity without change in the results. Since the charging can be due to electron transfer even in cases where conditions for ion transfer are favourable, Bauzer (1974) concluded that it is justifiable to concentrate on some electron model unless there are strong indications of ion transfer.

2.3 Electron transfer

2.3.1 Thermodynamical equilibrium

Two pieces of different material at the same temperature and in electrical contact will reach thermodynamic equilibrium in the sense that the Gibbs free energy, $G$, is a minimum for the entire system. According to thermodynamics (for instance Callen (1960)) in a single component system at constant temperature and pressure $G$ can be written
\[ G = \mu N \]  

where \( \mu \) is the electrochemical potential and \( N \) is the number of particles. \( G \) can be separated into terms related to each piece of material. Differentiation of equation (2.1) then results in

\[ dG = dG_1 + dG_2 = \nu_1 dN_1 + \nu_2 dN_2 \]  

where the subscripts stand for the different pieces of material. Electrons escaping from material 1 are transferred to material 2 and vice versa which gives, \( dN_1 = -dN_2 \). Since \( G \) has a minimum at equilibrium, the right hand side of equation (2.2) must equal zero. This happens if and only if \( \nu_1 \) is equal to \( \nu_2 \). Hence, the thermodynamic condition for equilibrium is constant electrochemical potential throughout the entire system.

The energy distribution of electrons is determined through the Fermi-Dirac distribution function

\[ f(w) = \frac{1}{\exp\left(\frac{w-E_p}{K_B T}\right) + 1} \]  

where \( w \) is the electron energy, \( K_B \) is the Boltzman constant and \( T \) is the temperature. The quantity \( \mu \) is to be chosen for a particular problem so as to keep the total number of electrons at the actual value and it can be shown that it has the thermodynamic meaning of electrochemical potential.

The terminology in this field is very confusing, various authors using different terminology. Following the terminology of Kittel (1969) for instance, the Fermi energy, \( E_F \), is defined as the energy of the topmost filled level at \( T = 0 \). Due to its normalizing task \( \mu \) is a function of \( T \). Hence \( \mu \) and \( E_F \) coincide at \( T = 0 \). For high temperature they may differ. At room temperature, however, the difference is expected to be negligible. For this reason, the Fermi level which actually according to Kittel (1969) should be referred to the energy level corresponding to the electrochemical potential is also treated as an equivalent to the energy level corresponding to the Fermi energy throughout this thesis.

In the presence of an external electric field \( w \) is changed but so is also \( \mu \). According to Kittel (1969) the influence from an electrostatic potential, \( U \), caused by an applied electric field, is given by
\[ \mu \rightarrow \mu - eU \]  \hspace{1cm} (2.4)

where \( e \) is the elementary charge.

### 2.3.2 Contact between metals

In a metal, the energy difference between the Fermi level and the vacuum level is referred to as the "work function", \( \phi \). If two adjacent pieces of metal with different work functions, \( \phi_{M_1} < \phi_{M_2} \), are connected electrically, as is illustrated in figure 2.1, they redistribute electrons between them so as to equate the Fermi levels.

\[
\begin{align*}
\phi_{M_1} & \quad \text{(a)} \\
\phi_{M_2} & \quad \text{(b)} \\
\end{align*}
\]

Figure 2.1 Simplified energy scheme for two metals  
(a) before contact, b) after contact is established.

There will then be a positive charge on metal 1, with the lower work function, and a negative charge on the other. The charge distributions are the cause of a potential difference between them, the contact potential (difference) or CPD, which is given by

\[ \text{CPD} = \frac{\phi_{M_1} - \phi_{M_2}}{e} \]  \hspace{1cm} (2.5)

where metal 1 is given as a reference.
2.3.3 Models for electron transfer at a metal-insulator contact

The first attempt to interpret equilibrium contact charge in terms of solid state theory was performed by Mott and Gurney (1940). They considered one dimensional charging by metal contact of an insulating slab extending to infinity as being analogous to the thermionic emission of electrons from levels near the Fermi level into a vacuum over a surface barrier of height $\Phi_M - x$, $x$ being the electron affinity (the energy required to lift an electron from bottom of the conduction band up to the vacuum level). They assumed that the electron cloud in the insulator conduction band will form a local electric field, given by the Poisson equation. When the charging is completed, the concentration gradient gives rise to a diffusion transport of electrons, which is balanced by the electrical current flowing down the potential gradient. Using this they obtained a form of Boltzman expression

$$\frac{n}{n_0} = \exp\left[-\frac{w}{k_B T}\right]$$  \hspace{1cm} (2.6)

where $n$ and $n_0$ are the electron densities in the insulator at a distance $x$ from the metal surface and quite near the metal respectively. In addition they found a differential equation

$$\frac{d^2w}{dx^2} = \frac{n_0 e^2}{\varepsilon} \exp\left(-\frac{w}{k_B T}\right)$$  \hspace{1cm} (2.7)

where $w$ is given by

$$w(x) = -e \int_0^x E \, dx$$  \hspace{1cm} (2.8)

the quantity $E$ being the electric field strength and $\varepsilon$ the permittivity of the insulator. The boundary condition used was the electric field to vanish at $x \to \infty$. The solution of the differential equation is given by

$$w = 2 k_B T \log\left\{\frac{x}{x_0} + 1\right\}$$  \hspace{1cm} (2.9)

where $x_0 = \left(\frac{2e k_B T}{n_0 e^2}\right)^{1/2}$. $w$ is seen to rise logarithmically with $x$.

By substitution of equation (2.9) into equation (2.6), $n$ is found to be

$$n = n_0 \left(\frac{x_0}{x_0 + x}\right)^2$$  \hspace{1cm} (2.10)
Mott and Gurney (1940) gave an estimate of the electron density, \( n_0 \), by assuming that \( n_0 \) is determined by the Fermi distribution function (equation 2.3) and by a density of states, \( s(w) \), varying as \( w^{1/2} \),

\[
\eta_0 = \int_0^\infty s(w) f(w) \, dw
\]  

(2.11)

They finally obtained from equation (2.11)

\[
\eta_0 = \exp\left(-\frac{\Phi_M - X}{k_B T}\right)
\]  

(2.12)

By using equation (2.10) and (2.12) the theory of Mott and Gurney (1940) may be extended to give the equivalent surface density of charge transferred, \( \sigma \), as

\[
\sigma = \int_0^\infty n \, dx = \exp\left(-\frac{\Phi_M - X}{2k_B T}\right)
\]

(2.13)

The treatment of Mott and Gurney (1940) were refined by Van Ostenburg and Montgomery (1958) in the sense that the difficulty of the infinite potential in equation (2.9) was removed. Their calculations were based on the assumption that the electrons escape by thermal agitation from the conduction band of the metal to the empty conduction band of the insulator leading to a Poisson equation of the form

\[
\frac{d^2U}{dx^2} = \sinh U
\]

(2.14)

by using Fermi-Dirac statistics. Figure 2.2 represents this situation when the metal Fermi level before contact is above the insulator Fermi level, which is assumed to lie midway between the filled valence band and the empty conduction band. At equilibrium the Fermi level is uniform throughout the entire system. By integrating equation (2.14) twice \( U \) is obtained using the boundary conditions that at infinity the field strength vanishes and that the field strength is continuous across the interface. The first boundary condition arises from electrical neutrality of the system and the second means that the volume charge density is finite. The solution gives the form of bends shown in figure 2.2 (b) with the condition
\[ \phi_M - \chi + eU_0 = \frac{1}{2} E_g \]  

(2.15)

where \( E_g \) is the band gap and the term \( eU_0 \) is defined in figure 2.2(b).

---

Figure 2.2 Schematic diagram of energy levels in a metal-insulator system. (a) Materials being separated before contact. (b) Contact is achieved and equilibrium is established (After Van Ostenburg and Montgomery (1958)).

Van Ostenburg and Montgomery (1958) calculated the equivalent surface charge density, \( \sigma \), by use of Gauss' law at \( x=0 \). They found \( \sigma \) to be of the same form as is found from the theory of Mott and Gurney (1940) (see equation 2.13).

Harper (1967) has made an analysis analogous to that of Van Ostenburg and Montgomery (1958) and in addition he found an expression for the width in space of the charge distribution which may be estimated from the conduction data of insulators. The charge layer was then shown to exceed a practical dimension for insulators used in electrification experiments. For that reason Harper (1967) tried the boundary condition of the electrical field strength being zero at \( x=t \) instead of at infinity. The quantity \( t \) is the thickness of the insulator sample. This assumption, however, does not alter the exponential dependence of the charge density on the metal work function (equation 2.13).
These calculations will not necessarily invoke localized trapping site levels situated in the insulator energy gap. A real insulator is very likely to possess electron traps in the vicinity of its surface because of defects such as broken chemical bonds, foreign atoms adsorbed and chemical impurities. According to Harper (1967), the existence of such electrons traps has to be postulated to explain the high resistivity for electrons moving into the insulator from outside and he also pointed out that the traps may be involved in the electrification process in the sense that they influence the boundary condition at a metal-insulator interface.

Insulators with a continuous and a uniform distribution of trapping sites have been considered by for example Rose (1956) and Many et. al. (1964). Both of these discussed the charge transfer as being an electron penetration into the bulk of the insulator. According to Many et. al. (1964) the charge density, $\rho$, at any point $\vec{r}$ in the space-charge region can be written

$$\rho = - e D_{V} \left[ \frac{E_{C} - eU}{E_{V} - eU} \right] \left( 1 + \exp \left( \frac{w - E_{F}}{k_{B}T} \right) \right)^{-1} dw - \left[ \frac{E_{C}}{E_{V}} \right] \left( 1 + \exp \left( \frac{w - E_{F}}{k_{B}T} \right) \right)^{-1} dw$$

(2.16)

where $U$ is the electrostatic potential at $\vec{r}$, $D_{V}$ is the trap density per unit energy and unit volume, $E_{V}$ is the energy of the upper valence band edge and $E_{C}$ is the energy of the lower conduction band edge. Assuming that the Fermi level is well removed from the band edges throughout the space charge region, the Fermi-Dirac function is very close to unity in the region between $E_{V} - eU$ and $E_{V}$ while it is negligibly small in the conduction band region. Hence the charge density reduces to

$$\rho = - e^{2} D_{V} U$$

(2.17)

By substitution of this expression into the Poisson equation, the solution becomes to be

$$U = U_{0} e^{-x/L}$$

(2.18)

where $U_{0}$ is the potential at the insulator surface ($x=0$) and $L$ is given by

$$L = \left( \frac{e^{2} D_{V}}{e^{2} D_{V}} \right)^{1/2}$$

(2.19)
L measures the extension of the space charge. The quantity $U_0$ in equation (2.18) is analogous to the contact potential between the metal and the insulator,

$$U_0 = - (\Phi_M - \Phi_I)/e$$  \hspace{1cm} (2.20)

The equivalent surface charge density, $\sigma$, is obtained from equation (2.17) with the expression for $U$ given by equation (2.18), yielding

$$\sigma \equiv \int_0^\infty \rho dx = -e^2D_VU_0 \int_0^\infty e^{-x/L} dx$$ \hspace{1cm} (2.21)

By integrating and making use of equations (2.20) and (2.19) equation (2.21) becomes

$$\sigma = (\varepsilon D_V)^{1/2}(\Phi_M - \Phi_I)$$ \hspace{1cm} (2.22)

It may be noted that this model results in a non-uniform volume charge density as a function of depth and in contrast to the trap-free models (see equation (2.13)) predicts a total charge transfer proportional to the difference in work functions.

A linear variation of the charge density with metal work function was also obtained in the theory of Davies (1967a). His theoretical approach was that of Schottky injection, except that he assumed a constant penetration depth, $\lambda$, instead of a constant volume charge density of the injection layer. This case is illustrated in figure 2.3.
A characteristic feature of this theory is that charge is supposed to be injected into the dielectric until the process is stopped by the field created by the charged layer. It is not supposed that there is any quantum statistical change of the local Fermi energy of the insulator. By integrating the Poisson equation twice and by using the boundary conditions, \( E_c = \phi_M - \chi \) at \( x = 0 \) and \( E_c = \phi_I - \chi \) at \( x = \lambda \) Davies (1967a) obtained

\[
\phi_M - \phi_I = \frac{\rho e}{2\varepsilon} \lambda^2 \tag{2.23}
\]

and the expression for equivalent surface charge density, \( \sigma \), was found to be

\[
\sigma = \rho \lambda = \frac{2e}{\varepsilon \lambda} (\phi_M - \phi_I) \tag{2.24}
\]

As pointed out by Chowdry and Westgate (1974), the unmodified Schottky barrier model on an insulator with one discrete trapping level predicts a value of \( \rho \) which does not depend on the difference, \( \phi_M - \phi_I \). This leads...
to the following expression for the equivalent surface charge density
\[ \sigma = \rho \lambda = \pm \left( \frac{2e\rho}{e} (\phi_M - \phi_I) \right)^{1/2} \] (2.25)

the positive sign being applicable for \( \phi_M > \phi_I \) and the negative sign for \( \phi_M < \phi_I \). However, several authors (see for instance Arridge (1967), Davies (1967a, 1969, 1970), Inculet and Wituschek (1967), Challande (1970), Bauser (1974), Wåhlin and Bäckström (1974)) have reported a linear relationship between \( \sigma \) and the difference, \( \phi_M - \phi_I \), the results being obtained from experiments performed in the lifting, rolling, or sliding mode of separation. It then seems that in many cases a quadratic relationship between the charge transferred and work function difference is far from the real situation.

Considering the time required for having the charge transfer completed and equilibrium established in a metal-insulator contact one is faced with an incompatibility between the theoretical prediction and the experimental results. Harper (1967) discussed the filling of empty trapping levels in the insulator band gap from the time scale point of view. Assuming that the charging is a diffusive process the electrons have to penetrate insulating material in which the resistivity is unaffected by the presence of traps. The equilibrium condition is then attained when diffusion transport is balanced by the electric current originated from the potential gradient. The equilibrium rate for the latter transport process may be estimated from the resistivity, \( \rho_I \), of the material. According to Harper (1967) the time constant \( k \) is simply defined as the ratio between the charge and the mean current giving

\[ k = \frac{2\rho IL}{U \sigma} \] (2.26)

where \( L \) is the extension of the charge layer and \( U \) is the potential difference to be attained. By putting in some relevant values of the parameters, Harper (1967) concluded that the value of \( k \) exceeds by several orders of magnitudes the real duration of contact in electrification experiments.

Bauser et. al. (1970) considered electron emission from the metal to the conduction band of the insulator and subsequent capture by traps. Tunnelling between trapping levels was neglected. A rough estimate for the charging current \( I \) was obtained from the Richardson equation for thermionic emission,
\[ I = BT^2 \exp \left[ - \frac{\phi_M - \chi}{K_B T} \right] \]  \hspace{1cm} (2.27)

\( B \) being the Richardson-Dushman constant. The relevant charging time, \( \tau_0 \), was then

\[ \tau_0 = \frac{\sigma}{T} \]  \hspace{1cm} (2.28)

By taking some practical values of \( \tau_0 \) and \( \sigma \) (of order 10 s and \( 10^{-8} \text{Ccm}^{-2} \) respectively) the value for \( \phi_M - \chi \) does not exceed 1 eV. This value is valid for insulators with a relatively deep-lying conduction band (3-4 eV). However, ESCA-studies (for instance Delhalle et al. (1974) and Pireaux et al. (1974)) on common insulating materials in electrification experiments resulted in conduction bands quite near the vacuum level. By doubling the difference \( \phi_M - \chi \) and keeping \( \sigma \) at the representative value \( 10^{-8} \text{Ccm}^{-2} \) the time for electron transfer will be \( 6 \cdot 10^{17} \text{days} \). Hence charging does not occur in a reasonable time, in contradiction to the real situation.

Instead, by assuming the mechanism of electron transfer to be direct tunnelling into traps close to the surface and subsequent tunnelling between traps to establish equilibrium, a charging time can be estimated which is noticeably shorter than that given by the estimates of Harper (1967) and Bauser et al. (1970). Heiman and Warfield (1965) for instance considered direct tunnelling from a semiconductor into traps in an insulator. Assuming typical values for the parameters involved they found that a charge density of approximately \( 10^{-8} \text{Ccm}^{-2} \) is injected in two minutes provided that the insulator trap level is energetically close to the semiconductor Fermi level. This process has been proposed as a possible conduction mechanism by for instance Munn and Siebrand (1970). However, there are indications that the charge transfer is completed in time \( \ll 1 \text{minute} \) (see for instance Hays and Donald (1972) and Wåhlin and Bäckström (1974)).

In order to avoid inconsistencies between experimental findings and expectations from the theoretical grounds above concerning time of charge transfer, Bauser et al. (1970) assumed that surface states are involved. These surface states will be filled up to an energy value which in equilibrium defines the Fermi level of the insulator. Making contact with a metal, surface states are instantaneously filled or emptied depending
on whether the metal Fermi level is situated above or below the insulator Fermi level. Considering the former case the energy schemes for contact are shown in figure 2.4.

Figure 2.4 Energy schemes for contact metal-insulator with surface states. (a) Before contact. (b) After bringing the solids into contact. After Bauser et. al. (1971).

According to Bauser et. al. (1970) and Krupp (1970) the insulator surface need not be in thermodynamical equilibrium with the bulk in the first phase of the charging. In a second phase, however, equilibrium may be maintained by the filling of bulk traps with a long time constant. Then band bending as in figure 2.3 occurs.

In this model it is assumed that the charge exchange during the first phase of the charging concerns only traps on the surface. Hence the charge transferred per unit area, $\sigma$, can be expressed as

$$\sigma = - e D S \Delta \phi_I$$  \hspace{1cm} (2.29)
when the surface state density per unit energy, $D_s$, is assumed to be uniformly distributed in energy. $\Delta \phi_1$ is the change of Fermi energy due to the filling of surface traps. The equilibrium condition is given by

$$\phi_M + eU = \phi_I - \Delta \phi_1$$  \hspace{1cm} (2.30)

i.e. the local Fermi level of the insulator surface coincides with the Fermi level of the metal. $U$ is the potential difference in the small region of separation of magnitude, $d$, between the insulator and the metal and is related to the surface charge density by

$$U = \frac{\sigma d}{\varepsilon_0}$$  \hspace{1cm} (2.31)

where $\varepsilon_0$ is the permittivity of free space. Combining equations (2.29), (2.30) and (2.31), the charge density is given by

$$\sigma = \frac{eD_s (\phi_M - \phi_I)}{e^2 d D_s + \varepsilon_0}$$  \hspace{1cm} (2.32)

In the limits of low and high surface charge density the expression for $\sigma$ is simplified to

$$\sigma = eD_s (\phi_M - \phi_I)$$  \hspace{1cm} (2.33)

and

$$\sigma = \frac{\varepsilon_0}{ed} (\phi_M - \phi_I)$$  \hspace{1cm} (2.34)

respectively.

In a study by Hays and Donald (1972) on the electrification of polyethylene by mercury the surface trap theory was extended to include the possibility of an applied electric field. They found that the external electric field, $E$, made the electronic energy levels shift by an amount $eEd$ relative those of the metal, and the charge density $\sigma$ is modified to

$$\sigma = eD_s (\phi_M - \phi_I + eEd)$$  \hspace{1cm} (2.35)

and
\[ \sigma = \frac{\varepsilon_0}{ed} (\phi_M - \phi_I + eEd) \]  
\hspace{1cm} (2.36)

in the limits of low and high surface charge density respectively.

In conclusion it can be said that trapping sites have to be invoked to explain the linear relationship between the charge transferred and the metal work function as found by many authors. The surface state theory according to Bauser et. al. (1970) correctly predicts this linear relationship but so do theories involving trapping sites in the bulk (Rose (1956) and Davies (1967a)). Chapter 7 in this thesis describes an experiment initiated in order to look for further support for one or the other of these current theories.
3 CHARGE MEASURING METHODS

On the purpose of clarifying the latent mechanisms causing charge transfer at a solid-solid contact, the experimenter is always faced to a choice of a suitable method for detecting or measuring static electric charge. Some methods are briefly reviewed in this chapter. The papers referred to should be consulted for full details of the experimental set-up.

In all measurements of charge stored on insulators the effect of the electric field created by the charge is detected in some way. Generally one distinguishes between (1) powder methods, (2) ponderomotive methods and (3) inductive methods. Besides these methods a current measuring technique, referred to as the galvanometric method, can be convenient in special cases.

3.1 Powder methods

These methods are going back as early as 1777 to Lichtenberg who discovered that fine powder of some materials adheres and forms a pattern on charged surfaces. By making use of selected powder materials of different colours, one of which develops a negative charge and the other a positive charge, it is possible to separate positively charged areas from negatively charged ones. Nearly as many different powder mixtures as there are users have been reported (see for instance Hull (1949), Webers (1963), Donald (1968) and van Turnhout (1970)).

The advantage of the powder methods is that they permit visualization of the presence and polarity of local charge densities simply and rapidly. The detection, however, is only qualitative and since the insulator surface is touched by the powder, it is not possible to study the variation with time of a charge distribution. The main application of the methods has been in the systematizing work of dielectric materials in triboelectric schemes.

3.2 Ponderomotive methods

By measuring the attractive force, $F$, on a suspended metal disk situated near a charged dielectric sample placed on a metal substrate the surface charge density, $\sigma$, can be calculated, since
Cross and Smalley (1969) and van Turnhout (1970) describe some working constructions of ponderomotive charge meters.

Van Turnhout (1970) points out that measurements with small area of the metal disk are difficult to perform. In practice then, the result is not a local charge density but some mean value on a piece of area defined by the dimension of the disk. As a matter of fact the R. M. S. - value is determined. This means that ponderomotive methods do not primarily distinguish between positive or negative sign of charge. However, the polarity can be obtained in a second stage, for instance by applying a small voltage of known polarity across the sample. The measured force increases if the applied potential to the substrate is the same sign as the surface charge and decreases in the opposite case.

The ponderomotive technique is rather uncommon, nevertheless it is useful in experiments where the force is important and knowledge of the value of the local charge density is of no interest.

3.3 Inductive methods

Charge studies with a so-called Faraday cage as performed by for instance Skinner et al. (1956) and Shashoua (1958) give an absolute value of the total excess charge of a sample. The equipment consists in principle of a closed metal electrode electrically insulated from a surrounding grounded electrode. The charged sample is put into the inner electrode. The inductive charge on it gives rise to a potential difference, $U$, between the electrodes to be measured by means of an electrometer. Knowledge of the capacitance, $C$, from the inner electrode to ground makes the total charge, $q$, calculable according to

$$q = CU$$

In experiments where no information about the distribution of the charge density is needed a Faraday cage is convenient. It is furthermore applicable as a calibrating instrument of other measuring devices, where the geometry does not permit the absolute value to be calculated.
The possibility of measurements of the surface charge density distribution is a gratifying quality of the potential probe technique. The principle is that the charged object is put near an optimally screened metal probe; hence, charge is induced on the probe. The resultant probe potential is measured by an electrometer. From values of the capacitances of the electrometer-probe-object system, the gain of the electrometer and the potential obtained the surface charge density can be calculated. The method is particularly applicable in decay studies of a surface charge density where only relative values are required, since the calibration procedure is then unnecessary.

Potential probes are described by several authors, e.g. Davies (1967b), Foord (1969), Wintle (1970), van Turnhout (1970) and Benninghoff et al. (1970). These devices, however, do not permit measurements to be taken continuously, as the probe is held stationary over a charged surface due to the finite input resistance of the electrometer used. This disadvantage is eliminated if the probe is periodically screened by a rotating vane, as in the field mill system according to Schwenkhagen (1953). Field mills have also been described by Czejja (1970) and Secker (1975). In a commercially available instrument (Monroe Isoprobe, Monroe Electronics, Inc.) feedback of the signal via an integrator to the frame of the probe is an improvement on the traditional field mill. In section 4.3 an additional inductive instrument is described. In this instrument the probe itself oscillates over a small aperture in a grounded envelope. This design is compact, mechanically simple and electrically reliable.

3.4 Galvanometric method

Since a continuous charge transfer is analogous to a current an electrometer in the current mode can be used in such cases. As a matter of fact this technique is very convenient and highly informative for the electrification experiments presented in later chapters, where a metal electrode which is connected to ground via an electrometer slides or rolls over a dielectric slab with constant velocity. The charge transferred from dielectric to metal during electrification is then at each area of contact registered as a current through the electrometer. A positive current is related to a negative charge deposited and vice versa. The total charge transfer in a track of a certain length is
obtained by integrating the current with time. Hence the galvanometric method applied to this particular case gives information about the total charge transfer as well as the local charge transfer without a laborious calibration procedure which would be necessary with any inductive method.
4 EXPERIMENTAL ARRANGEMENTS IN SLIDING ELECTRIFICATION

This chapter describes the equipment and technique used in the experiments reported in the chapters 5, 6 and 7. The preparation of the insulator surface which is specific to the insulator investigated is given in the chapter concerned.

4.1 Electrification details

4.1.1 Electrification apparatus

The sliding electrification was performed in an apparatus which is shown in figure 4.1. The electrification device was put up on a L-profiled beam. Along two steel guide rods (A) a grounded carriage (B) is mobile and on the plane upper surface the insulating sample (C) is fastened. A microswitch arrangement makes it possible to adjust the carriage travel to a desired length giving an automatic stop at the ends. The metal electrode (D) has a spherical end surface which, during measurements, makes contact with the insulator surface. The electrode is mounted in a Teflon bush which provides electrical insulation from the metal parts of the electrode holder (E). The holder is attached to one end of a balance arm (F), the middle of which is mounted in a fork by tip bearings (G). The other end of the arm is provided with a balance screw (H) in order to balance out the weights of the electrode and its holder. The vertical force exerted by the electrode against the insulator surface is variable by means of different weights (I) placed on the balance arm above the electrode. An eccentrically pivoted disc (K) on the axis from a step motor (M₁) enables lifting or lowering of the electrode. Another motor (M₂) can be used to move the balance arm sideways along a guide rod (L) and the resultant position is registered by a linear transducer.

Between the guide rods (A) a play-free leadscrew (N) is mounted so as to move the carriage at constant velocity. The leadscrew is rotated from outside the right flange by means of a synchronous motor with exchangeable gear box units for different carriage velocities. The L-profiled beam may be pushed to the left into an aluminium tank (P) in order to screen the experiment chamber electrostatically and make a vacuum-tight joint between the flanges.
Figure 4.1 Electrification apparatus: A, guide rods; B, carriage; C, sample; D, metal electrode; E, electrode holder; F, balance arm; G, tip bearing; H, balance screw; I, weight; K, eccentric disc; L, guide rod; M₁ and M₂, motors; N, lead screw; P, tank.
The system was evacuated to a vacuum better than $10^{-5}$ torr by a pump combination consisting of an oil diffusion pump (Edwards Diffstak model 100-300) backed by a mechanical rotation pump (Edwards ES 100). A baffle and a liquid nitrogen cold trap is mounted between the vapour pump and the chamber for the purpose of minimizing back-streaming of organic molecules and increasing the pumping speed for moisture. An activated alumina oil trap in the fore-pump pipeline ensured that clean vacuum was also obtained during the rough pumping stage.

4.1.2 Measuring principle

Whatever the preparation treatment of the insulator surface, there was nearly always spurious charge left. Since the electric field due to excess charge influenced the results, neutralization of the insulator surface was performed by exposing the insulator fastened to the carriage to irradiation by a $\beta$-source ($^{85}$Kr, $\sim 1$ mC). The effect of the treatment was checked by the instrument described in section 4.3 and the spurious charge was shown to be unmeasurable small after treatment.

The height position of the balance arm was adjusted by hand so as to make the balance arm parallel to the insulator surface with the metal electrode in contact. Newly machined metal electrodes were used. After the choice of material of the electrode and the magnitude of the weight producing the contact, the vessel was closed and evacuated. A charged track on the insulator was produced by driving the carriage between the previously adjusted end stops with the metal electrode sliding on the insulator surface. After the microswitch had stopped the run the electrode was lifted up from the surface by the eccentrically pivoted disc. The carriage was then moved back to start position and the electrification device was pushed sideways a few millimeters to present for electrification adjacent and parallel area of the insulator. The electrode was then lowered and a new run made. Two or three such runs could be performed without breaking the vacuum, since the charge on a given track was found to be independent of the presence of adjacent tracks. After this, the vacuum was broken and the insulator discharged with the $\beta$-source before re-evacuation. In comparative measurement series equal numbers of runs were performed with each value of the parameter to be varied on one sample before exchange of sample to avoid influence from random scatter of charge transfer from one sample to another.
The metal electrode was connected to ground via an external electrometer (Keithley model 640) which permitted the charge transferred to be measured continuously along the track on the insulator. The measurement range chosen on the electrometer made the potential difference to ground of the electrode less than 300 mV. The unity gain output of the electrometer was connected to an integrator so that the total charge could be read as well as the current which was registered by a potentiometer recorder. (An example of current recording is shown in figure 4.6(a)).

The tracks after electrification could be observed in a workshop microscope and the widths of the tracks measured. These apparent widths were used to estimate the surface charge density on the insulator after separation.

4.1.3 Sources of error

It is by no means evident that the charge flow as measured by the present method is the real charge transferred at contact. This section will give a short discussion of a few of the possible mechanisms which may decrease the charge measured and consequently may cause an underestimation of the charge transfer at contact.

As is observed in figure 4.6(a), which is a current recording from an electrification experiment, the rise is rather slow at the beginning. This is due mainly to creation of induced charge on the metal electrode during the first phase of electrification. Induced charge also appears on the top surface of the grounded carriage. Wåhlin (1973) made a rough estimate of the extent to which the induced charge on the electrode may affect the total charge measured without taking into account the induced charge on the carriage. He approximated the charge track on the insulator by a line charge of density \(q_L\) and the metal electrode by a sphere with radius \(a\) in a position such that the extension of the line charge crosses the centre of the sphere. He obtained for the total induced charge, \(q_{in}\)

\[
q_{in} = -q_La \frac{2}{\varepsilon (\varepsilon + 1)} \ln \left(1 + \frac{L}{a}\right)
\]

where \(\varepsilon\) and \(\varepsilon_0\) are the permittivities of the insulator and free space respectively and \(L\) is the total length of the track. The total charge deposited on the insulator, \(q\), is expressed by
\( q = q_L L \) \hspace{1cm} (4.2)

It is clearly seen that \(|q| >> |q_{in}|\) for large values of \(L\) (for example \(L = 100\) and \(a = 1.5\) mm, which is a possible experimental situation). It seems plausible to consider the induced charge creation on the metal electrode during electrification as a saturation process since, in addition, surface charges far removed from the electrode tend to turn their field lines against the carriage thereby decreasing the value of \(q_{in}\) as estimated from equation (4.1). However, in the earliest part of a track (i.e., \(L\) is small), the induced charge is increasing and of the same order of magnitude as the charge deposited.

From the slope of the initial portion of the current curve the contribution from the induced charge may be estimated experimentally. It was found that the associated error was \(\leq 3\%\). Since this error is small compared to the random scatter in electrification experiments the results have not been corrected for the effect of induced charge.

After separation, and before the distance between the pieces of material has become too large, electrons deposited on one piece may leak back to the other by tunnelling. The driving mechanism for this back leakage is the rise of contact potential difference due to decreasing capacitance resulting from increasing distance between the pieces of material. The tunnelling mechanism can be effective at atomic distances only, and, if a non-negligible probability of tunnelling exists, it would be expected to affect the sliding as well as the rolling and lifting modes of separation. However, although it would be interesting, tunnelling \textit{per se} has not been investigated in these experiments.

Further separation makes the contact potential difference rise even more and the dielectric strength of the ambient atmosphere may be exceeded, resulting in electrical breakdown. By employing a high vacuum and/or using thin insulating samples on a conducting substrate the likelihood for air breakdown is minimized. By the present simultaneous electrifying-measuring method discharging by breakdown will be observed as transients in the electrification current which makes the method advantageous to any inductive method in this sense.
Back leakage by conduction is very likely in a tangential mode of separation if the insulator in the electrification system does not have a sufficiently high resistivity. The amount of charge transported back a certain distance increases with time. Since the metal electrode continuously leaves the freshly charged region, a low velocity of separation should cause a greater amount of back leakage than a higher velocity. Hence charge transfer independent of velocity over a wide range gives an indication that back leakage by conduction is negligible.

4.2 Contact potential difference measurements

The contact potentials relative to Pt of the metal electrodes used were measured by a modified Kelvin method (Wåhlin (1973)), the principle of which is shown in figure 4.2.

The reference electrode (R) was mounted on a magnetic coil movable inside a cylindrical permanent magnet. By feeding the coil with an alternating current a vibrating motion of the reference electrode was generated. Hence, the distance and consequently the capacitance between the electrodes (E) and (R) varies with time with the same frequency as the alternating current. Since (E) and (R) are connected via an external circuit a constant contact potential difference exists between them. Owing to the time variation of the capacitance the charge on the electrodes varies in the same way causing an alternating current at the amplifier input. The output signal of this amplifier is fed in turn to a selective amplifier which amplifies the second harmonic which is then viewed on an oscilloscope. For a special value of voltage from the direct voltage supply the signal on the oscilloscope vanishes. This value of voltage with opposite sign is the contact potential difference between the electrode and the reference electrode. A check can be made by turning the switch so as to reverse the polarity of the detected signal. The discrepancy between two such measurements was always less than 0.01 V.

For practical reasons this equipment was placed in a separate tank which was evacuated to a pressure $< 10^{-5}$ torr. The measurements of contact potential difference were performed before the electrification experiments.
Figure 4.2  Block diagram of the circuit for contact potential measurements. After Wählin (1973).
4.3 Probe for charge density measurements

With the purpose of being capable of studying charge distributions on insulator surfaces an inductive charge measuring instrument was constructed, and is described in this section.

The heart of the instrument is a piano wire, 0.5 mm in diameter, fixed at one end and free to oscillate over a small hole (0.4 mm in diameter) in the bottom plate of the grounded metal envelope (see figure 4.3(a)). The wire was ground nearly flat over a portion of its length close to the support in order to stabilize the plane of vibration. The oscillation is sustained by means of a small magnet (see figure 4.3(b)), creating an inhomogeneous field over the wire, and operating at approximately 40 Hz. As the wire passes over the hole it is exposed to the electric field of the external charge and an alternating induced charge is produced at the tip. The resulting potential is measured by a one-stage transistor (3N128) preamplifier, where a 100 MΩ bleeder is connected from gate to ground. The output is connected to a PAR HR-8 lock-in amplifier. It should be noted that the frequency of vibration is twice the frequency of the magnet current and that therefore the second harmonic voltage across the magnet coil is to be used as reference voltage to the lock-in amplifier, as shown in figure 4.4. After calibration, the sign as well as the magnitude of the charge is obtained from this circuitry.

The output voltage was shown to be proportional to the potential of a metal test plate used under the probe. The constant of proportionality may drift, however, by approximately 1 percent per hour, probably due to instabilities in the various electronic circuits, which were by no means optimized. This drift was not a serious disadvantage, however, since recurrent calibration against a reference potential could easily be made.

The noise voltage at the oscillating wire was 6 µV peak-to-peak, which corresponds to 0.5 V on a metal surface 0.25 mm under the bottom of the apparatus. Signals, with a typical value of 5 mV, were obtained by measuring the charge density of electrified tracks on Teflon. In such a case the width of the charged track could be 0.15 mm and the surface density $2 \times 10^{-8} \text{Ccm}^{-2}$. 
Figure 4.3 A semi-schematic representation of the essential parts of the charge detector. (a) Vertical projection. (b) Horizontal projection.
Figure 4.4 Block diagram of equipment for charge density measurements.
Tests of the geometrical resolving power were carried out by scanning over a potential step produced by two metal plates cemented edge to edge. Figure 4.5 shows one of these results, where the distance of the envelope bottom from the metal surfaces was 0.25 mm. The resolution, of course, depends on the distance as well as on the diameter of the hole. For the investigations of charge distributions depending on one coordinate only, a slit would yield even better results than the circular aperture used, because of the more efficient penetration of the field into the envelope.

![Graph](image)

**Figure 4.5** Resolution of a step potential of 50 V.

The detector may be calibrated by scanning over a charged track, where the current leaving the electrifying metal pin has been recorded continuously during the electrification process by an electrometer (see section 4.1). Figure 4.6(a) shows a charge distribution inferred from the electrification current. The same distribution observed shortly afterwards with the charge detector is shown in figure 4.6(b).
Figure 4.6 Linear charge density of a charged track on Teflon.
(a) Measured by a Keithley Model 640 electrometer during the electrification experiment. (b) As seen by the charge detector immediately after the electrification.
The initial rise is sharper in figure 4.6(a) than in 4.6(b), presumably due to an image built up during the first phase of the electrification as discussed in section 4.1.3. The distance between the Teflon surface and the probe was chosen so as to match the resolution. Shorter distance proved to yield more pronounced peaks and valleys.

No attempts were made to find optimal working conditions for this instrument. Improvements may, no doubt, be made in several respects, if this should prove desirable. The preamplifier used is quite rudimentary, and could be substituted by an FET operational amplifier having an input bias current of 0.1 pA. Possibly a higher operating frequency could yield an increased sensitivity. The optimal area of the wire tip for a given aperture could be determined, and a much thinner bottom plate than the present one (0.4 mm) could be made from a platinum foil. The size of the total probe arrangement could also be much reduced to suit certain applications. Finally, internal calibration could be introduced, of the type found in the field mill meter described by Pollard and Chubb (1975).
5 SLIDING ELECTRIFICATION OF SODIUM CHLORIDE

As mentioned in the first chapter one reason for choosing single crystalline NaCl as the insulator part in an insulator-metal electrification system was that, as a result of its simple structure, existing electron band calculations are reasonably satisfactory. The experimental results presented in this and in the subsequent chapter show that the electrification of NaCl is due to transport of electrons. For this reason the presentation of the electrification measurements on NaCl is preceded by a short introduction to the structure of NaCl in order to relate the electronic energy levels of metals to those of NaCl.

5.1 Electronic structure of NaCl

NaCl is an ionic crystal and the well-known structure can be described as two interleaved arrays, one of sodium atoms, the other of chloride atoms, each in face-centered cubic arrangement. Consider the electron states in NaCl by imagining the formation of the crystal from a state where the atoms are arranged as in the NaCl-structure but with a very large separation between each other as illustrated in figure 5.1.

Figure 5.1 Sodium and chloride atoms in a widely spaced NaCl-configuration. After Harrison (1970).
The atoms in this pattern do not affect each other and they remain neutral atoms. The sodium atom possesses an valence electron in a 3s state outside a filled 2p shell while there is an electron missing to fill the 3p shell of the chlorine atom. A net expenditure of energy is required to remove a 3s electron from a sodium atom and carry it against the electric field of the sodium ion created to a neighbour chlorine atom in order to produce a chlorine ion. Decreasing the separation distance between atoms there is a shorter distance for the electron to be carried and the energy expenditure becomes smaller. In addition, by ionizing all sodium atoms at the same time, there will be energy gain in moving the electrons to the chlorine sites, which are then surrounded entirely by positive sodium ions. Thus, even at interatomic distances where there is negligible band formation, due to wave function overlap, the more stable electron configuration becomes that of sodium ions and chlorine ions. This point is illustrated in figure 5.2 where the shift of the electron levels is plotted against the internuclear distance. At distances less than $a_1$ in the figure the formation of ions is energetically favourable.

![Figure 5.2](image)

**Figure 5.2** Schematic diagram of the bands in NaCl as a function of the internuclear distance. The curve denoted Na gives the energy for an electron in the 3s state of Na while Cl$^-$ stands for the electron energy in the 3p state of Cl. After Harrison (1970).
Further decrease of the internuclear distance to values less than $a_1$ will broaden the ion levels into bands because of the overlap of the wave functions. The electrons centred on the chlorine ions will form a completely filled valence band corresponding to a filled shell in the atomic case. Furthermore the formation of an empty conduction band from the broadening of the unoccupied sodium atom states will occur. There is still a reduction of energy in decreasing the distance, until the outer electron shells of nearest neighbours are more or less in contact. These shells, 2p for the sodium ions and 3p for the chlorine ions, are completely filled and as a result of the orbital overlap the energy increases rapidly for further decrease of the internuclear distance. The real crystal will then come to equilibrium at a distance between the ions which is roughly equal to the sum of the radii of the ions (marked as $a_0$ in figure 5.2).

In recent years the electronic energy bands of NaCl have been investigated extensively. Several authors, i.e. Fong and Cohen (1969), Lipari and Kunz (1971), Kunz and Lipari (1971) and Perrot (1972), have reported theoretical calculations on the band structure of NaCl. Various methods have been used, and their results for the bandgap vary between 8.4 eV and 10.0 eV. These theoretical findings may be compared to some experimental measurements of the bandgap. For instance Eby et al (1959) obtained 8.5 eV from absorption measurements in the UV-range. By interpreting the threshold for luminescence as a band to band transition Timusk and Martienssen (1962) obtained a value 8.0 eV for the band gap. Roessler and Walker (1968) studied reflectance spectra in the ultraviolet and concluded that the bandgap is 9.0 eV. Concerning the electron affinity there is less consistency between various contributors. Some authors (i.e. Eby et al (1959) and Pong and Smith (1974)) have reported the conduction band edge above the vacuum level, while others (i.e. Lipari and Kunz (1971), Kunz and Lipari (1971), Gilleo (1954) and Timusk and Martienssen (1962)) have found the electron affinity in the range 0.0 to 0.8 eV. Summarizing now the theoretical and experimental results above taking the value 9.0 eV for the band gap and 0.4 eV for the electron affinity a simplified energy band scheme of pure NaCl can be constructed and related to that of a typical metal as shown in figure 5.3.
Figure 5.3 Schematic diagram of energy bands of NaCl compared to that of a metal with work function 4.0 eV.

It may be noted that the Fermi level of a metal roughly 4 eV below the vacuum level before contact with NaCl is well separated from the insulator band edges.

5.2 Experimental details

The apparatus described in pp 34 - 36 was used. The metal electrodes had a radius of curvature of 1.5 mm at the tip throughout the study. The NaCl crystals were cut along a (100) plane but a separate investigation with other orientations was also carried out. The sizes were approximately 50 x 25 x 10 mm³. The surfaces were prepared by cutting with a microtome, followed by baking for 6 hours in a vacuum oven at a temperature slightly above 100°C. The baking appeared to be essential to the reproducibility. The spurious charges remaining after this treatment were eliminated by a brief irradiation with a 1 mC ⁸⁵Kr source. The rest charge was then
unmeasurably small. The crystal to be investigated was fixed to the plane carriage with an epoxy resin and was then placed in vacuum for about eight hours. Two electrification tracks could be generated without breaking the vacuum, after which the crystal had to be discharged in atmospheric pressure. The tracks on the insulator surfaces could be seen in a workshop microscope, and their widths were measured in order to obtain the surface charge densities.

5.3 Results

5.3.1 Velocity dependence

As a start of the investigation a series of experiments was performed on (100) faces by sliding a gold electrode with various velocities between 0.01 mm/s and 2.5 mm/s and at a constant load of 50 g. Twenty measurements were made with all velocities but the lowest, which was used in nine runs. The results are shown in table 5.1.

Table 5.1

<table>
<thead>
<tr>
<th>Velocity (mm s⁻¹)</th>
<th>Charge density (10⁻⁸ C cm⁻²)</th>
<th>Standard error of the mean (10⁻⁸ C cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>+3.5</td>
<td>0.4</td>
</tr>
<tr>
<td>0.05</td>
<td>+4.2</td>
<td>0.3</td>
</tr>
<tr>
<td>0.5</td>
<td>+4.2</td>
<td>0.3</td>
</tr>
<tr>
<td>2.5</td>
<td>+4.1</td>
<td>0.2</td>
</tr>
</tbody>
</table>

There seems to be no systematic variation of the surface charge with velocity at least for velocities greater than 0.05 mm s⁻¹. On the basis of these findings, the following investigations were performed at the velocity 0.5 mm s⁻¹, in the middle of the range of independency.

5.3.2 Dependence of the metal work function

In the next series of experiments on (100) oriented surfaces different metals were used while the velocity was kept constant at 0.5 mm s⁻¹ and the load at 50 g. The purity of the metals was better than 99.95 percent in the cases of aluminium, copper, gold, magnesium and platinum. One electrode was made of duraluminium. The contact potentials between the metal electrodes and a platinum reference electrode were measured by a modified
Kelvin method as described in chapter 4. The contact potential measuring device is for practical reasons placed in a separate tank evacuated to a pressure below $10^{-5}$ torr. Twenty runs were made by each electrode material and the means of the surface charge density transferred to the NaCl crystals are plotted in figure 5.4 against the measured work function differences relative to platinum. The bars give the standard deviation of the mean value.

![Graph](image)

**Figure 5.4** Plot of surface charge density on (100) surfaces of NaCl against metal work function measured relative to Pt. The metals are from the left Mg, Al, duraluminium, Pt, Au and Cu.
Figure 5.4 shows an evident correlation between the surface charge and the metal work function. The point for duraluminium marked by an open dot is disregarded in the least square fitting to a straight line.

5.3.3 Influence of the force

Charge transfer as a function of the load on an electrode of gold was also measured and the results are presented in figure 5.5. Ten tracks were electrified for each value of the load. Curve (a) gives the best-fitting function of the form $q_L = F^n$, where $q_L$ is linear charge density and $F$ is the normal force. The fitting requires an exponent $n = 0.36$. Curve (b) corresponds to $q_L = \log F$, where the point for the load 0.7 gram is excluded. There were some measurements taken at even lower load (0.25 gram), which resulted in smaller electrification charge than for the higher loads, but definitively of positive sign.
Figure 5.5 is a plot of the linear charge density, $q_L$, against the load, $F$. The continuous curve, (a), is the fit of the form $q_L \propto F^{0.36}$ and the curve of the short dashes, (b), corresponds to the best fitting function $q_L \alpha \log F$. 
5.3.4 Electrification of different crystallographic faces

In order to investigate whether the charge transfer between metals and NaCl was affected by the crystallographic orientation of the insulator, some crystals were cut along (110) planes and (111) planes. Twenty measurements were performed with each of the metals aluminium, gold and magnesium keeping the load constant at 50 g. Table 5.2 shows a summary of the surface charge densities on the different crystallographic planes. The errors are expressed by the standard deviation of the mean value. The charge densities are given in the unit 10^{-8} C cm^{-2}.

Table 5.2

<table>
<thead>
<tr>
<th>Plane</th>
<th>Au</th>
<th>Al</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>4.6 ± 0.2</td>
<td>1.9 ± 0.1</td>
<td>1.4 ± 0.1</td>
</tr>
<tr>
<td>(110)</td>
<td>4.7 ± 0.3</td>
<td>1.9 ± 0.2</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>(111)</td>
<td>4.5 ± 0.5</td>
<td>2.2 ± 0.1</td>
<td>1.6 ± 0.1</td>
</tr>
</tbody>
</table>

The results are obviously the same for the three planes within the experiment errors.

One of the (111) surfaces showed an interesting anomalous behaviour in such a way that a specific small area of the surface attained an extremely high charge density when electrified with gold, while magnesium gave a noticeably lower charge density on this spot than in its vicinity. Tracks from aluminium, however, did not give rise to any remarkable change of the electrification properties. Figure 5.6 show a set of typical electrification recordings of closely-spaced tracks for the three metals.
Figure 5.6 Current recordings from electrification of a specific (111) surface showing an anomalous charge transfer behavior. The tracks are electrified by from the left Au, Al and Mg respectively.
5.4 Discussion

Summarizing the experimental results from sliding electrification of NaCl it is seen that the charge density is independent of the relative velocity, it varies linearly with the metal work function and the variation of the charge transferred with the force can be described by a power law but a logarithmic function may express the dependence for higher forces. The crystallographic orientation seems to have no influence on the electrification charge density.

The constancy of the electrification charge with the velocity is interpreted as a sign of no back conduction occurring. The back conduction effect may, however, influence the result at very low velocities, which is indicated from the runs at the velocity of 0.01 mm s\(^{-1}\). It may also be inferred that the time of contact was sufficiently large for full injection to occur, even at the highest velocity. The contact durations related to the velocities used are in the range 0.03 - 7.5 s as estimated from the track width measured by a microscope. Hence the charging process seems to be finished in a few hundredth of a second. This is in accordance with the findings of Wåhlin and Bäckström (1974) in their sliding electrification study of Teflon. There are, however, no comparable data published for alkali halides.

The approximately linear dependence of charge density with metal work function when the crystals are thoroughly dried and electrified in vacuum is consistent with electron transfer (Arridge (1967), Davies (1967a, 1969, 1970)). If the outgassing stage in the preparation treatment was excluded, the reproducibility for the metal-NaCl electrification system was completely missing. Some parts of a crystal were charged negatively while others showed a positive sign for the charge deposited. Besides, the absolute magnitude of charge transferred was much smaller in this case than in cases where the complete preparation procedure was carried out. The same observations were made in electrification experiments performed in ambient atmosphere. NaCl is known to be hygroscopic and the absorbed moisture probably raises the surface conductivity and thereby limits the charging. In addition, such aqueous films probably include ions which may contribute to the charging and may cause the irregular electrification behavior of the metal-moistened NaCl system. Although it cannot be excluded that there may be
cases where ion transfer predominates, it seems justified to abandon this effect in my measurements.

The NaCl crystals were charged entirely positively by the metals used. Hence the contact potential theory states that the Fermi level of NaCl is situated above that of all electrifying metals. By extrapolating the straight line fitted in figure 5.4, zero charge is attained with a hypothetical metal which has the Fermi level 1.6 eV above that of Pt. (See further chapter 6). The work function of NaCl would then be about 3 eV. Considering figure 5.3 the Fermi level of NaCl is then experimentally found at roughly 2 eV above the value calculated for a trap-free crystal.

The positive electrification charge attained on NaCl is quite in accordance with other studies of metal-alkalihalide systems. Wagner (1956) generated charge by rolling spherical samples of NaCl and other alkalihalides on a nickel surface in high vacuum. The charge on the spheres raised with rolling time and reached a "saturation" value after more than ten minutes. This raise was mainly due to increase of the area which had been in contact with the nickel surface. There was nothing in his experiment which contradicted electron transfer but the possibility of loss of negative ions was considered quite likely.

Investigations on KCl in the vertical separation mode have been performed by Weingärtner et al (1968) and Kasai and Nishi (1974). The alkalihalide attained an increasing amount of charge by repeating the contact-separation process several times. The charge increase is probably, as in the case of Wagner (1956), a consequence of new areas being touched during each contact, but charge diffusion along the surface and into the bulk by ionic and electronic conduction may also interfere. The latter hypothesis was supported by the observation that the charge increment at each contact increased with increasing time between successive contacts as shown by Kasai and Nishi (1974). Although there was great variation in their results for different pieces of pure KCl they obtained a correlation between the charging rate and the work function of the metal which was explained in terms of the energy band model by introducing electron trapping levels in KCl. Weingärtner et al (1968), however, could not draw such a conclusion in their study.
Challande (1970) studied the electrification of the alkali halides NaCl, KCl, KBr and KI upon rubbing with metals. He obtained positive charge on the insulators but in contradiction to my measurements the charge acquired was greater for Pt than for Au. This inconsistency between our results does not oppose the idea of electrons being the charge carriers because the platinum which was used by Challande (1970) possessed a higher work function than the gold in the experiment.

The main purpose of the study of Challande (1970) and also of an earlier study (Challande (1967)) was to find out how the electrification charge varied with the force between the substances. He found that the amount of charge created on NaCl was proportional to the logarithm of the normal force in contradiction to the results from Al_2O_3 which gave a linear relationship. The theoretical explanation given was based upon the occurrence of lattice defects. As is shown from curve (b) in figure 5.5 such a logarithmic relation may describe my experimental points for loads higher than 5 gram. At low loads, however, the logarithmic fit breaks down completely since there is in fact no charge sign reversal as would be required by the logarithmic dependence. It seems then that the plot (a) of the form \( q_L \propto F^n \) best describes the variation of the electrification charge with the normal force. It may be noted that in the study of Challande (1970) true low loads are not investigated. In addition the low load measurements of NaCl (\( < 40 \) gram) can be satisfactorily fitted to a function of the form \( q_L \propto F^n \).

The idea of relating the charge transferred to some power of the force is based upon the behavior of the real area of contact between a spherical formed and a flat surface, which theoretically shows such a relationship. The value of the power \( n \) depends on the assumptions made about the origin of the deformation. For example, with a classical elastic theory approach, Hertz (1881) derived an expression for the area of contact, \( A \)

\[
A \propto F^{2/3} 
\]  

(5.1)

By assuming plastic deformation, as did Meyer (1908), we find the relation,

\[
A \propto F
\]  

(5.2)

Since real surfaces always show roughness in the microscopic scale it is very difficult to predict the real area of contact. Calculations were made by Archard (1957), where he introduced a model of a rough sphere in which
the roughness consisted of equal spherical asperities evenly distributed over the surface and with equal protrusion. By covering the asperities with smaller spheres and these with even smaller ones and so on he obtained in each stage a closer approach to the law of direct proportionality, even in the elastic theory. Archard (1957) also pointed out that as the total area of contact increases nearly proportional to the load, so does the number of individual contacts. If, however, the increase in load does not create any new individual points of contact, but instead increases the size of the existing ones, the elastic theory gives the relation (5.1) as found by Hertz (1881).

The asperity argumentation by Archard (1957) has been extended by among others Greenwood and Tripp (1967, 1970/71). Their first assumption was that the asperity heights follow the normal, Gaussian, distribution about a mean surface. They also assumed that the tops of the asperities are spherical, all with the same radius, which deform elastically according to the law of Hertz (1881). They then concluded that the behavior of rough surfaces in contact is determined primarily by the statistical distribution of asperity heights and is only secondarily influenced by the mode of deformation and their calculating gave as a result that the total real area of contact is approximately proportional to the load. Their solution points out that the classical Hertzian solution is the high load limit for a rough surface. This limit is nearly reached with loads in the range used in this investigation by assuming a low value of the roughness (standard deviation of the asperity heights) and/or a large value of the asperity radius. Since NaCl shows easy cleavage in the (100) plane, giving relatively plane asperity tops, it is probable that the surface parameters will take values in the direction of the Hertzian solution.

A pure Hertzian contact between the insulator and the metal electrode will then give a width of real contact, \( \omega \), varying as \( \omega \propto f^{0.33} \). This power relationship should appear between the linear charge density in the sliding electrification mode and the normal force, as well, if there is proportionallity between charge transferred and area of contact. My measurements, however, show a slightly higher value of the exponent, 0.36 in fact. (Figure 5.5). The discrepancy may be due to the creation of some new contact asperities besides the enlarging of the real contact area of
those already existing, as a consequence of increasing load. (Archard (1957)). The plastic deformation mode will tend to raise the value of the exponent towards 0.50. Hence a combination of the elastic and the plastic mode of deformation is expected to result in a value of the exponent somewhere between 0.33 and 0.50. Irrespective of whether the deformation is pure elastic or contains some plastic mode contributions it then seems plausible that the exponent in the power law connecting real track width and normal force takes the value 0.36, as deduced from figure 5.5. These findings are consistent with the idea of the charge transferred being proportional to the real area of contact.

Similar interpretations have been made on recent electrification experiments on polymers. For instance Wählin and Bäckström (1974) found in a sliding electrification study of Teflon that the charge varied as $F^{0.50}$. The real width of contact varies in the same way if the deformation is plastic and/or if the asperity model (Greenwood and Tripp (1970/71)) is applicable to Teflon. The latter alternative is plausible taking the preparation method (grinding) into consideration since the surface parameters probably take values in the range where the direct proportionality between real contact area and force is theoretically predicted.

Davies (1973) made experiments on the contact electrification between a metal sphere and plane samples of the polymer polyethylene terephthalate as a function of the contact pressure in the vertical separation mode. He used a probe technique to measure the area of contact and the results indicate that the surface charge density even in this case is not primarily dependent on the normal force exerted but on the increasing area due to the increasing load. Polyethylene terephthalate, however, seems to follow the Hertzian model of deformation in contrast with Teflon (Wählin and Bäckström (1974)) and NaCl in the present investigation.

The electrification of different crystallographic faces does not show any significative differences between the orientations chosen. Hence the electrification properties of NaCl are determined merely by the composition of the insulator material and not from the specific geometrical structure of the surface. This may indicate that the bulk of NaCl takes part in the electrification as is concluded for polyethylene in chapter 7. If
the electrification process, however, is considered as a pure surface phenomenon, as proposed by Bauser et al. (1970), the controlling parameters then must be independent of the orientation of the surface of NaCl.

As is seen from figure 5.6 there were peaks in the electrification current on a specific small area on one of the (111) surfaces when electrifying with Au. Near-lying tracks generated with the Mg-electrode showed dips in the charge transfer from the corresponding area, while the current recordings from the Al-electrode experiments did not exhibit any such irregularities on the area in question. Let us assume that there are electron trapping levels continuously distributed in the energy gap of the NaCl sample and that for simplicity these normally have the same density for all energies in the gap. If for some reason the density of traps on this specific spot was lower than normal for energies corresponding to the work function of Mg but had higher values deeper in the energy gap the results shown in figure 5.6 can be explained from a model based on an electron trap density, for instance that of Bauser et al. (1970), equation (2.32), or the model treated in chapter 7, which is expressed in equation (7.19). The number of traps available for emptying would then be below the normal value with Mg and above the normal value with Au as electrifying electrode. Since the work function of Al is between that of Au and Mg it is plausible that charge transfer with Al as electrifying electrode would be unaffected by such a non-constant distribution of trapping levels. The findings in figure 5.6 may then give an indication that there is an electron trap distribution involved in the electrification of NaCl.

In conclusion it can be said that the electrification in the sliding mode of NaCl by metals is well described by electron transfer as a consequence of the difference of the Fermi energy between the materials. It seems plausible that the bulk of the alkali halide takes part in the charge transfer if it is assumed that the controlling parameters on the surface depend on the orientation. There is also an indication that the emptying of electronic trapping levels in the band gap of NaCl is one of the fundamental mechanisms.
When considering contact charging of insulators by sliding metal electrodes, the role of friction is by no means known. By rolling the metal electrode over the insulator surface there would be no slip between the materials if the surfaces are undeformed. But even in free rolling there is in fact deformation due to the loading normal to the point of contact. This deformation always involves a finite amount of slip (relative motion of contacting surfaces) somewhere within the area of contact. Bowden and Tabor (1966), however, have shown that the extent of slip is negligible and this conclusion still holds in the case of a partly normal and a partly tangential load. Hence the electrification by rolling will be affected by friction to a lesser extent than can be expected from electrification by sliding and consequently rolling electrification gives a more genuine contact charging case. This chapter gives a comparison and discussion of electrification in the sliding and rolling modes of separation.

6.1 General experimental details

The electrification apparatus as shown in figure 4.1 was used. The mounting equipment for the electrode, however, was changed to that shown in figure 6.1. It consists of a fork (A) and the electrodes, now made from gold, aluminium and magnesium were in the form of circular wheels (B) of 10 mm diameter and the peripheral surface of the wheel was ground to a radius of 1.5 mm. Through the center of each wheel a thin steel axis (C) was pressed. Use of tip bearings ensured free rolling of the wheel. The electrical connection between wheels and fork was improved by a blade spring (E) fastened to the fork and rubbing on the axis. The sliding mode of electrification could be examined as well by pinning the wheel to the fork.

The experiments were performed at a load of 50 gram and a relative velocity of 0.5 mm s\(^{-1}\). The charge was measured in the way described in chapter 4.
Figure 6.1 Electrode arrangement. A, fork; B, wheel electrode; C, steel axis; D, tip bearing; E, blade spring; F, rod for pinning the electrode; G, holes for electrode pinning.

6.2 Measurements on NaCl

Crystals of NaCl cut along the (100) plane and prepared as described in section 5.2 were electrified in the rolling as well as in the sliding mode of separation. As discussed in chapter 4, the image charge built up on the metal electrode during the first phase of electrification increases with increasing size of electrode (see equation 4.1)), and so the electrification current has a slower rise with wheel electrodes than is the case with metal rods. In order to diminish the influence of the image charge build-up on the total measured charge, two crystals of length of about 50 mm were placed in series on the carriage. Ten tracks were electrified in the two modes with the metals Au, Al and Mg. The track width was measured
by means of a microscope. The results for the charge densities on NaCl are given in figure 6.2.

Figure 6.2 Plots of surface charge density on NaCl against metal work function relative to Pt. Open circles refer to sliding electrification while filled circles stand for results from rolling electrification. The error bars shown are the standard deviations of the mean value.
6.3 Measurements on Teflon

Teflon was investigated for comparison between rolling electrification and sliding electrification. The Teflon was produced by Habia AB, Knivsta, Sweden and had a crystallinity of about 60% (the same quality as was used by Wåhlin and Bäckström (1974)). The Teflon samples, 12 cm long, 3 cm wide and 0.2 cm thick, were cemented on the carriage shown in figure 4.1. The surfaces of the samples were prepared by grinding with carborundum paper with gradually finer grain and the preparation was finished by wet grinding and rinsing with distilled water. Finally the spurious charge was removed by exposing the surface to a β-ray source.

Ten measurements were made in the sliding mode of separation with a Au electrode and in the rolling mode with Au, Al and Mg electrodes. Irrespective of the mode of separation and the metal used the electrification charge was always negative. The means of the results are plotted against the work function of metal as measured by the Kelvin method in figure 6.3, where for both present results and those of Wåhlin and Bäckström (1974) electrification charge density for the sliding mode of separation with Au electrode is arbitrarily set equal to unity. The absolute magnitude of the charge density from electrification by rolling was found to be 17% lower than that obtained in the sliding mode of electrification when the electrode was made of Au.
Figure 6.3 Plots of relative charge density against metal work function relative to Pt. Filled circles refer to the present rolling electrification results. Open circles are sliding electrification results from Wählin and Bäckström (1974).

6.4 Discussion

The charge densities acquired by rolling electrification of NaCl are found to be much different from those in the sliding mode experiments. A remarkable discrepancy is observed with Mg electrodes as shown in figure 6.2 since the sliding method resulted in a positive charge deposited while the sign of the charge was negative in rolling electrification experiments. However, it may be noted that a linear relationship between the charge density measured and the metal work function appeared in the rolling mode as well as in the sliding mode of separation.
It is well known that deformation of a crystalline solid may produce charging. Disregarding the piezoelectric effect, which requires the crystal be non-centrosymmetric, there is the effect from the formation and movement of dislocations. Fröhlich and Suisky (1964) measured the charge redistribution appearing in the bulk of NaCl and KCl oriented crystals when the samples were stressed between two metal plates. They interpreted their results as movement of dislocations towards the measuring electrodes. Dislocations may carry an excess charge concentration. Electrical neutrality is maintained by a charge distribution of the opposite kind around the dislocation line. Schottky disorder due to equal numbers of both sodium and chloride ion vacancies is the dominant type of defects in NaCl. The result of Fröhlich and Suisky (1964) showed that when a dislocation moves in a pure NaCl crystal there is preference for the chloride ion vacancies to follow and the sodium ion vacancies to be left behind. Hence the dislocations will carry negative charges to the crystal surface, while a positive space charge distribution remains in the bulk. Similar observations have also been made by Toth and Kiss (1973).

It is to be expected that material transfer from rolling is negligible in comparison with that from sliding since contact is broken nearly vertically. Material transfer from the NaCl surface by sliding the metal electrode would then according to the findings of Fröhlich and Suisky (1964) preferentially influence the electrification in such a ways as to charge the insulator more positively. If this effect alone causes the discrepancy between the charge transfer obtained in the two modes of electrification the results of sliding electrification experiments would be obtained from those of the rolling electrification experiments by simply adding a constant term. As is seen in figure 6.2 this is clearly not true, since the fitted straight lines have different slopes. It may be noted, however, that the surface charge density is based upon the contour width of the tracks. Hence the slopes are dependent on the fraction of real contact inside the boundaries of the tracks and we argue that the contact is larger in the sliding case. The rolling separation creates a nearly one-to-one point contact between the metal electrode and the NaCl surface, while a particular spot on the NaCl surface may be touched several times by the metal during sliding. In addition, there is a possibility of some areas of NaCl remaining untouched by metal, and this may be more likely in the case of rolling contact.
Both these effects tend to increase the real area of contact in the sliding mode of electrification relative to that in the rolling mode of electrification. The charge density, $\sigma$, plotted in figure 6.2 can be expressed,

$$\sigma = \frac{q}{A_{\text{app}}} = \frac{A_{\text{real}}}{A_{\text{app}}} \times \sigma_{\text{real}} \quad (6.1)$$

where $q$ is the total charge measured along the track, $\sigma_{\text{real}}$ is the charge density based upon the real area of contact, $A_{\text{app}}$ is the apparent area of contact estimated from the contour of the track and $A_{\text{real}}$ is the real area of contact, which is presumably larger in the sliding case than in the rolling case. Since

$$\frac{A_{\text{real}}}{A_{\text{app}}} \leq 1 \quad (6.2)$$

it can be concluded that the experimental charge density is underestimated by the factor $A_{\text{real}}/A_{\text{app}}$. From the arguments above it follows that this factor is probable to be larger in sliding than in rolling contacts. Hence it is justified that the slope of the straight line fitted to the sliding electrification results in figure 6.2 is the steepest one.

It has recently been verified that the electrification charge density obtained on Teflon in both the rolling mode of electrification (Davies (1969)) and the sliding mode of electrification (Wåhlin and Bäckström (1977)) is linearly related to the work functions of electrifying metals as measured by the contact potential method. The present rolling electrification investigation of Teflon, however, does not show such a linear dependence. The absolute magnitudes of the charge densities obtained from electrifying by Al and Mg electrodes are in fact less than the charge density obtained with Au electrode electrification, which seems to be in contradiction to the contact potential theory since Au possesses the largest work function of these metals. The experimental equipment was thoroughly investigated in order to search for indications of bad electrical contacts in the circuit from the wheel to ground, but no such indications were found.

It is well-known that nearly all clean metals acquire an invisible protective layer of oxide not only when exposed to a laboratory atmosphere, but even in a vacuum of the order of $10^{-6}$ torr. The noble metals such as Au
and Pt are much more resistant to oxidation than Al and Mg. Since the electrodes are formed in ambient atmosphere such oxide layers are created, no doubt, and may interfere the electrification process. It is plausible that in the sliding mode of electrification (Wåhlin and Bäckström (1974)) there is break-up of the oxide layer shortly after the beginning of slip giving contact between the clean metal and the insulator. Even in rolling electrification, as in the results of Davies (1969), there seems to be no interference from oxide layers. In his investigation, however, the contact wheel was rolled over the same area many times and made many revolutions while the wheel in my investigation steadily changed the area of contact and made only three revolutions along the track. Since some sliding cannot be excluded during rolling contact, many revolutions may result in greater breakage of oxide layers than only a few revolutions. This argument may account for the discrepancy between my results for Teflon and those of Davies (1969).

Rolling electrification of Teflon by a gold electrode showed charge transfer 17% lower than that obtained in the sliding mode (see figure 6.3). Since the formation of surface films is slower on Au than on Al or Mg, the rolling mode electrification by freshly formed Au is more probable to be unaffected by an oxide film. The slightly higher charge transfer in the sliding mode of electrification may be due to larger real area of contact in this case than what is reached in the rolling electrification case.

At first sight it is to be expected that an oxide layer on the metal electrode will affect rolling electrification of NaCl and Teflon in the same way. Obviously this is not the case, the charge transfer being linearly dependent on the metal work function in the case of NaCl but not in the case of Teflon (see figures 6.2 and 6.3). However, break-up of the oxide layer is more likely when rolling an electrode on a NaCl surface than on a Teflon surface, since however smooth the NaCl surface there are always steps with sharp edges to be climbed over by the rolling wheel while the Teflon surface is a soft one. This justifies the linear relationship obtained in the rolling mode of electrification in the case of NaCl.

The formation of oxide films on metals has been theoretically investigated by Cabrera and Mott (1949) and Bloomer (1957) has experimentally confirmed their theoretical predictions. Cabrera and Mott (1949) assumed that there
is an adsorbed layer of oxygen atoms on the outside of the oxide layer and that there are deep acceptor levels in these oxygen atoms. These levels are situated below the Fermi level of the metal and electrons may tunnel from the metal through the oxide layer so as to partially fill the oxygen acceptor levels. The Fermi level on the outer surface of the oxide layer is then shifted to coincide with that of the metal. As far as contact charging is concerned, the role of an oxide layer with adsorbed oxygen atoms is to change the effective work function of the metal to a value equal to the depth of the acceptor levels in the adsorbed oxygen. According to Cabrera and Mott (1949), this value is about 5.5 eV, roughly independent of the work function of the metal. This explains my results from rolling electrification of Teflon by Al and Mg, metals which in this case behave as if their work functions are near equal and somewhat larger than that of Au.

The question now arises, how is the contact potential difference as measured by the Kelvin method affected in general by an adsorbed layer on the metal surface? It is very difficult to make reliable theoretical predictions. There is, however, some experimental evidence that what is measured is not far from the true values of the clean metals at least if the water vapour concentration of the ambient atmosphere is reduced to a minimum. Huber and Kirk (1966) investigated changes in contact potential differences of Al and they concluded that thin contaminating layers of oxygen or oxide have very little effect on the contact potential difference. Water adsorption, however, gave 1 eV increase of the contact potential difference of Al relative to Au. Similar results were obtained by Wåhlin (1973). He studied the variation of contact potential difference of metals relative to Pt by cycling the pressure from $2 \times 10^{-5}$ to 760 torr. The values of the contact potential differences reached maxima at atmospheric pressure but for pressures lower than $10^{-2}$ torr no variation could be seen. The cyclic variation of contact potential difference was probably due to the release and the adsorption of water molecules. Wåhlin (1973) also measured contact potential differences in connection with sliding electrification experiments. As a consequence of sliding the metal electrode over the Teflon surface, the electrode has been smoothly ground in a vacuum and the metal surface is assumed to be comparatively clean. He did not detect any difference between values of contact potential difference measured either before or after electrification unless charged fragments of Teflon were found to be attached to the electrode after electrification.
Such attachment could be detected by a dependence of the contact potential difference on the distance between the electrodes in the measuring equipment. It may be concluded from these results that contact potential difference is roughly unaffected by the presence of an oxide layer.

Returning to the case of NaCl, figure 6.2, it is found that the Fermi level is 0.8 eV above that of Pt since this difference is expected to be given approximately by the intersection of the line for rolling electrification with the axis corresponding to zero charge density. There will of course exist dislocation movement due to the contact pressure even in the rolling mode of electrification. Since the dislocation lines carry negative charge, this component of the charge distribution will tend to raise the levels of the undisturbed insulator relative to those of the metal. The Fermi level difference obtained, 0.8 eV, may then be overestimated, but is probably more near the true value than 1.6 eV as obtained from electrification in the sliding mode (section 5.3.2). By assuming that the dislocation line movement does not greatly interfere in the rolling mode of electrification and taking the work function of Pt ≈ 5 eV it can be concluded from figure 5.3 that the Fermi level of NaCl experimentally is found to be situated at about 1 eV above the value calculated for the ideal insulator, in which the Fermi level is found midway between valence and conduction bands.

For both Teflon (Wåhlin and Bäckström (1974)) and NaCl (section 5.3.1) charge transfer is independent of velocity, so for these materials it is unlikely that frictional heating causes electrification, by contrast with the case of pyrene (Zimmer (1970)). A secondary effect of friction, material transfer, may contribute to the charging of NaCl. Otherwise the action of friction seems to be break-up of contamination layers. Furthermore, separation by sliding instead of rolling has been argued to have the effect of enlarging the real area of contact. It may then be concluded that in broad outline electrification in the sliding and rolling modes are consistent.
The experimental series described in this chapter was initiated in order to test the theory of contact charging. For this purpose a model is presented which includes the possibility of an impressed voltage across the insulator.

7.1 The model

The insulator is placed between the electrifying metal probe to the left and a metallic substrate to the right, as shown in figure 7.1.
There is a region of thickness $d$ just outside the metal surface. It has no charge, and it may consist of a layer of the dielectric or simply a vacuum interspace. Next, to the right, is a charged layer of thickness $\lambda$, having a volume charge density $\rho$ which is constant in space. Finally, there is the main bulk of the dielectric, which is uncharged and extends to $x=t$, where a metallic substrate carrying the voltage $U_t$ with respect to the electrode is positioned. The potential drop due to the charge injected from the substrate is neglected. In the uncharged region $0 < x < d$ the potential, $U$, is

$$U = Ax \quad (7.1)$$

where $A$ is a constant. The potential is thus taken to be zero at $x = 0$.

In the region $d < x < d+\lambda$ the Poisson equation will be $d^2U/dx^2 = -\rho/\varepsilon$, where $\varepsilon$ is the dielectric constant of the insulator. Integrating twice with $P$ and $Q$ as constants we have

$$U = -\frac{\rho}{2\varepsilon} x^2 + Px + Q \quad (7.2)$$

Since the potential is continuous at $x=d$, equations (7.1) and (7.2) yield

$$Ad = -\frac{\rho}{2\varepsilon} d^2 + Pd + Q \quad (7.3)$$

By differentiating equations (7.1) and (7.2) and using the continuity of the electric displacement at $x=d$ and $x=d+\lambda$ one obtains

$$\varepsilon_d A = -\rho d + \varepsilon P \quad (7.4)$$

$$-\frac{\rho}{\varepsilon} (d + \lambda) + P = \frac{U_t + \frac{\rho}{2\varepsilon} (d + \lambda)^2 - P (d + \lambda) - Q}{t - d - \lambda} \quad (7.5)$$

where $\varepsilon_d$ is the dielectric constant in the region $0 < x < d$. Equations (7.3) and (7.4) permit $P$ and $Q$ to be written in terms of $A$:

$$P = \frac{\varepsilon_d}{\varepsilon} A + \frac{\rho}{\varepsilon} d \quad (7.6)$$

$$Q = Ad \left(1 - \frac{\varepsilon_d}{\varepsilon}\right) - \frac{\rho d^2}{2\varepsilon} \quad (7.7)$$

Equations (7.5), (7.6) and (7.7) yield

$$A = \frac{1}{\varepsilon_d \left(\frac{t-d}{\varepsilon} + \frac{d}{\varepsilon_d}\right)} \left[U_t + \frac{\rho \lambda^2}{2\varepsilon} + \frac{\rho \lambda}{\varepsilon} (t - d - \lambda)\right] \quad (7.8)$$
Furthermore the electrochemical potentials are equated at \( x = 0 \) (metal probe) and at \( x = d + \lambda \). In addition, a continuous distribution of trap levels with a constant density \( D_v (\text{m}^{-3}\text{J}^{-1}) \) is introduced. The local Fermi energy will then change, with respect to that of the uncharged insulator, by the amount \( \Delta E_{FI} \) given by

\[
\rho = -eD_v \Delta E_{FI}
\]  

(7.9)

The equality of the electrochemical potentials will then take the form

\[
\frac{\rho}{2e} \left( d + \lambda \right)^2 + P \left( d + \lambda \right) + Q = \frac{1}{e} \left( \phi_M - \phi_I \right) - \frac{\rho}{e^2 D_v}
\]  

(7.10)

where \( \phi_M \) and \( \phi_I \) are the work functions of the metal and the insulator respectively and \( e \) is the modulus of the elementary charge. Finally from equations (7.6), (7.7), (7.8) and (7.10) the resultant expression for the effective surface charge density is

\[
\sigma = \frac{\phi_M - \phi_I}{e} - U_t \left( \frac{\lambda}{e} + \frac{d}{\varepsilon d} \right) / \left( \frac{d}{\varepsilon d} + \frac{t - d}{\varepsilon} \right)
\]

(7.11)

\[\]  

\[
\left( \frac{t - d}{\varepsilon} - \frac{\lambda}{2\varepsilon} \right) \left( \frac{\lambda}{e} + \frac{d}{\varepsilon d} \right) / \left( \frac{d}{\varepsilon d} + \frac{t - d}{\varepsilon} \right) - \frac{\lambda}{2\varepsilon} + \frac{1}{e^2 \lambda D_v}
\]

This result may of course be modified to accommodate other assumptions about the trap distribution.

Expression (7.11) can now be simplified by setting the voltage \( U_t = 0 \) and neglecting the interspace \( d \). In addition, assuming \( D_v \gg 2e/e^2 \lambda^2 \), \( \sigma \) then becomes

\[
\sigma = 2e \left( \phi_M - \phi_I \right) / e\lambda
\]  

(7.12)

which is identical to an expression due to Davies (1967 a) and previously quoted in equation (2.24).

Another interesting situation arises when \( d \) remains finite and \( \lambda \to 0 \). Then the term \( \lambda D_v \) has to be interpreted as a surface charge density, \( D_s \), resulting in
\[ \sigma = \frac{eD_s (\phi_M - \phi_I)}{1 + e^2d D_s / \varepsilon_d} - \frac{U_t e^2d D_s \varepsilon / \varepsilon_d}{1 + e^2d D_s / \varepsilon_d} \]  

(7.13)

The first term becomes identical to the expression of Bauser et al. (1970) given in equation (2.32). The second term, which is proportional to the applied field, has not yet appeared in the literature. However, letting \( D_s \rightarrow 0 \) or \( D_s \gg \varepsilon_d / e^2d \), the second term becomes

\[ - \frac{U_t}{t} \times \frac{e^2d D_s \varepsilon}{\varepsilon_d} \text{ and } - \frac{U_t}{t} \times \varepsilon \text{ respectively.} \]

These expressions agree with those of Hays and Donald (1972) which are given in equations (2.35) and (2.36).

Equation (7.13) may be used to form two derivatives

\[ \frac{\partial \sigma}{\partial \phi_M} = \frac{eD_s}{1 + e^2d D_s / \varepsilon_d} \]  

(7.14)

\[ \frac{\partial \sigma}{\partial U_t} = - \left( \frac{e^2d D_s \varepsilon}{\varepsilon_d} t \right) / \left( 1 + e^2d D_s / \varepsilon_d \right) \]  

(7.15)

From the expressions (7.14) and (7.15) the parameter \( d \) may be extracted in terms of measurable quantities

\[ d = - \left( \frac{t \varepsilon_d}{\varepsilon \varepsilon} \right) \frac{\partial \sigma}{\partial U_t} / \frac{\partial \sigma}{\partial \phi_M} \]  

(7.16)

One gratifying fact is that one does not need to know the real area of contact, which is presumably less than the contour area.

7.2 Experiments and results

In order to determine \( d \) experimentally, electrification measurements were made on a polyethylene foil 0.095 mm thick, using the apparatus shown in figure 4.1. The foil was mounted on an insulated metal plate fixed to the top of the carriage which was driven at a velocity of 0.5 mm s\(^{-1}\). The metal electrodes had a radius of curvature of 1.5 mm at the tip. The purity of the metals was better than 99.95\%. The electrode was loaded by a weight of 0.05 kg. The work functions relative to Pt of the metal electrodes were derived from contact potential difference measurements as described in section 4.2. The surface charge densities were estimated on the basis of the track width measured in a workshop microscope.
The polyethylene foil (unmodified quality DFDS-6600, low-density) was produced by Unifos Kemi AB, Stenungsund, Sweden, and had a crystallinity of about 50%. The foil was prepared by a light polish with carborundum paper (grain size 600) to expose a fresh surface layer and was then dusted off by means of a clean brush. The mechanical treatment was followed by discharging with β-rays and the foil was then left in vacuum for a few hours for outgassing before electrification.

The metal substrate was connected to a voltage source to get an impressed voltage across the polyethylene foil. Ten tracks were charged with each of the metals Au and Pt for each of six different applied voltages. The measurements with Al were limited to three voltages. The results are shown in figure 7.2. The slope is about 30% higher for Al than for Au and Pt.

![Figure 7.2 Plots of surface charge density versus applied voltage.](image)

Error bars given are the standard deviations of the mean value.
A series of experiments was also made at zero voltage, and in this case a Mg electrode was included. Figure 7.3 shows the results of these measurements.

![Graph](image)

**Figure 7.3** Plot of surface charge density versus metal work function measured relative to Pt. From the left the points are referred to Mg, Al, Pt and Au respectively. Error bars shown are the standard deviations of the mean value.

It may be noted that the work function of polyethylene is found to be about 0.1 eV larger than that of Au and about 0.3 eV larger than that
of Pt. These values are in fair agreement with the results reported by Strelia (unpublished) and Davies (1967) according to which polyethylene has a 0.2 eV larger work function than Au and a 0.1 eV larger work function than Pt respectively.

7.3 Sources of error due to geometry

Before the discussion of the experimental findings it is of interest to consider in what sense the present geometry may influence the results from electrification in an electric field.

The electric field in the foil of insulating material between the metal electrode and the metal substrate is not homogeneous because of the spherical curvature of the electrode. A capacitive system consisting of a plane at a distance, \( t \), from a sphere can be replaced by two identical spheres distanced 2\( t \). The radius of the spheres is the same as that of the original sphere and in order to preserve the electrostatic situation the potential difference between them must be taken double that between the sphere and the plane. U. Thwaites (1962) has calculated the spatial variation of the electric field in the gap between two identical spheres with the quotient between sphere distance and sphere diameter as a parameter. By applying the results of Thwaites (1962) to the present case the electric field at the tip of the electrode is found to exceed the electric field in the plane case, \( U/t \), by about 3%. At the contour of the track, however, the actual electric field is about 2% lower than \( U/t \). It then seems reasonable to approximate the variable electric field in the region of contact by simply \( U/t \) throughout the region.

The thickness of the foil of insulating material and hence the magnitude of the capacitive charge may vary slightly between the beginning and the end of a track. In unfavourable cases such variation may contribute appreciably to the electrification charge measured. In order to estimate this error in the present case two identical spheres with radius, \( a \), and at a distance, 2\( t \), from each other are considered. The capacitance, \( C \), of such a system has been expressed by Cho (1964),

\[
C = 2\pi e a \sinh B \sum_{n=1}^{\infty} \frac{1}{\sinh nB} 
\]

(7.17)
where $\beta$ is given from

$$\cosh \beta = \frac{a + t}{a}$$  \hspace{1cm} (7.18)

Taking the relative permittivity of polyethylene as 2.3 and the radius of the sphere as 1.5 mm the capacitance is calculated to be $(4.5 \pm 0.1) \times 10^{-13} \text{F}$, the limits representing a 0.01 mm decrease or increase of $t$ (i.e. change of insulator thickness in the real case). The change of the capacitive charge at a potential difference of 600 V between the spheres (which corresponds to a potential difference of 300 V between the electrode and the plane) and corresponding to such a distance change was estimated to be $3 \times 10^{-12} \text{C}$. This value has to be compared to the total charge acquired in a track of length 100 mm which is about $1 \times 10^{-10} \text{C}$ in the minimum case (i.e. electrification with Au at -300 V). Hence, in most cases, the error originating from the change in capacitive charge is negligible.

7.4 Conclusions concerning the surface trap model

The distance, $d$, may now be computed from the empirically known derivatives. One should expect $d$ to be of the order of an atomic radius, and therefore it is justified to put $\varepsilon_d$ equal to the vacuum value $\varepsilon_0$. The results for $d$ are shown in the third column of table 7.1.

Table 7.1

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\frac{3\sigma}{3U_t}$ (C m$^{-2}$V$^{-1}$)</th>
<th>$d_1$ (nm)</th>
<th>$d_2$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$(\varepsilon_d=\varepsilon_0)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>$-6.0 \cdot 10^{-8}$</td>
<td>15</td>
<td>36</td>
</tr>
<tr>
<td>Pt</td>
<td>$-6.5 \cdot 10^{-8}$</td>
<td>17</td>
<td>38</td>
</tr>
<tr>
<td>Al</td>
<td>$-8.1 \cdot 10^{-8}$</td>
<td>21</td>
<td>48</td>
</tr>
</tbody>
</table>

Since these values are larger than atomic dimensions by a factor of nearly 100, it is clear that a two-dimensional surface charge, if it exists, must be far inside the bulk of the polymer. It may be argued that in this case $\varepsilon_d$ should be chosen equal to $\varepsilon$, the dielectric constant.
of the bulk insulator. The value of d then becomes even larger, however, as seen in column 4, and the final average for d is 40 nm. Thus, a contradiction exists, and it seems, therefore, that the idea of charge being deposited only on the surface has to be abandoned.

7.5 Discussion of the volume injection model

If it is accepted that the charged layer has a finite thickness, what can be learned about the electrification process by using equation (7.11). The first simplification arises by stating that $\lambda >> d$. It may also safely be assumed that $t >> \lambda$, and after these simplifications the following expression for $\sigma$ is found

$$\sigma \equiv \rho \lambda = \left( \frac{\phi_M - \phi_I}{e} - U_t \frac{\lambda}{t} \right) / \left( \frac{\lambda}{2e} + \frac{1}{e^2 \lambda D_v} \right)$$

(7.19)

In this model $\lambda$ is expressed by

$$\lambda = - \frac{t}{e} \frac{\delta \sigma}{\delta U_t} \left/ \frac{\delta \sigma}{\delta \phi_M} \right.$$  

(7.20)

When calculating $\lambda$ from equation (7.20) for the different cases the results become $\lambda$(Pt) = 38 nm, $\lambda$(Au) = 35 nm and $\lambda$(Al) = 48 nm. Thus, values of about 40 nm for polyethylene are found, whereas Davies (1967 a) has found 1800 nm by putting his charge density into equation (7.12).

In a later study by a modified method (see Davies (1970)) the penetration depths ranged from 10 to 50 nm. In the case of polyethylene the discrepancy probably means that the real contact area in the case of a plane electrode, as used by Davies (1967 a), would be only 2 percent. It seems that a spherical end surface as used in this experiment makes more efficient contact than a flat one. For Al for instance, the charge density in the present study is $-1.7 \times 10^{-8}$ C cm$^{-2}$, and Davies (1967 a) reports $-0.27 \times 10^{-8}$ C cm$^{-2}$, which is smaller by a factor of 6. Generally, one would expect sliding to provide more efficient contact than a vertical approach, since a surface element of the insulator is passed over by a much larger surface element of the metal electrode. The real areas are, however, probably smaller than those which were measured on the basis of the track contours. Information about the real area can be obtained by putting the value of the penetration depth into equation (7.19), calculating for the charge density, and then comparing to the experimental value. However, the quantity $D_v$ is unknown so the result is an inequality which
asserts that the real area is at least 16% of the contour area.

Similarly, by utilizing the fact that the theoretical charge density must be larger than the measured one it is found that $D_y$ must be larger than $3 \times 10^{22} \text{m}^{-3} \text{(eV)}^{-1}$. Equation (7.9) gives that this limit corresponds to an energy shift of the Fermi level of 0.86 eV for Al, and, consequently, it is doubtful whether the term containing $D_y$ in the expression for the charge may really be neglected. This point is best illustrated by figure 7.4, which shows how the energy of the Fermi surface is influenced by the assumption made concerning the effective area. The ratio of real to apparent area is represented on the axis of abscissa and the shift in Fermi energy on the axis of ordinates. At the left edge of the figure the metal Fermi levels relative to that of polyethylene are drawn for comparison. In most of the allowed range on the axis of abscissa the energy shift is comparatively large.
Figure 7.4 Plots of insulator Fermi energy shift versus the effective area for the metals used.
The formalism developed can also be used for the case when there is an uncharged layer of thickness \( d \) at the surface, followed by a charged layer of thickness \( \lambda \). Replacing \( \epsilon d \) by \( \epsilon \) in equation (7.11) and neglecting \( \lambda \) and \( d \) in comparison to \( t \), will give

\[
\sigma = \left( \frac{\phi_M - \phi_I}{\epsilon} - U_t \left( \frac{\lambda + d}{t} \right) \right) / \frac{\lambda}{2\epsilon} + \frac{1}{\epsilon^2 \lambda D_V} \tag{7.21}
\]

It is then seen that equation (7.20) is modified to

\[
(\lambda + d) = -\frac{t}{\epsilon} \frac{\partial \sigma}{\partial U_t} / \frac{\partial \sigma}{\partial \phi_M} \tag{7.22}
\]

Using the experimental data as before, it is found that \( d + \lambda = 40 \text{ nm} \), i.e. the total penetration depth is unchanged even if the surface has been discharged by back-conduction. Note that, as a consequence of the result \( d + \lambda = \text{constant} \), the trap density must increase.

There is no fundamental reason for assuming that the injection depth, \( \lambda \), should be independent of the metal work function \( \phi_M \). It is legitimate and quite simple to adapt the formalism to the alternative assumption that the charge density remains constant, while \( \lambda \) depends on \( \phi_M \). Solving equation (7.11) for \( \lambda \) instead of \( \rho \), with \( d = 0 \) and \( \lambda \ll t \), the following equation of second order in \( \rho \lambda \) is found

\[
(\rho \lambda)^2 + \frac{2\epsilon U_t}{t} (\rho \lambda) + 2\epsilon \rho \left( \frac{\rho}{\epsilon^2 D_V} - \frac{\phi_M - \phi_I}{\epsilon} \right) = 0 \tag{7.23}
\]

The solution of equation (7.23) becomes

\[
\sigma = \rho \lambda = -\frac{\epsilon U_t}{t} \left[ \left(\frac{\epsilon U_t}{t} \right)^2 + \frac{2\epsilon \rho (\phi_M - \phi_I)}{\epsilon^2 D_V} - \frac{2\epsilon \rho^2}{\epsilon^2 D_V} \right]^{1/2} \tag{7.24}
\]

where the minus sign stands for the case \( \phi_I > \phi_M \) and conversely.

If the applied voltage \( U_t \) is zero and \( D_V \) is very large, \( \sigma \) is simplified to become

\[
\sigma = \frac{1}{2} \left[ \frac{2\epsilon \rho (\phi_M - \phi_I)}{\epsilon} \right]^{1/2} \tag{7.25}
\]

This expression is identical to that presented by Chowdry and Westgate (1974) given in equation (2.25). The proportionality between \( \sigma \) and the square root of the work function difference, predicted by equation (7.25), is, however, far from the real situation.
Although there is no fundamental reason for assuming a constant injection depth independent of $\phi_M$, an empirical justification for this assumption may be found. By accepting as an experimental fact that the charge density is proportional to the work function difference, it is easily shown by equation (7.24) that $\lambda$ must be independent of the metal work function. Hence $\lambda$ is a constant, characteristic of the polymer.

The assumption of a volume charge density which is independent of the depth coordinate, $x$, is, however, unsatisfactory from the thermodynamical point of view, since the electrochemical potential varies with $x$. A reasonable starting point in this respect would be to have a constant chemical potential from the electrode and throughout the injection layer, $0 < x < L$. From equation (2.4) the equilibrium condition becomes,

$$E_{PI} + \Delta E_{PI} - eU = E_{FM} \quad (7.26)$$

Here $E_F$ is the local Fermi energy, and the subscripts $I$ and $M$ stand for insulator and metal, respectively. The Fermi energy shift, $\Delta E_{PI}$, arises from putting electrons into the trap levels. The relationship between the charge density, $\rho$, and the density of traps, $D_V$, which is assumed to be constant in space and energy, is still given by equation (7.9). Equations (7.9) and (7.26) lead to the following Poisson equation

$$\frac{d^2U}{dx^2} = - \frac{eD_V}{\varepsilon} (\phi_M - \phi_I) + \frac{e^2D_V}{\varepsilon} U \quad (7.27)$$

which under the appropriate boundary conditions that the electric displacement is continuous at $x = L$ and that the potential is continuous at $x = 0$ has the solution

$$U(x) = M + \frac{(U_t/\alpha t - Me^{-\alpha L}) e^{\alpha x} - (U_t/\alpha t + Me^{\alpha L}) e^{-\alpha x}}{e^{\alpha L} + e^{-\alpha L}} \quad (7.28)$$

where $\alpha = e(D_V/\varepsilon)^{1/2}$ and $M = (\phi_M - \phi_I)/e$

From equations (7.9), (7.26) and (7.28) the volume charge density, $\rho(x)$, is found to be

$$\rho(x) = \frac{e\alpha^2[(U_t/\alpha t + Me^{\alpha L}) e^{-\alpha x} - (U_t/\alpha t - Me^{-\alpha L}) e^{\alpha x}]}{2 \cosh \alpha L} \quad (7.29)$$

It may be noted that in the limit of large $\alpha L$ and vanishing $U_t$ equation...
(7.29) can be written

$$\rho(x) = e^{D_{v}M - \phi_{I}} \exp[-(\frac{e^{2D_{v}}}{\varepsilon}) \frac{1}{2} x]$$

(7.30)

An identical expression for $\rho$ may be derived from the equations due to Many et al. (1964) previously quoted as equations (2.17) - (2.20).

Integrated from 0 to L equation (7.29) yields the effective surface charge density

$$\sigma = \frac{e\alpha}{\cosh \alpha L} \left[ \frac{\phi_{M} - \phi_{I}}{e} \sinh \alpha L - U_t \times 2 \sinh^{2}(\alpha L/2)/\alpha t \right]$$

(7.31)

In this case the ratio of derivatives previously used becomes

$$\frac{\partial \sigma}{\partial U_t} / \frac{\partial \sigma}{\partial \phi_{v}} = -\frac{e}{\alpha t} \tanh(\frac{\alpha L}{2})$$

(7.32)

Unfortunately the experimentally determined ratio does not permit calculation of both $D_{v}$ and L, but equation (7.32) does yield the inequality $D_{v} < 7.7 \times 10^{22} m^{-3}(eV)^{-1}$. Furthermore, by assuming that the effective area is as large as the contour area, it is found that $L = 100$ nm and $D_{v} = 3 \times 10^{22} m^{-3}(eV)^{-1}$. Although the exact value of the depth of injection thus depends on the details of the model adopted, it is concluded that the charged layer has a finite thickness of 40-100 nm in polyethylene.
The results of chapter 7 clearly demonstrates that the injection charge varies with the applied field in the insulator. The charge is not likely to redistribute instantaneously. In principle, the injection charge should be measurable as a time dependent current by simply changing the potential difference between two metal substrates on either side of a dielectric. Such a straightforward method will, however, include a contribution from the classical charging which is several orders of magnitude larger than the injection charging. On the other hand the injection charge may be accessible by making the capacitor fully charged in the classical sense by a potential step and at a later time connecting the measuring circuit. This chapter describes measurements of delayed current in some polymeric materials and it is shown that the injection current may be extracted.

8.1 Theoretical analysis

Consider the capacitor in figure 8.1 in which a dielectric foil of thickness \( t \) and permittivity \( \varepsilon \) is situated between two metal plates.

![Figure 8.1 Model for injection charging of capacitors.](image-url)
Since the metal makes contact with the insulator there are assumed to be charged layers of thickness $\lambda$ near both metal surfaces. The volume charge densities are denoted $\rho_1(x)$ and $\rho_2(x)$ respectively. Between the charged layers the dielectric is electrically neutral. The grounded metal plate carries a surface charge density $\sigma_0$. The applied voltage $U(t)$ is a step function of time, $t$.

As the capacitor has a large area and a small plate distance the electric displacement, $D(x)$, is perpendicular to the plates and is obtained at each point by Gauss law,

$$D(x) = \begin{cases} 
  \int_0^x \rho_1(x')dx' + \sigma_0 & 0 \leq x \leq \lambda \\
  \lambda \int_0^x \rho_1(x')dx' + \sigma_0 & \lambda \leq x \leq t-\lambda \\
  \int_{t-\lambda}^x \rho_2(x')dx' + \int_0^\lambda \rho_1(x')dx' + \sigma_0 & t-\lambda \leq x \leq t
\end{cases} \quad (8.1)$$

The potential difference between the plates, $U$, may be written

$$-U = \frac{1}{\varepsilon} \int_0^t D(x)dx \quad (8.2)$$

or using expression (8.1)

$$-\varepsilon U = \sigma_0 t + \int_0^\lambda x \rho_1(x')dx' + \int_0^t \rho_1(x')dx' + \int_0^{t-\lambda} \rho_2(x')dx' \quad (8.3)$$

In the special case of constant volume charge density equation (8.3) becomes

$$-\varepsilon U = \sigma_0 t + \rho_1 \lambda t - \frac{\lambda}{2}(\rho_1 \lambda - \rho_2 \lambda) \quad (8.4)$$

By substituting for the terms $\rho_1 \lambda$ and $\rho_2 \lambda$ the equivalent surface charge densities $\sigma_1$ and $\sigma_2$, and rearranging equation (8.4) the following expression is found

$$\sigma_0 + \sigma_1 = -\frac{\varepsilon U}{t} + \frac{\lambda}{2t} (\sigma_1 - \sigma_2) \quad (8.5)$$

The left side of equation (8.5) represents the total charge, $\sigma$, on the grounded metal plate and in its vicinity. The time derivative, $\dot{\sigma}$, may
be measured as the current entering the lower metal plate. Differentiating equation (8.5) at constant $\varepsilon U/t$, results in

$$\dot{\sigma} = \frac{\lambda}{2\varepsilon t} (\dot{\sigma}_1 - \dot{\sigma}_2) \quad (8.6)$$

The charge densities $\sigma_1$ and $\sigma_2$ should be equal in the case $U=0$ if the insulator surfaces make contact to metals of the same kind and hence $\sigma$ should vanish. The time derivatives with an applied electric field, however, are of opposite sign since electrons penetrate into the insulator at one metal plate and leave the insulator at the other plate. It seems reasonable to assume that at least the total time integrals of $\dot{\sigma}_1$ and $\dot{\sigma}_2$ are equal in absolute magnitude, i.e.

$$\int_0^\infty \dot{\sigma}_1 d\tau = \frac{t}{\lambda} \int_0^\infty \dot{\sigma} d\tau \quad (8.7)$$

From this relationship the polarization by injection, $\frac{1}{2\lambda} \int_0^\infty \sigma_1 d\tau$, may be calculated in terms of observables. Thus, if $\lambda$ is known the injected charge may also be computed.

The insulators treated in this paper are non-polar materials (see Ritchie (1965)), which do not exhibit the rather slow orientational polarization. The polarization due to displacement of bound electrons is certain to be completed within a time of, say 1 ms. There is also a relatively slow process called interfacial polarization as described by for instance Birks (1960) which may interfere. This type of polarization has its origin in migration of charge carriers over short distances. The designation "interfacial" is intended to convey the idea that the charge is stored at boundaries between different phases of the material. In principle the charge redistribution in the surface layer of thickness $\lambda$ may be classified as interfacial polarization but it is of interest to separate this process from any volume polarization effect occurring.

If the permittivity is allowed to vary slightly with the time it can be written

$$\varepsilon = \varepsilon^1 + \Delta\varepsilon(\tau) \quad (8.8)$$

where $\varepsilon^1$ is the value at the beginning of the measurement and $\Delta\varepsilon(\tau)$ is the contribution to the permittivity from interfacial polarization in
the volume. Since the measuring circuit does not respond to variations in $\varepsilon$ due to other polarization types, $\varepsilon'$ can be said to be a valid approximation for the value of the dielectric constant at $\tau = 0$. Equation (8.7) is then modified,

$$\int_0^\infty \delta \sigma \, dt = - \frac{U}{t} \int_0^\infty \Delta \varepsilon (\tau) \, d\tau + \frac{\lambda}{t} \int_0^\infty \sigma_i \, d\tau$$  \hspace{1cm} (8.9)

Equation (8.9) is simplified to become,

$$\frac{1}{U} \int_0^\infty \delta \sigma \, dt = - \frac{\Delta \varepsilon (\infty)}{t} + \frac{\lambda}{t} \int_0^\infty \sigma_i \, d\tau$$  \hspace{1cm} (8.10)

The volume polarization term is seen to be of the same sign as the injection charging term, and will then tend to raise the measured value.

8.2 Experimental set-up

The principle of the experiment is to apply a voltage, $U$, from a source of low impedance for approximately 1 ms, an interval sufficiently long for classical charging to be completed. The current due to injection is then measured by means of a resistor switched into the circuit. The experimental arrangements are shown in figure 8.2.

In the alternative circuit shown in figure 8.2(b) an operational amplifier (Burr-Brown 3523) is used as a low impedance amplifier, its impedance being low enough for $U$ to be considered as constant. Unfortunately this circuit produced damped oscillations, which degraded the measurements for small signals.
Figure 8.2 Block diagrams for investigation of injection charging.  
(a) The current measured directly by an oscilloscope.  
(b) The measurement performed by a current to voltage converting operational amplifier.
8.3 Experimental tests

Tests were first made with commercial polyester capacitors in order to explore whether identical results would be obtained from the two different measuring amplifiers.

Denote the input voltage to the amplifier in figure 8.2(a) or 8.2(b) by \( U_i(\tau) \). Then

\[
\frac{dU_i(\tau)}{d\tau} = -RC \frac{dU_i(\tau)}{d\tau} + I_i(\tau) \times R
\]

(8.11)

where \( R \) is the input resistance of the amplifier and \( C \) is the external capacitance. It was found empirically that \( I_i(\tau) \) could be written in the form

\[
I_i(\tau) = I_k e^{-\tau/k} + I_r e^{-\tau/r}
\]

(8.12)

where the constant \( r \) is much larger than \( k \). If the time for connecting the measuring circuit is defined to be \( \tau = 0 \), the solution to the equation (8.11) becomes

\[
U_i(\tau) = C_k e^{-\tau/k} + C_r e^{-\tau/r} - (C_k + C_r) e^{-\tau/RC} \]

(8.13)

where

\[
C_k = I_k/C (R^{-1}C^{-1} - k^{-1}) \]

(8.14)

\[
C_r = I_r/C (R^{-1}C^{-1} - r^{-1}) \]

(8.15)

The last term of expression (8.13) becomes vanishingly small when the circuit in figure 8.2(b) is used. With the circuit in figure 8.2(a), however, it becomes comparable in magnitude to the other terms.

For comparison of the two amplifying methods measurements were carried out using both circuits with a polyester capacitor of 10 nF and five such capacitors connected in series. Current curves as obtained with the capacitor chain are shown in figure 8.3.
Figure 8.3 Photographs of the current pulse from five 10 nF polyester capacitors in series. Plate voltage was 30 V.
(a) Measured by an oscilloscope.
(b) Measured by the experimental equipment according to figure 8.2(b).

It is seen that the current curve as measured by the circuit according to figure 8.2(a) possesses a pronounced maximum. Equation (8.13) may be differentiated to give
\[
\frac{d(U_i(\tau))}{d\tau} = \frac{C_k + C_r}{RC} e^{-\tau/RC} - \frac{C_k}{k} e^{-\tau/k} - \frac{C_r}{r} e^{-\tau/r}
\]  
(8.16)

The value of the time at maximum, \(\tau_0\), makes the derivative in equation (8.16) equal zero, yielding

\[
\frac{C_k + C_r}{RC} e^{-\tau_0/RC} - \frac{C_k}{k} e^{-\tau_0/k} - \frac{C_r}{r} e^{-\tau_0/r} = 0
\]  
(8.17)

which has four unknown quantities, i.e. \(k\), \(I_k\), \(r\) and \(I_r\). The current \(I_k\) is eliminated by replacing \(\tau\) and \(U_i(\tau)\) in equation (8.13) by the coordinates of the maximum, \((\tau_0, U_i(\tau)_0)\), solving for \(C_k\), thus,

\[
C_k = \frac{(U_i)_0 + C_r(\exp(-\tau_0/RC) - \exp(-\tau_0/r))}{\exp(-\tau_0/k) - \exp(-\tau_0/rc)}
\]  
(8.18)

and then substituting expression (8.18) for \(C_k\) in equation (8.17). The tail of the current as measured by the operational amplifier yields \(I_r\) and \(r\) to be put into equation (8.17). Hence \(k\) may be obtained and equation (8.14) may be solved for \(I_k\). Finally the sum of \(I_k\) and \(I_r\) can be compared to the maximum current, \(I_{op}\), as obtained with the operational amplifier.

Table 8.1 shows the results of the fitting procedure in the testing experiment.

**Table 8.1**

<table>
<thead>
<tr>
<th>Capacitance (nF)</th>
<th>(k) (ms)</th>
<th>(r) (ms)</th>
<th>(I_k) (nA)</th>
<th>(I_r) (nA)</th>
<th>(I_k + I_r) (nA)</th>
<th>(I_{op}) (nA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.9</td>
<td>35</td>
<td>64</td>
<td>14</td>
<td>78</td>
<td>85</td>
</tr>
<tr>
<td>2 (10/5)</td>
<td>2.9</td>
<td>35</td>
<td>15</td>
<td>3</td>
<td>18</td>
<td>16</td>
</tr>
</tbody>
</table>
It is seen that the single capacitor yields five times as large values of \(I_k\) and \(I_r\) as the capacitor chain. This is a reasonable result, since the contact area between the grounded metal foil and the polymer is the same in both cases, the electrical field at the grounded plate in the case of the capacitor chain being only 1/5 of that in the 10 nF case. It may also be noted that the time constants agree in the two cases. The techniques for making these measurements thus seem to be reliable.

The procedure described above for comparing the measuring methods was found capable of being used in the analysis of current pulses in general. A flow diagram of the analysis method is shown in figure 8.4.

Figure 8.4 Flow diagram of the analysis method.
8.4 Experimental results

Layers of gold were evaporated on both sides of Teflon and polyethylene foils about 0.1 mm thick and 50 cm$^2$ in area. Measurements were performed with an applied voltage $U = 30$ V on these laboratory capacitors as well as on commercial polystyrene and polyester capacitors. Some of the commercial capacitors were demounted for area measurements.

The currents obtained according to the analysis method described in section 8.3 were extrapolated to the time of initial charging of the capacitors and then integrated. In table 8.2 the results for the different polymeric materials are presented. $\sigma_k$ and $\sigma_r$ denote the time integrated charge densities per unit voltage corresponding to the transfer processes with time constants $k$ and $r$ respectively.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$k$ (ms)</th>
<th>$r$ (ms)</th>
<th>$\sigma_k$ (C m$^{-2}$ V$^{-1}$)</th>
<th>$\sigma_r$ (C m$^{-2}$ V$^{-1}$)</th>
<th>$\sigma_k + \sigma_r$ (C m$^{-2}$ V$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>3.0</td>
<td>29</td>
<td>$1.4 \times 10^{-10}$</td>
<td>$3.0 \times 10^{-10}$</td>
<td>$4.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>Teflon</td>
<td>1.3</td>
<td>10</td>
<td>$6.9 \times 10^{-11}$</td>
<td>$5.0 \times 10^{-11}$</td>
<td>$1.2 \times 10^{-10}$</td>
</tr>
<tr>
<td>Polyester</td>
<td>2.9</td>
<td>35</td>
<td>$16 \times 10^{-10}$</td>
<td>$27 \times 10^{-10}$</td>
<td>$43 \times 10^{-10}$</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>1.5</td>
<td>51</td>
<td>$4.8 \times 10^{-11}$</td>
<td>$27 \times 10^{-11}$</td>
<td>$3.2 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Capacitors were also made from metal plates and a foil of polyethylene or Teflon. The foil was stretched over a support ring to prevent motion of the dielectric with respect to the metal plates. In order to provide a controlled air gap, inserts of brass, 0.025 mm thick, were positioned between the foil and the plates. The total area of the inserts was only 1% of the plate area. The electric field in the dielectric was held at approximately the same value as in the experiments with the evaporated foil. Unfortunately, the observed signals were obscured by interference and therefore no quantitative analysis of the time dependence could be made. It was possible, however, to measure the initial current, and for both kinds of polymers this was found to agree with the value $I_r$, corresponding to the larger time constant. This strongly indicates that the short time constant, $k$, is absent in cases in which contact is lacking between metal and dielectric.
8.5 Discussion

The time constants for Teflon given in table 8.2 indicate that the charging process is completed in a few hundredth of a second, which is in accordance with the findings of Wåhlin and Bäckström (1974). The results of the investigation of the combined air-dielectric capacitor clearly show that for Teflon and polyethylene there is a contribution besides the volume polarization effect. This has to be a true injection charge, since it requires intimate contact between the metal and the dielectric. There are also indications that the term with the shorter time constant should be assigned to this injection charge.

Owing to lack of knowledge of the variation of the electrification charge with an applied electric field nothing can be said as to whether the charge obtained for Teflon is reasonable or not. The result for polyethylene, however, may be further discussed in this sense.

By considering only the injection charge contribution, equation (8.10) may be written

\[ \int_0^\infty \dot{\sigma} \, d\tau = \frac{\lambda}{\varepsilon_0} \int_0^\infty \dot{\sigma}_1 \, d\tau \]  

(8.19)

The surface charge densities in equation (8.19) as well as in table 8.2 are expressed per unit voltage. This is experimentally justified, since the currents measured were found to be linearly dependent on the applied voltage in the range 0 to 30 V.

By replacing \( \int_0^\infty \dot{\sigma} \, d\tau \) in equation (8.19) by the value for \( \sigma_k \) in table 8.2 and choosing \( \dot{\sigma}_1 \) the mean value, 40 nm, as obtained from the model expressed by equation (7.19) for the penetration depth, the value for \( \int_0^\infty \dot{\sigma}_1 \, d\tau \) is calculated to be \( 3.3 \times 10^{-7} \text{ C m}^{-2} \text{ V}^{-1} \), where the evaporated layer of Au is assumed to contact the full area. Since the injection charge measurements and the electrification measurements as described in chapter 7 were performed on polyethylene foils of the same quality and thickness, the results from these measurements are accessible for comparison. From table 7.1 it is found that the absolute magnitude of the electrification charge density per unit potential difference across the polyethylene foil is \( \geq 6.9 \times 10^{-8} \text{ C m}^{-2} \text{ V}^{-1} \) (mean value for the three metals used). This inequality has its origin in the estimation of the contact area on the basis of the contour area, which
is probably much larger than the real area of contact. Note that this value \((\geq 6.9 \times 10^{-8} \text{ C m}^{-2} \text{ V}^{-1})\) is consistent with the value of the field dependent surface charge density \((3.3 \times 10^{-7} \text{ C m}^{-2} \text{ V}^{-1})\) calculated above from the injection charge measurements. From the crude model with constant charge density (section 7.1) the ratio between real area and contour area \((\equiv \text{the fractional area})\) is \(\geq 0.16\). The present results make it possible to estimate the fractional area on another basis by simply taking the ratio between the limiting value of the surface charge density from the electrification experiments, \(6.9 \times 10^{-8} \text{ C m}^{-2} \text{ V}^{-1}\), and the value, \(3.3 \times 10^{-7} \text{ C m}^{-2} \text{ V}^{-1}\), resulting from the measurements on evaporated capacitors. The resultant value of this ratio is found to be 0.21, which is greater than the lower limit of 0.16 obtained from the constant charge density model. It is therefore concluded that the charge obtained for polyethylene is reasonable.

Concerning the dielectric materials in the commercial capacitors only qualitative conclusions can be drawn, since no experiments has been performed in order to separate the charge injection contribution from the volume contribution to the polarization. Table 8.2 shows that the equivalent surface charge density per unit voltage transferred into polyester is 10 times greater than that transferred into polystyrene. If the surface charge densities had been expressed per unit electric field, the ratio would have been a factor of two less, since the thickness of the polyester foil was found to be half that of the polystyrene foil. Such relative charge densities in polyester and polystyrene are consistent with the fact that polyester capacitors have a larger dissipation factor than polystyrene capacitors. It may also be noted that according to a capacitor manufacturer (Rifa AB, Kalmar, Sweden) polystyrene capacitors are always wound with metal foils, since evaporation of metal layers creates a considerable increase of the dissipation factor. It is plausible that the effect of evaporation is mainly an increase of the area of intimate contact between metal and dielectric indicating that there is charge injection into polystyrene as well as into Teflon and polyethylene.

The results presented in this chapter are consistent with those obtained in chapter 7 and they support the idea of charge penetrating into a surface layer. The kinetics of the transfer mechanism, however, remain unclear.
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Appendix. Charge Decay Due to Exposure to UV-Light

Generally it can be shown that electrification charge remains on an insulator surface for a long time owing to the insulating properties. For instance surface charge on Teflon electrified by a gold electrode has been observed to decay less than 1% in 24 hours when stored in a vacuum better than $10^{-5}$ torr. It is clear that the local trapping sites suggested earlier bind the excess electrons strongly. The interpretation of the results from the electrification experiments described in chapters 5 - 7 are based on the assumption that the trapping levels are distributed continuously in energy and hence that the topmost filled level at equilibrium is related to the work function of the contacting metal by the assumed density of trapping sites (see equation (7.19)). It would be of great value to make an independent measurement of the energy of this topmost filled level. In theory this is possible by supplying the electrified surface with quanta of known energy. If this energy is sufficient for excitation of electrons from the trapping levels to the insulator conduction band, or alternatively the lowest permitted level above the vacuum level, the trapped electrons may escape which will be seen as a charge decay. The lower limit of energy required to obtain charge decay would then measure the relative energy of the topmost filled level. The amount of energy would be expected to be in the range 4 - 6 eV, depending on the work function of the electrifying metal used. This energy range is found as the photon energy in UV-light.

This appendix tells about attempts to investigate insulators by releasing electrification charge by means of UV-light. The experiments were found to be unexpectedly troublesome and time-consuming, much more than can be understood from this brief report. Unfortunately, all ways tried led to a blind alley and consequently the project is at an inconclusive stage. Although it is reasonable to suppose that attempts have been made to tackle electrification problems from this starting-point, the author is not aware of any published study in this subject. Hence the following may be taken as the status of the UV-exposing technique to create a charge decay for investigation of electrification properties of insulators.

The experimental equipment described in section 4.1.1 and figure 4.1 was modified by mounting a suprasil quartz window from above on the aluminum tank (P) so as to make it possible to expose the insulator slab on the
carriage (B) by light from a UV-source outside the tank. An additional window of CaF$_2$ was mounted on the side of the tank. Hence the insulator surface could be illuminated obliquely from above as well. To the latter window a vacuum photo tube with a spectral response for wave lengths in the range 200 nm - 550 nm (Phillips UV 150) could be fixed. By use of the reflected light from inside walls of the tank the stability with time of the light source could be checked. The charge of the track was measured by means of the oscillating probe described in section 4.3.

Since this technique is based on the release of excess electrons it is applicable only to insulators with negative charge deposited i.e. to insulators which possess a larger work function than that of the electrifying metal. At the time of this investigation Teflon alone among the insulators with this property had been thoroughly investigated in our laboratory (see Wåhlin (1973)) and hence the effort was concentrated on Teflon.

The first choice of UV-source was a high pressure Xenon lamp (Osram XBO 450) with continuous spectrum from the vacuum limit (200 nm) to the IR-region. By exposing charged tracks to the integral spectrum from the source a decay of charge was observed. In order to eliminate the influence from ions in air, the investigation was after some preliminary experiments performed in a vacuum better than 10$^{-5}$ torr. After pump-down the Penning gauge was switched off since it was noticed that ions from the Penning gauge head could interfere with the charge decay.

The role of neutralization by ions was at this early phase of the project extensively investigated. The decay due to illumination of charged tracks on polyethylene and on Teflon were compared and it was found that the half-life of the electrification charge on Teflon was about twenty times longer than that of the charge on polyethylene. This would not have been the case if neutralization alone had caused the charge decay. Furthermore the vacuum chamber was flushed with the noble gas Argon which has ionization energy of about 14 eV. The charge decay was studied as a function of pressure. The same charge decay rate was observed in an Argon atmosphere in the range 10$^{-6}$ - 10$^{-4}$ torr as at a normal pump-down to 10$^{-5}$ torr. It then was concluded that the charge decay obtained was due to some excitation processes.
In order to determine the threshold for photo excitation the light from the Xenon UV-source was monochromatized by a Jarrel-Ash Monochromator. Unfortunately, the bringing in of the monochromator lowered the intensity of the light striking upon the charged track to such an extent that no charge decay was observed even with hours of illumination. It was then tried to cut the integral spectrum by glass filters. While exposure with the integral spectrum resulted in a 50% charge decay a filter with about 1% transmission at wave length 200 nm (corresponding to a photon energy of 6.2 eV) and about 20% transmission at wave length 240 nm (5.2 eV) reduced the charge decay to about 2%. It is then concluded that the magnitude of energy needed to excite electrification charge is above 5 eV.

Since the Xenon light source combined with the monochromator was shown to be of insufficient intensity another kind of light source had to be tried. A resonance line of a discrete spectrum has a well-defined wave length. However, resonance lines with energies larger than 5 eV are not common. The Hg-spectrum has a line in the vacuum UV (at wave length 185 nm corresponding to a photon energy of 6.7 eV). A mercury lamp (Phillips OZ 4W) was mounted instead of the quartz window on the top of the tank. The 185 nm line was transmitted through the bulb directly into the vacuum of the tank and on the charged tracks. In order to be able to examine a larger part of the charged tracks the carriage (B) in figure 4.1 was moved forward and back several times under the light source during exposure. This made it possible to integrate the charge as measured by the oscillating probe over a part of the track which was illuminated with homogenous intensity. In order to get reproducible results for the charge decay with flux it was found necessary to omit the usual preparatory exposure of the Teflon surface to a β-source. It was found that washing in distilled water eliminated the spurious charge due to the mechanical preparation besides giving proper reproducability. Five measurements were made on tracks electrified by Au and Mg respectively. Figure A.1 shows the remaining charge relative to the charge deposited against the flux (in arbitrary unit).
It is seen that the decay of the tracks electrified by Mg has a slightly steeper slope than that of those electrified by Au. The same qualitative result was obtained in exposure experiments using a Zn-lamp (Phillips) provided with an interference filter with peak transmission at 214 nm (corresponding to a photon energy of 5.7 eV) as shown in figure A.2.
Figure A.2 The relative rest charge against exposure by the 214 nm line of the Zn-spectrum.

The interpretation of these results is not yet understood since there is confusion about the mechanism of charge decay. Can two-step processes be neglected? In what way does the probability of the processes depend on the initial state and the final state of the electrons? Are the electrons escaping by a kind of photo effect and/or are they transported away in the conduction band? There are experimental indications that excitation above the vacuum level of Teflon is important. For instance by exposing a track in atmospheric pressure the charge decay was observed to be about 25 times slower than if the experiment was performed in vacuum, indicating that a space charge is built up in the atmosphere preventing the charge decay. Exposure with an applied magnetic field, which affects the escape of photo electrons, has also been studied. It was found that the effect of the field was to decrease the decay rate.

Perhaps the question marks concerning these phenomena can be straightened by using an intense light source with continuously varying wave length which now is commercially available.