COLLECTIVE RESPONSE OF ELECTRONS AND SURFACE PROPERTIES OF METALS

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by

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PREFACE

Excluding Chapter 1, which deals with the elementary concepts involved in this thesis, most of the material presented here is my original contribution to the subject. While doing the calculations and writing the thesis, I have closely interacted with my supervisor, Dr J. Mahanty, who has encouraged me to work on the problems discussed here. The reference to other workers is given wherever it is necessary.

Rakesh Mehrotra
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ABSTRACT

The application of Bloch's hydrodynamic formalism to the electronic properties of a metal surface has been of considerable interest in recent years. This thesis embodies the results of a study of some of the bulk and surface properties of metals using the same formalism.

The basic hydrodynamic equations for an electron gas are obtained from the action principle. As an illustration of the use of these equations the dielectric response function and the bulk plasmon dispersion for a homogeneous electron gas are calculated. The limitations of the model are mentioned.

The charge response of a metal surface to an external oscillating charge source is calculated. It is used to find the effective polarizability of an ad-atom, and also the effect of mediation of the metal surface on the interaction between ad-ions. The screening action of the electron gas near the surface is studied.

The free electron contribution to the work function of metals is estimated. It is shown to be inversely proportional to $\sqrt{F_0}$. The numerical values obtained for various metals show reasonable agreement with experimental results, as also with previous theoretical calculations based on the density-functional approach, despite the simplicity of the model adopted here.

The phenomenon of physisorption on metal surfaces is briefly discussed, and van der Waals interaction of an atom with a metal surface is calculated for planar as well as spherical
geometries of the surface. The results are obtained from the charge response of the metal surface mentioned earlier. The dispersion formulae for plasma oscillations follow as a direct consequence of the analysis. The cases for a metallic sphere and a metal having a spherical void are described separately.

The above analysis is extended for a bimetallic junction, and the dynamic response of electrons to an oscillating charge source near the junction is calculated. The analytical expressions for the induced potentials are given for planar as well as spherical junctions, and are employed to evaluate the van der Waals interaction of a molecule with the interface. The dispersion formulae for interface plasma oscillations are discussed for both planar and spherical geometries.

The calculations referred to earlier deal with a sharp interface. The effect of diffuseness of a planar bimetallic interface is also studied using a simple iterative method, which is applicable when the electron densities of the two constituent metals differ only slightly. It is shown that the dispersion force field on an atomic system at a very small separation from the interface is divergence-free if the electron density profile is diffuse. The same analysis is also carried out for a sharp spherical interface.
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CHAPTER 1
HYDRODYNAMIC MODEL OF COLLECTIVE RESPONSE

1.1 Introductory Remarks

The hydrodynamic theory of the collective response of an electron gas was advanced some forty years ago by Bloch (1933, 1934) in connection with atomic problems. The formalism has also been proved useful in nuclear and solid state physics. Bloch (1933) has employed his theory, with considerable success, to the problem of slowing down of fast moving ions in a scattering medium. Ball et al (1973) have solved Bloch's hydrodynamic equations for the charge oscillations of a neutral Thomas-Fermi atom and used the solutions to calculate the atomic photoabsorption cross-section successfully. More recently, Monaghan (1973) has considered the collective oscillations in many electron atoms using Bloch's (1933) model. He has calculated the classical oscillator strengths and the polarizability for both ions and atoms. The formalism has also been applied to study the slowing down of fast charged particles by their interaction with many electron atoms (Monaghan 1974). The compressible oscillations of heavy nuclei have been studied using the statistical model and the hydrodynamic approximation (Ishidzu and Kawarada 1964).

Because of the development of more detailed microscopic theories (Pines and Bohm 1952), the hydrodynamic model did not attract much attention in solid state physics until about the last decade. However, growing interest in inhomogeneous and finite metallic systems, such as metal surfaces (Lang 1973, Brown and March 1976), have generated renewed interest in the
hydrodynamic model of the electron gas in a solid (Heinrichs 1973 a,b,c,d, 1975 a,b; Boardman et al 1975, Eguiluz and Quinn 1976), as microscopic theories prove to be extremely complicated in such situations (Feibelman et al 1972). A drawback of the hydrodynamic formulation is that it is semi-classical and it over-simplifies the excitation spectrum neglecting many details. Recently, Mukhopadhyay and Lundqvist (1975) have formulated the problem of the electron density response in inhomogeneous systems using linear response theory in such a way that the terms which depend on the detailed nature of the excitation spectrum of the electrons appear separately from the classical hydrodynamic terms. This separation makes it easier to see the relative contribution of the classical density oscillations and the single-particle excitation spectrum in a given problem. A general theoretical framework has also been developed by March and Tosi (1972) which yields results similar to those of the hydrodynamic model in the long wavelength and low frequency limit.

Given the difficulty of applying many-body techniques to highly inhomogeneous systems, the hydrodynamic approach offers a workable approximate alternative treatment. Owing to its directness and simplicity, Bloch's theory is very appealing in dealing with homogeneous as well as inhomogeneous systems. This is the main motivation for several recent papers using the hydrodynamic formulation of the electron gas (Eguiluz and Quinn 1976, Mahanty and Paranjape 1977). Some of the merits of the hydrodynamic model are:
(i) It accounts for the current experimental results on the surface plasmon dispersion as is discussed in Chapter 4.

(ii) It yields good results for the interactions involving metal surfaces, which can be easily visualised physically. Its importance in the calculation of the response of metal surfaces to perturbing charge distribution is discussed in Chapter 2. Its application to calculate the free electron contribution to the work function of metals is described in Chapter 3 (Mehrotra and Mahanty 1978b). Its relevance to bimetallic junctions is studied in Chapters 5 and 6 (Mehrotra and Mahanty 1978c, a).

(iii) It can be used under more complex situations, such as in the presence of an external magnetic field. Nakamura and Paranjape (1975) have used it to calculate the dispersion relation for surface plasmons in an external magnetic field parallel to the surface, when the wave propagates perpendicular to the magnetic field.

The theoretical problems concerned with metal surfaces become especially intricate when one allows for spatial dispersion in the dielectric response function of the electron gas (Zaremba and Kohn 1976). This property of spatial dispersion can easily be accommodated within the framework of the hydrodynamic model by the introduction of a finite particle pressure (Boardman et al 1976). The effect of spatial dispersion on the van der Waals interaction between two metal surfaces is to remove the divergence, as obtained by Lifshitz (1956) in the local approximation, when their separation goes to zero (Heinrichs 1975a). Its consequence on the plasmon contribution to the surface energy of metals is discussed by Heinrichs (1973b).
The specific effects of spatial dispersion on some surface phenomena are studied in the present thesis by assuming that the metal surface forms an infinite-barrier, from which the electrons are reflected speculally. The advantages and the shortcomings of the infinite-barrier model are discussed in Sections 5.1 and 6.1.

The present Chapter is constructed as follows. Section 1.2 defines the hydrodynamic model and sets up its basic equations of motion. Section 1.3 deals with the simple applications of the model to a homogeneous electron gas. The limitations of the model are discussed in Section 1.4.

1.2 Equations of Motion

The basic hydrodynamic equations for an electron gas can be derived by following Bloch's (1933) pioneering approach. The electron gas is regarded as a fluid which is characterized by a space-time dependent density \( n(r,t) \) and a drift velocity \( \mathbf{v}(r,t) \). The motion of the fluid is assumed to be irrotational so that \( \mathbf{v} = -\nabla \psi \), \( \psi \) being the velocity potential. The electrons are supposed to move in a smeared out positive background so as to ensure charge neutrality of the system. In order to describe the dynamics of the electron gas in a systematic way, the interaction between the particles is included on the basis of the Thomas-Fermi model (March 1957). In the Thomas-Fermi theory, the interaction between the particles is taken care of by the field to which they give rise (Lindhard 1954). By making an adiabatic generalization of the Thomas-Fermi model and using hydrodynamic concepts, the equations of motion for the electron gas can be derived.
Ying (1974) has proposed an extension of the original Bloch's (1933) model, starting with the Hohenberg-Kohn (1964) density-functional approach. In this approach, the ground-state energy of an inhomogeneous electron gas can be written as a unique functional of the density. The idea has been proved very useful in dealing with the static properties of an inhomogeneous electron gas (Lang 1973). By doing a quasi-static generalization of the ground-state density-functional in the hydrodynamic approximation, the total energy, $H$, of the electron gas can be expressed as:

$$H = \frac{m}{2} \int n(r,t) v^2 d^3r - e \int \frac{n_+(r)n(r',t)}{|r-r'|} d^3rd^3r' +$$

$$\frac{e^2}{2} \int \frac{n(r,t)n(r',t)}{|r-r'|} d^3rd^3r' + G[n(r,t)]$$ (1.1)

where $-e$ and $m$ are, respectively, the charge and mass of the electron and $n_+(r)$ is the charge density of the positive background. $G[n(r,t)]$ is the universal energy functional which includes the kinetic, exchange, and correlation energies of the inhomogeneous electron system. The use of the full energy functional provides, in principle, a better treatment of the pressure due to the electron gas (Mukhopadhyay and Lundqvist 1975). The first term in equation (1.1) represents the macroscopic kinetic energy which should not be confused with the internal kinetic energy included in $G[n]$.

The equations of motion for the density fluctuations in the electron gas can be obtained from the action principle, starting with the Lagrangian
\[ L = m \int n \frac{\partial \psi}{\partial t} d^3r - H \tag{1.2} \]

and treating \( n \) and \( m \psi \) as the generalized coordinates (Goldstein 1964). The Lagrange equation for the variable \( n \) gives

\[ mn \frac{dv}{dt} = -en \mathbf{E} - n \nabla \left( \frac{\delta G}{\delta n} \right) \tag{1.3} \]

where \( \mathbf{E} \) is the electric field which is given by Poisson's equation

\[ \nabla \cdot \mathbf{E} = 4\pi (n_+ - en) \tag{1.4} \]

Equation (1.3) is known as the Euler's equation. Here the quantity \( n \nabla \left( \frac{\delta G}{\delta n} \right) \) takes the role of the gradient of the pressure for a classical fluid and provides a constitutive relation between the pressure due to the electron gas and the density fluctuations. This relation is of central importance in the hydrodynamic model and is normally treated in a phenomenological manner (Bennett 1970). The Lagrange equation for the variable \( m \psi \) yields the equation of continuity

\[ \frac{\partial n}{\partial t} + \nabla \cdot (nv) = 0 \tag{1.5} \]

Equations (1.3) - (1.5) form the basis of the hydrodynamic model. These equations can easily be linearized for small deviations from the equilibrium state. The linearized hydrodynamic equations are:
\[ mn_0 \frac{\partial v}{\partial t} = en_0 v \phi - n_0 v (P(n_0) n_1) \]

\[ \nabla^2 \phi = 4\pi en_1 \]  \hspace{1cm} (1.6)

\[ \frac{\partial n_1}{\partial t} + \nabla \cdot (n_0 v) = 0 \]

where \( n_1 \) is the departure from the equilibrium electron density \( n_0 \), \( \phi \) is the potential arising out of the density deviation \( n_1 \), and the drift velocity \( v \) is taken to be of the first-order. The system carries no current in the equilibrium.

If the density functional \( G[n] \), introduced in equation (1.1), contains only the kinetic and exchange energies of the electron gas, then the particular form of \( P(n_0) \) used in the first of equations (1.6) is given by (Jensen 1937):

\[ P(n_0) = \frac{10}{9} x_k n_0^{-1/3} - \frac{4}{9} x_A n_0^{-2/3} \]  \hspace{1cm} (1.7)

where

\[ x_k = \left( \frac{3h^2}{10m} \right) (3\pi^2)^{2/3} \]

\[ x_A = \left( \frac{3e^2}{4} \right) (\frac{3}{\pi})^{1/3} \]  \hspace{1cm} (1.8)

An alternative way to obtain the linearized Bloch's equations (1.6) is to work with the Lagrangian

\[ L = m \int n_1 \frac{\partial \psi}{\partial t} \, d^3x - (H-H_0) \]  \hspace{1cm} (1.9)

where \( H_0 \) is the equilibrium energy functional of the electron gas. By treating \( n_1 \) and \( m \psi \) as the generalized coordinates, the linearized Euler's equation and the equation of continuity may be obtained. The linearized equations (1.6) can be used to study self-oscillations of the electron gas around the equilibrium density \( n_0 \).
The time-dependent response of the electron gas to a weak charge source of strength $q$ and frequency $\omega$, located at a point $r_0$, can be studied by modifying equations (1.6) as:

$$(-i\omega)\mathbf{m}_{\mathbf{n}} = e_0 \nabla \psi - n_0 \nabla (P(n_0)n_1)$$

$$\nabla^2 \psi = 4\pi e n_1 - 4\pi q \delta (\mathbf{r} - \mathbf{r}_0) \quad (1.10)$$

$$(-i\omega)n_1 + \nabla (n_0 \nabla) = 0$$

where the explicit time-dependence of the form $\exp(-i\omega t)$ is omitted from all oscillating quantities. Equation (1.10) can also be generalized to find the response of the electron gas to a prescribed density of perturbing charge. If the system is homogeneous, then in the linear response theory followed here, a Fourier decomposition of the perturbing charge density can be made, and the response to each Fourier component can be calculated separately. In the presence of boundaries the solutions of coupled equations (1.10) are to be determined by using appropriate boundary conditions.

For simplicity and in order to understand the physical concepts involved, it may be assumed that the pressure term $n_0 \nabla (P(n_0)n_1)$, in the first of equations (1.6) or (1.10) has the form:

$$n_0 \nabla (P(n_0)n_1) = m^2 \nabla n_1 \quad (1.11)$$

where $m^2$ is a constant. A similar ansatz has also been made by Eguiluz et al (1975). Equation (1.11) is justified for a homogeneous electron gas or for a metal with an abrupt change of
the electron density at the surface, and will be used here only in these cases.

In the original Bloch's (1933) theory, which starts with the Thomas-Fermi model, the second term in the expression for $P(n_0)$, given in equation (1.7), is dropped, and thus, using equation (1.11), for a homogeneous system $\beta^2 = (1/3) v_F^2$, $v_F$ being the Fermi velocity. However, it will be shown in Section 1.3.2 that this value of $\beta^2$ does not lead to the RPA result for the bulk plasmon dispersion to the order $k^2$, $k$ being the wave vector, and hence needs to be modified appropriately at high frequencies. This is a trouble with the Bloch's theory which is correct in order of magnitude, but gets $\beta^2$ wrong by about a factor of 2, when applied to calculate the plasmon dispersion in a homogeneous electron gas (March 1974).

1.3 Homogeneous Electron Gas

The idea of a gas of free electrons embedded in a uniform positive background has been found useful to account for many properties of metals which are characteristics of valence electrons. The picture may be refined by introducing the periodic potential due to the lattice, but this will not be considered here. In this Section we illustrate the application of basic hydrodynamic equations (1.10) and (1.11) to calculate the dielectric response function and bulk plasmon dispersion for a homogeneous electron gas. The former describes the screening action of the electron gas and is useful in an elementary theory of metals (Kittel 1967, Harrison 1970), whereas the latter is of both experimental and theoretical interest (Pines 1963, Raether 1965). It will be seen that a vanishing of the dielectric
response function leads directly to the bulk plasmon dispersion.

1.3.1 Dielectric Response Function

We consider the time-dependent response of a homogeneous electron gas to a weak external charge source of strength \( q \) and frequency \( \omega \), located at a point \( r_0 \). This is a typical case of a perturbing field in a metal due to a charge impurity. Although the impurity represents a static source, here, for generality, it will be regarded as an oscillating charge. The effect of the impurity on the electron gas can be easily studied by using the hydrodynamic equations (1.10). For a homogeneous electron gas, equations (1.10) and (1.11) can be combined to give

\[
(\nabla^2 - \lambda^2) n_1 = -\frac{q}{\epsilon} \left(\frac{\omega p^2}{p} \right)^2 \delta(r-r_0)
\]

where

\[
\lambda^2 = (\omega_p^2 - \omega^2) / \beta^2 ; \quad \omega_p^2 = 4\pi n_0 e^2 / m .
\]

Using the Fourier transform of the perturbing charge density, the solution of equation (1.12) for \( n_1 \) can be found. On substituting this in the second of equations (1.10), the potential, \( \phi \), due to the charge source can be expressed as

\[
\phi = \frac{q \omega_p^2}{\omega^2 - \omega_p^2} \frac{1}{|r-r_0|} + \frac{q \omega_p^2}{\omega^2 - \omega_p^2} \frac{\exp(-\lambda |r-r_0|)}{|r-r_0|} .
\]

Equation (1.14) describes the screening of an oscillating point charge by the electron gas. In the static limit of \( \omega=0 \), the first term in equation (1.14) drops out, whereas the second falls off exponentially with distance with a screening radius
\[ \lambda_0^{-1} = \beta/\omega_p, \] obtainable from the value of \( \lambda \), given in equation (1.13), by setting \( \omega=0 \). This is the usual Thomas-Fermi screening length (Ziman 1965) provided the value of \( \beta^2 = (1/3)v_F^2 \), given in Section 1.2, is used.

We have seen that the effective potential due to an oscillating charge source in a homogeneous electron gas is modified because of the screening action of the electron gas. If \( \phi_{\text{ext}}(k,\omega) \) is the Fourier transform of the applied potential, then the effective potential \( \phi(r,t) \) can be written as

\[
\phi(r,t) = \left( \frac{1}{2\pi} \right)^4 \int \frac{\phi_{\text{ext}}(k,\omega)}{\varepsilon(k,\omega)} \exp(i(k \cdot r - \omega t)) d^3k d\omega \tag{1.15}
\]

where \( \varepsilon(k,\omega) \) is a function of the wave vector \( k \) and frequency \( \omega \), and is known as the dielectric response function of the system. By taking the applied potential to be due to a point charge and considering only a single frequency \( \omega \), it can be shown that

\[
\varepsilon(k,\omega) = 1 - \frac{\omega^2}{\omega^2 - \beta^2 k^2} \tag{1.16}
\]

which is the well-known result (Heinrichs 1975a). There is no loss of generality in deriving equation (1.16) by taking the perturbing potential to be due to a point charge as the above analysis is linear, and is carried out in terms of the Fourier components. The large value of \( \varepsilon(k,\omega) \) for \( \omega=0 \) indicates that a low frequency charge distribution is strongly screened. For \( \omega=0 \), equation (1.16) reduces to the Thomas-Fermi result for the dielectric function (Ziman 1965). It is clear from equation (1.16) that the quantity \( \beta^2 \), which arises because of the finite
pressure gradient, leads to spatial dispersion in the dielectric response function $\varepsilon(k,\omega)$. An improvement over the hydrodynamic form of $\varepsilon(k,\omega)$ has been carried out by Lindhard (1954). Recently Taylor (1978) has suggested a simple, useful analytical form of the static dielectric function.

1.3.2 Bulk Plasma Oscillations

The interacting electron gas in metals is capable of collective oscillations which resemble classical plasma (Pines 1963). A typical difference is that in metals rather high densities and low temperatures are involved, and hence quantum statistics for the electrons is to be employed. The restoring force in the plasma oscillations is governed by the force field of many other particles. In the random phase approximation (RPA), which includes microscopic details, the dispersion relation for plasma oscillations in metals, to the order $k^2$, is given by (Pines and Bohm 1952, Pines 1963)

$$\omega^2 = \omega_p^2 + \frac{3}{5}v_F^2k^2 \quad (1.17)$$

where $\omega_p$ is the bulk plasma frequency, defined in equation (1.13).

Bloch's hydrodynamic theory of the electron gas provides a considerably simplified picture to study this phenomenon. By taking all oscillating quantities as $\exp(-i\omega t)$ in equations (1.6), using equation (1.11), and assuming a plane wave type of solution for the density fluctuation $n_1$, the following result for the bulk plasmon dispersion can be obtained
\[ \omega^2 = \omega_p^2 + \beta^2 k^2. \] (1.18)

To the order \( k^2 \), the dispersion formula, given in equation (1.18), is qualitatively the same as equation (1.17). However, for \( \beta^2 = (1/3) v_F^2 \), given in Section 1.2, Bloch's theory brings an error of roughly a factor of two in the coefficient of \( k^2 \). The difficulty may be avoided by parametrizing the quantity \( \beta^2 \) as

\[
\begin{align*}
\beta^2 &= (1/3) v_F^2 & \text{low frequencies} \\
&= (3/5) v_F^2 & \text{high frequencies}. 
\end{align*}
\] (1.19)

The low frequency value of \( \beta^2 \) leads to the Thomas-Fermi result for the dielectric response function, as is found in Section 1.3.1, while the high frequency value gives the RPA result for the bulk plasmon dispersion to the order \( k^2 \). The parametrization, given in equation (1.19), is well known (Heinrichs 1975a).

The definition of \( \epsilon(k, \omega) \), given in equation (1.15), shows that the zeros of \( \epsilon(k, \omega) \) correspond to the self-sustaining collective oscillations in the system. Using equation (1.16), it can be seen that the vanishing of \( \epsilon(k, \omega) \) leads to equation (1.18) for the bulk plasmon dispersion.

A review article by Raether (1965) gives an account of experimental determination of the bulk plasmon dispersion by energy loss measurements using fast electrons. Recently Krane (1978) has measured dispersion of the bulk plasmons for aluminium and indium. The experimental results are in agreement with equation (1.17). The propagation of plasmons in periodic lattices has been described by March and Tosi (1972).
1.4 Limitations of the Model

The hydrodynamic approach, although gives many useful and instructive results concerning the collective properties of an electron gas, represents an abstraction. The major limitations of the model arise due to the following reasons:

(i) It leads to an uncertainty in the value of $\beta$ which arises due to the parametrization given in equation (1.19).

(ii) It considers only long-wave collective oscillations of the electron gas and neglects particle-hole excitations (Mukhopadhyay and Lundqvist 1975). This limitation is, however, not always very serious. For instance, it has been found that the collective excitations dominate the van der Waals interaction energy between two coupled metal films, and that the single-particle excitations give rise to a relatively small correction (Harris and Griffin 1975).

(iii) A cut-off wave vector for the collective oscillations is to be introduced in a somewhat arbitrary manner, as is discussed in Section 3.4. The cut-off may occur at a point where the plasmons become degenerate with the single-particle excitations (Heinrichs 1973b). This effectively means that beyond the cut-off wave vector the plasmons are unstable against decay into the particle-hole pairs. More realistic treatments include the full excitation spectrum (Harris and Griffin 1975).

(iv) The effects which lead to the damping of plasmon oscillations are ignored here. Thus it is implicitly assumed that the collective excitations dealt within the framework of the hydrodynamic model are sufficiently long lived. Although
the damping effects can be introduced in a phenomenological manner by means of an effective collision time and associated viscous force in Euler's equation, but the use of the hydrodynamic formulation means that the electron-hole pairs are left out, and hence a genuine damping, which arises due to the decay of collective excitations into single-particle excitations cannot be introduced here (Eguiluz and Quinn 1976).

The answer to these objections is, as usual, that the model will find its ultimate usefulness if it is able to account for the results obtained from more reliable theories, and experiments. It will be seen that the model indeed provides a good basis to study many properties of a metal surface.
CHAPTER 2

RESPONSE OF A METAL SURFACE

2.1 Introduction

In Chapter 1 we have obtained the basic hydrodynamic equations (1.10) to calculate the response of an inhomogeneous electron gas to a perturbing charge. Here we use these equations to describe the response of a metal surface. The problem of finding the response of a metal surface to some perturbing charge distribution has been of considerable interest (Newns 1970, Heinrichs 1973d). The interaction energy between an ion a short distance outside the surface and the induced charge density is important in ionic chemisorption, and is also useful for an understanding of field evaporation and desorption (Newns 1970, Heinrichs 1973d). It will be seen in Section 4.2 that the induced potential due to an oscillating charge source is of interest in the van der Waals interaction of a molecule with the surface. The mutual interaction between ad-atoms can also be studied (Mahanty and March 1976, Duniec et al 1977).

Some of the earlier methods, which have been used to study the response of a metal surface to a perturbing charge density, can be broadly classified into following categories:

(i) Classical image theory
(ii) Thomas-Fermi approximation
(iii) Hartree approximation
(iv) Dielectric approach
(v) Quantum mechanical linear response theory
(vi) Self-consistent and variational calculations
(vii) Surface plasmon field and the hydrodynamic model.

This classification is not complete as other methods are also available (Inkson 1971). However, here we briefly discuss in succession some of the applications of the above techniques.

The image theory of classical electrostatics (Jackson 1962) has been widely used to study the interactions involving metal surfaces (Lennard-Jones 1932, Remy 1970, Mahanty and March 1976). An application of the theory has been made by Kohn and Lau (1976) to find that the interaction energy between two dipoles on a metal surface is twice the classical interaction energy between the parallel dipoles in the same configuration in vacuum. Antoniewicz (1974) has considered the instantaneous potential due to the image charges to show that an atom adsorbed on a metal surface acquires an induced dipole moment.

The classical image theory is a poor approximation as it ignores many details concerning the metal surface. The linearized Thomas-Fermi approximation, which allows for the finite screening in the metal, provides a better way to study the response of a metal surface (Newns 1969, Antoniewicz 1972, Heinrichs 1973d). Newns (1969) has employed this to calculate the interaction energy of an external point charge with a metal surface. He has found that the classical point image charge may be generalized to a line charge with an oscillatory charge distribution extending from the image point to infinity along the inward normal to the surface. His analysis has been extended by Antoniewicz (1972) who has calculated the response of a metal
surface to an external point dipole and used the result to find the effective polarizability of an atom near the surface. This is discussed in detail in Section 2.4.

The Thomas-Fermi method discussed above refers to the static limit. Newns (1970) has employed the Hartree approximation to calculate the time-dependent response of a metal with two plane parallel surfaces, and a semi-infinite metal to a perturbing source. He has introduced a 'surface dielectric function' which generalizes the classical image law.

The dielectric approach has been used by Heinrichs (1973d) to study the response of a metal surface to an oscillating point charge. The advantage of this treatment is that all quantities of interest are expressed in terms of the wave number and frequency dependent bulk dielectric function of the metal.

A quantum mechanical calculation of the response of a metal to an external charge distribution has been carried out by Beck and Celli (1970). Using the RPA, they have obtained approximate expressions for the induced potential and the electric field outside the metal. The surface is assumed to be perfectly reflecting in their analysis. The formalism has also been used by Beck et al (1970) to study the response of a metal to a charged impurity embedded near the surface. They have presented graphs for the potential and the electric field at the surface for several values of the distance of the impurity from the surface.

The above approaches to find the response of a metal surface to some perturbing charge distribution are based on the
infinite-barrier model of the metal surface, which by its nature is not self-consistent. Ying et al (1972) have presented a self-consistent treatment of the screening charge induced in an inhomogeneous electron gas by a small perturbing charge. They have also extended this analysis to present a density-functional theory of chemisorption (Ying et al 1975). The restriction arising due to the artificial nature of the surface, having a step-function density profile, has been partially removed by Appelbaum and Hamann (1972), who have performed a variational calculation of the image potential near a metal surface for a static point charge. A similar calculation has also been carried out by Lang and Kohn (1973) in a self-consistent manner. The response of a metal surface to an external perturbing dipole has recently been studied self-consistently by Meixner and Antoniewicz (1976) using the density-functional formalism. The results have been used to yield the effective polarizability of an atom or a molecule adsorbed on a metal surface.

The importance of surface plasmons in dealing with the interaction of a point charge with a metal surface has been pointed out by Ritchie (1972). He has suggested that a classical point charge at a fixed distance from a metal surface produces the surface plasmon field which in turn gives rise to the classical image potential. The hydrodynamic theory has been employed by Ying (1974) to study the response of an inhomogeneous metallic system to a perturbing potential in a formal way.

In this Chapter we study the response of a metal surface to a time-dependent perturbing charge distribution using the hydrodynamic model of the electron gas. The analysis is
based on the assumption that the equilibrium electron density at the metal surface forms a step-function. The assumption is equivalent to the infinite-barrier model of the surface, and is discussed in detail in Sections 5.1 and 6.1. The specular boundary condition, which corresponds to the vanishing of the normal component of the drift velocity at the surface, is used. It is found that the model gives many interesting results in a direct and simple manner.

The Chapter is arranged as follows. In Section 2.2 the interaction of a metal surface with an external charge source is discussed. The consequence of the surface on the screening action of the electron gas is described in Section 2.3. The effective polarizability of an ad-atom is calculated in Section 2.4, and the mutual interaction between ad-ions is considered in Section 2.5.

2.2 Interaction with a Charge Source

We consider a semi-infinite metal occupying the half-space $Z < 0$ and assume that the half-space $Z > 0$ is unoccupied. An oscillating charge source of strength $q$ and frequency $\omega$, located at a point $r_0$ outside the metal, induces density fluctuation $n_1(r,t)$ which is superposed on the equilibrium electron density $n_0(r)$ of the metal. If $n_0$ is a constant upto the metal surface then, using equations (1.10) and (1.11), the equation satisfied by $n_1$ in the metallic region in the time-independent form becomes

$$(\nabla^2 - \lambda^2) n_1 = 0 , \quad Z < 0 \quad (2.1)$$
where $\lambda^2$ is defined in equation (1.13). In the vacuum $n_1$ is taken as zero. The solution of equation (2.1) can be put in the form

$$n_1 = \left(\frac{1}{2\pi}\right)^2 \int C(K) \exp(iKR + \gamma Z) d^2K, \quad Z < 0 \quad (2.2)$$

where

$$\gamma^2 = K^2 + \lambda^2 \quad (2.3)$$

$R$ and $Z$ are the components of $\vec{r}$ along and perpendicular to the surface respectively, and $K$ is a two-dimensional wave vector parallel to the surface. The coefficient $C(K)$ is to be determined with the help of the condition for specular reflection. This is a natural boundary condition in the hydrodynamic model, and corresponds to the vanishing of the normal component of the drift velocity at the surface (Mahanty and Paranjape 1977, Forstmann and Stenschke 1978). The condition can be expressed as

$$en_0 \frac{\partial \phi}{\partial Z} \bigg|_{Z=0} - m^* \beta^2 \frac{\partial n_1}{\partial Z} \bigg|_{Z=0} = 0 \quad (2.4)$$

where we have used the first of equations (1.10) in conjunction with equation (1.11).

The potential, $\phi$, due to the oscillating charge source can be determined in terms of the coefficient $C(K)$ by using the second of equations (1.10), and the boundary conditions that $\phi$ and its normal derivative across the surface are continuous (Heinrichs 1973d). The use of equations (2.2) and (2.4) then gives
\[ \phi = -q \frac{w_s^2}{\lambda^2} \left\{ \frac{J_0(|R-R_0|)}{\beta^2 \gamma (\gamma+K) - \omega_s^2} \right\} dK + \frac{q}{|\mathbf{r}-\Sigma_0|} \quad Z > 0 \]

\[ = -q \frac{w_s^2}{\lambda^2} \left\{ \frac{J_0(|R-R_0|)}{\beta^2 \gamma (\gamma+K) - \omega_s^2/(\gamma+K)} \right\} dK \]

\[ + \frac{q}{|\mathbf{r}-\Sigma_0|} \quad Z < 0 \]

Equation (2.5) is a generalization of the corresponding static result obtained by Newns (1969) in the linearized Thomas-Fermi approximation.

The use of the image theory of classical electrostatics for a non dispersive medium leads to the familiar result (Jackson 1962)

\[ \phi = -\left( \frac{\varepsilon_0 - 1}{\varepsilon_0 + 1} \right) \frac{q}{|\mathbf{r}-\Sigma_0|} + \frac{q}{|\mathbf{r}-\Sigma_0|} \quad Z > 0 \]

\[ = \frac{2q}{\varepsilon_0 + 1} \frac{1}{|\mathbf{r}-\Sigma_0|} \quad Z < 0 \]

where \( \Sigma_0 = (R_0, -Z_0) \), and \( \varepsilon_0 \) is a dielectric constant of the medium. By taking \( \varepsilon_0 \) to be the local dielectric response function of the medium, obtainable from equation (1.16) by setting \( \beta = 0 \), equation (2.6) may be recovered from equation (2.5) by expanding the algebraic parts of the integrands in powers of \( K \) and retaining only the leading order terms.

We can introduce a 'surface dielectric function'
\[ \varepsilon_s(K, \omega), \text{ to write equation (2.5) for } Z > 0 \text{ as} \]

\[ \phi = -q \int_0^1 \frac{\varepsilon_s(K, \omega)-1}{\varepsilon_s(K, \omega)+1} J_0(K|R-R_0|) \exp(-K(Z+Z_0)) dK + \frac{q}{|r-R_0|}. \quad (2.7) \]

The surface dielectric function, defined in equation (2.7), establishes a close similarity between the Fourier components in equation (2.7) and the reduction factor \((\varepsilon_0-1)/(\varepsilon_0+1)\) of the classical image result, given in equation (2.6). Equation (2.7) when compared with equation (2.5) gives the known result (Heinrichs 1973d)

\[ \varepsilon_s(K, \omega) = \frac{\omega^2 - \omega^2_p}{\omega^2 - K\omega^2_p/\gamma}. \quad (2.8) \]

The induced potential, \(\phi_i\), due to the charge source may be obtained from equation (2.5) for \(Z > 0\) by dropping the last term as it represents the direct contribution. In the linear response theory followed here, the interaction energy, \(W\), of the charge source with the metal surface is thus given by (Newns 1969)

\[ W = \frac{1}{2} q \phi_i \bigg|_{r=R_0} \]

\[ = -\frac{q^2 \omega^2_s}{2} \int \frac{\exp(-2\beta K \varepsilon)}{\beta^2 (\gamma + K) - \omega^2_s} dK. \quad (2.9) \]

In the static limit of \(\omega=0\), equation (2.9) coincides with the corresponding result obtained by Newns (1969) in the linearized Thomas-Fermi approximation. The classical image result for the interaction energy may be obtained from equation (2.6), and for the static case we get
By expanding the algebraic part of the integrand in equation (2.9) for \( \omega = 0 \) in powers of \( K \), it is found that the classical image result, given in equation (2.10), can be a good approximation to the interaction energy at large distances from the surface, provided the effective surface is recessed by the Thomas-Fermi screening length, \( \lambda_0^{-1} \), defined in Section 1.3.1. A similar conclusion has also been drawn by Newns (1969), and Beck and Celli (1970) who have regarded the metal surface as an infinite-barrier in their treatments. However, in the self-consistent calculations, the effective surface has been found to be outside the discontinuity in the positive background (Appelbaum and Hamann 1972, Lang and Kohn 1973).

The correction to the image result for \( W \) arises due to the inclusion of spatial dispersion through the parameter \( \beta \). The divergence in the classical interaction energy for \( \mathbf{z} \rightarrow 0 \) is removed, when equation (2.9) for \( W \) is used. The cut-off in the \( K \)-integration is disregarded here. It will be seen in Section 3.4 that the cut-off plays an important role in estimating the work function of metals.

The external charge source and the induced charge constitute a dipole, \( p \), which is oriented normal to the surface, and is given by

\[
p = q \left[ \mathbf{z} + \frac{\omega^2 \lambda_0^{-1}}{\mathbf{S} - \omega^2} \right].
\]

(2.11)

For \( \omega = 0 \) and \( q > 0 \), the induced dipole points out of the surface. The dipole formed in this manner is responsible for changes in
the work function of metals due to an adsorbed layer of ions (Heinrichs 1973d).

2.3 Screening near a Metal Surface

When a charged particle is embedded near a metal surface, the screening which occurs is different from when it is in the bulk. The screening action of a homogeneous electron gas is examined in Section 1.3.1. Here we study the response of a semi-infinite metal to a charged impurity embedded near the surface. The impurity affects binding of the surface atoms which may be detectable in field ion microscopy experiments (Beck et al 1970).

The formalism is based on the basic hydrodynamic equations (1.10) and (1.11). For a semi-infinite metal confined in the half-space $Z < 0$, the equation satisfied by the density fluctuation $n_1$, induced by an embedded charge source of strength $q$ and frequency $\omega$ located at a point $r_0$ inside the metal, becomes

$$ (V^2 - \lambda^2) n_1 = -\frac{q}{e} \left(\frac{\omega}{\beta}\right)^2 \delta(r - r_0), \quad Z < 0 \quad (2.12) $$

where $\lambda^2$ is defined in equation (1.13). For $Z > 0$, $n_1$ is taken as zero. Equation (2.12) can easily be solved to give

$$ n_1 = \left(\frac{1}{2\pi}\right)^2 \int D(K) \exp(iK \cdot R + \gamma Z) d^2K + \frac{q\omega^2}{4\pi e\beta^2} \frac{\exp(-\lambda |r - r_0|)}{|r - r_0|}, \quad Z < 0 \quad (2.13) $$

where $\gamma$ is given by equation (2.3), and $D(K)$ is an arbitrary coefficient which is to be determined using equation (2.4) in
conjunction with the second of equations (1.10).

The potential, $\phi$, due to the charge source can be calculated with the help of Poisson's equation, given in equations (1.10). In the metallic region, a part of the potential arises because of the screening of the charge source by the homogeneous electron gas, and resembles equation (1.14). If we drop this part then, for $Z < 0$, the induced potential, $\phi_i$, which is a consequence of the presence of the surface can be expressed as

$$\phi_i = q \omega^2 \left[ J_0(K|\mathbf{R}-\mathbf{R}_0|) \left\{ \frac{\exp(KZ)}{(\gamma-K)} - \frac{2K}{\lambda^2} \exp(\gamma Z) \right\} \right. $$

$$ \times \left\{ \frac{\omega^2}{\omega^2-\omega_0^2} \exp(KZ_0) + \frac{\omega^2}{\beta^2\gamma(\gamma-K)} \exp(\gamma Z_0) \right\} + $$

$$ \frac{(\gamma-K)}{\beta^2\lambda^2\gamma} \exp(KZ+\gamma Z_0) \right] dK \quad \text{(2.14)} $$

If the effect of spatial dispersion is ignored by setting $\beta = 0$, then equation (2.14) becomes

$$\phi_i = -\frac{q}{\varepsilon_0} \frac{1-\varepsilon_0}{1+\varepsilon_0} \frac{1}{|\mathbf{r}-\mathbf{r}_0^{\text{im}}|} \quad \text{(2.15)} $$

where $\mathbf{r}_0^{\text{im}}$ and $\varepsilon_0$ are defined in connection with equation (2.6). Equation (2.15) can also be obtained using the image theory of classical electrostatics provided $\varepsilon_0$ is treated as a dielectric constant of the medium (Jackson 1962).

The interaction energy, $W$, of the charge source with the metal surface, defined in the first line of equation (2.9), can be calculated using equation (2.14), and for the static case
we get

\[ W = \frac{q^2}{2\lambda_0^2} \left( \gamma_0 - K \right)^2 \exp(-2\gamma_0 |Z|) \, dK \]  

(2.16)

where \( \lambda_0 \) and \( \gamma_0 \) are the static values of \( \lambda \) and \( \gamma \), defined in equations (1.13) and (2.3) respectively. For large \( |Z| \) the algebraic part of the integrand in equation (2.16) can be expanded in powers of \( K \) and various integrals can be evaluated term by term to give

\[ W = \frac{q^2}{4|Z|^2} \left[ 1 - \left( \frac{\pi}{\lambda_0 |Z|} \right)^\frac{1}{2} + \frac{2}{\lambda_0 |Z|} \ldots \ldots \right] \exp(-2\lambda_0 |Z|) \]

(2.17)

which shows that the interaction energy is localized, and vanishes when the effect of spatial dispersion is disregarded. Equations (2.16) and (2.17) are known results (Heinrichs 1973d).

2.4 Effective Polarizability of an Ad-atom

In Section 2.2 we have studied the response of a metal surface to an external charge source. When the charge source is replaced by an oscillating dipole, some modifications occur in the response. Here we analyse this problem using the hydrodynamic model of the electron gas, when the dipole is oriented normal to the surface, and use the results to find the effective polarizability of an adsorbed atom.

For a charge source external to the metal surface, the potential in the vacuum region is given by equation (2.5) for \( Z > 0 \). In order to find the potential due to a dipole, oriented normal to the surface, we place another charge of strength \(-q\) at a point \((R_0, Z_0 - dZ_0)\). In the limit when \( q \to \infty \),
\[ dq_0 \to 0 \] such that the product \( qdZ \) remains finite, the two charges constitute a dipole of moment \( p = qdZ \). By superposing the potentials due to these charges using equation (2.5), the induced potential, \( \phi_d \), due to the dipole for \( Z > 0 \) can be written as

\[
\phi_d = p \omega^2_s \left\{ \frac{KJ_0(K|R-R_0|)\exp(-K(Z+Z_0))}{\beta^2\gamma(\gamma+K)-\omega^2_s} \right\} dK, \quad Z > 0 \tag{2.18}
\]

where we have dropped the direct contribution from the dipole. The induced electric field, \( E_d \), due to the induced charges is normal to the surface, and is given by the negative derivative of \( \phi_d \) with respect to \( Z \).

The above analysis can be used to calculate the effective polarizability of a polarizable atom in the vicinity of a metal surface. The effective polarizability, \( \alpha_e \), is the apparent polarizability of an atom near the surface, and is found to be appreciably different from the free atomic polarizability, \( \alpha \) (Antoniewicz 1972, Heinrichs 1973d, Meixner and Antoniewicz 1976). In order to calculate \( \alpha_e \), we consider a nonpolar atom near a metal surface. On applying a small spatially uniform electric field \( E_0 \exp(-i\omega t) \) normal to the surface, a small dipole moment can be induced on the atom, which in the time-independent form is \( p = \alpha E_0 \). This dipole induces a charge density deviation in the metal which gives rise to an additional electric field, \( E_d \). In the linear response theory followed here, \( E_d \) is directly proportional to \( p \). Since the electric field near the atom is altered due to the induced electric field \( E_d \), the dipole moment of the ad-atom is given by
\[ p = \alpha \left( E_0 + E_d \right) \bigg|_{r=r_0} \quad (2.19) \]

The effective polarizability, \( \alpha_e \), at frequency \( \omega \) can be calculated from the relation \( p = \alpha_e E_0 \), and is found to be

\[
\alpha_e = \frac{\alpha}{1 - \frac{\omega^2}{\omega^2 - \omega^2} \frac{aS(Z)}{4Z^3}} \quad (2.20)
\]

where

\[
S(Z) = 4(\omega^2 - \omega^2)Z^3 \int \frac{K^2 \exp(-2KZ) dK}{\beta^2 \gamma(\gamma + K) - \omega_s^2} \quad (2.21)
\]

Equation (2.20) shows a strong dependence of the effective polarizability on the distance from the surface. The factor \( S(Z) \) in equation (2.20) is because of spatial dispersion, and becomes equal to one when the effect of spatial dispersion is neglected. The dispersion less expression for \( \alpha_e \) can also be derived from the classical image result for the induced electric field \( E_d \), obtainable from equation (2.6) for \( Z > 0 \). Equation (2.20) is a generalization of the static result obtained by Antoniewicz (1972) in the linearized Thomas-Fermi approximation.

A detailed self-consistent analysis of the effective polarizability, using the density-functional formalism of the electron gas, has recently been made by Meixner and Antoniewicz (1976). The effective polarizability has also been obtained experimentally by Palmberg (1971) for xenon atom adsorbed on palladium surface from variations in the work function with coverage.
2.5 Mutual Interaction between Ad-ions

When two charged particles are brought near a metal surface, besides the direct interaction between them an indirect interaction mediated by the metal surface also appears. This mediation arises due to the induced charge density in the metal and weakens the original direct interaction between the charged particles. A similar phenomenon has also been found when two atoms are in the proximity of a metal surface (Mahanty and Ninham 1973b, Mahanty and March 1976, Duniec et al 1977, Schmeits and Lucas 1978). Here we briefly discuss the mechanism of how a metal surface mediates in the interaction between two charged particles.

Let there be two charged particles $q_1$ and $q_2$ located outside a metal surface at the points $r_1$ and $r_2$, respectively. The induced potential in the vacuum region due to these charges are denoted by $\phi_{q_1}$ and $\phi_{q_2}$ respectively, and may be obtained from equation (2.5) for $Z > 0$ by dropping the last term. The interaction energy of the charge $q_1$ alone with the metal surface can be found from equation (2.9). When the charge $q_2$ is also brought near the surface, the interaction energy, $W$, of both the charges with the metal surface is given by

$$W = \frac{1}{2} q_1 \phi_{q_1} \bigg|_{r=r_1} + \frac{1}{2} q_2 \phi_{q_2} \bigg|_{r=r_2} + q_2 \phi_{q_1} \bigg|_{r=r_2}$$

$$= -\frac{\omega^2}{2} \int \frac{dK}{\beta^2 \gamma (\gamma + K) - \omega^2} \left[ q_1^2 \exp(-2KZ_1) + q_2^2 \exp(-2KZ_2) + 2q_1q_2 J_0(K|R_1-R_2|) \exp(-K(Z_1+Z_2)) \right]$$

(2.22)
where the direct interaction between the charges $q_1$ and $q_2$ is ignored. For $r_1 = r_2$, the two charged particles coincide, and thus equation (2.22) becomes the same as equation (2.9). The first two terms in equation (2.22) represent the direct interaction of the external charges with the metal surface, whereas the last term is the indirect interaction between the two charges and arises due to the mediation of the metal surface. The interaction energy, $W_m$, between the two charges, as mediated by the metal surface, can thus be written in the static limit as

$$W_m = -q_1q_2\lambda_0^2 \int \frac{J_0(K|R_1-R_2|)\exp(-K(Z_1+Z_2))}{(K+\gamma_0)^2} \, dk \quad (2.23)$$

where $\lambda_0$ and $\gamma_0$ are defined earlier in connection with equation (2.16). The interaction energy, given in equation (2.23), is negative of the product $q_1q_2$, and thus the mediation of the metal surface clearly weakens the interaction between the charged particles.
CHAPTER 3

THE WORK FUNCTION OF METALS

3.1 Introduction

In Chapter 2 we have seen that the hydrodynamic theory of the electron gas provides a good basis to study the response of a metal surface to a perturbing charge density. Several interesting results are derived there and it is found that in the static limit they reduce to the well-known results of the linearized Thomas-Fermi approximation. The cut-off in the K-integrations is disregarded, and thus it is implicitly assumed that the distances involved are rather large. Here we explicitly introduce the cut-off, and use the hydrodynamic formalism to estimate the work function of metals.

The concept of the work function is somewhat old and it is rather difficult to pinpoint its origin. The early research on the work function has been carried out mainly due to the following two reasons:

1. The need for more efficient cathodes for the rapidly expanding electronic tube industry.
2. The realization that the work function is a fundamental feature of the then new electronic theories of metals.

There are several methods available for the experimental determination of the work function of a particular material and thus a huge quantity of data is available in literature. Fomenko (1966) has collected these pieces of information in a
handbook which also contains the theoretically calculated values. On the basis of this information, the recommended experimental values of the work function for most of the chemical elements in the periodic table are listed. In making a choice of the recommended values, some consideration is given to the experimental procedure, the systematic nature of the measurements, and the purity of the materials. Rivière (1969) has also discussed the measurement of work function by various methods and has given the results that have been obtained until 1966.

The work function is related to both the surface and bulk properties of the material (Seitz 1949). To a large extent, the work function is determined by the top few layers of atoms, and not by the material as a whole (Bardeen 1936). For instance, the work function can be altered appreciably if the surface is oxidised or there is a deposition of atoms of another material. Changes in the work function due to adsorption of alkali atoms by a metallic substrate are studied by Lang (1971) who has used a jellium model of the substrate-adsorbate system. On completion of one full layer, the work function has been found to be very nearly equal to that of the corresponding bulk sample of the adsorbate. The effect of deposition of carbon monoxide on the work function of titanium and erbium has recently been reported by Surplice and Brearley (1978). They have found that the work function is sensitive to the doses of CO.

The work function may be defined as the difference in energy between a lattice with an equal number of ions and electrons, and the lattice with the same number of ions, but with one electron removed. Using this definition Bardeen (1936) has made an early and sophisticated attempt to calculate the work
function of sodium by treating the ions as a continuous distribution of charges. To determine the work function, he has solved Fock's equations in an approximately self-consistent way. The approach is an extension of the analysis presented by Wigner and Bardeen (1935) for the calculation of the work function of monovalent metals where they have omitted the effect due to the electric double layer at the surface and still obtained reasonably good results. This suggests that the double layer of these metals are probably small. The inner contribution to the work function of metals has also been calculated by Schneider (1969).

Smith (1969) has presented a formalism to calculate the work function of metals from first-principles without considering the grain orientation effects. The analysis is not fully self-consistent and starts with an expression for the total energy as a functional of the electron number density. The actual computation has been done for those metals which may be amenable to the free-electron picture and thus the characteristics of the metals enter only through the electron density. The theoretical results for the work function are found to increase with the increase in the electron density and show a reasonably good agreement with the experimental values recommended by Fomenko (1966). This approach is discussed briefly in Section 3.3.

A self-consistent calculation of the work function of simple and noble metals has been performed by Lang and Kohn (1971) using density-functional formalism. They have carried out their analysis in the uniform-background model and also included the effect of the discrete ions using first order perturbation theory. For simple metals the contribution arising from the
discrete nature of the ions has been found to be of the order of 10% of the average work function, and so is the anisotropy among different faces. The agreement of their final results with the experimental data is good (5-10%) for simple metals, but for noble metals the calculated values are 15-30% too low. This is to be expected because noble metals are not amenable to the perturbation theory approximation.

Here we discuss an application of the hydrodynamic model to estimate the free electron contribution to the work function of metals. The approach has recently been developed by Mehrotra and Mahanty (1978b) and is based on the charge response properties of a metal surface. Before describing this method in Section 3.4, we first show in Section 3.2 that the work function of any physical system is zero in the simple Thomas-Fermi theory. A concise discussion of the density-functional formalism, which has been employed by Smith (1969) to calculate the work function is given in Section 3.3.

3.2 Thomas-Fermi Theory

The Thomas-Fermi method has been found to be useful for a simple description of inhomogeneous systems (March 1957). However, here we show that the method is inadequate for a quantitative estimate of the work function of metals. We consider a model of a metal surface in which the positive ions are replaced by a uniform positive charge background filling the half-space $Z \leq 0$. The electron density, $n_0(r)$, at the metal surface is assumed to be a slowly varying function of the distance. If $\phi_0(r)$ is the potential at a point $r$, then the classical energy equation for the fastest electron can be written...
as

\[ E_f = \frac{p_f^2(r)}{2m} - e\Phi_0(r) \]

\[ = \frac{\hbar^2}{2m} \left( 3\pi^2 n_0(r) \right)^{2/3} - e\Phi_0(r) \]  (3.1)

where \( p_f(r) \) is the Fermi momentum, and \( E_f \) is the Fermi energy measured with respect to the zero of energy outside the metal. In the second line of equation (3.1) we have used a local relationship between Fermi momentum and electron density. The Fermi energy, \( E_f \), must be a constant, for otherwise the electrons can re-adjust themselves to lower the energy.

Equation (3.1) forms the basis of the Thomas-Fermi approximation and, when supplemented with Poisson's equation, may be used to calculate the electron density distribution at the metal surface.

The work function, \( \psi_e \), may be defined as the smallest amount of energy which is required to liberate an electron from a metal. Qualitative considerations suggest that

\[ \psi_e = -e(\Phi_0(\infty) - \Phi_0(-\infty)) - \frac{p_f^2}{2m} \]  (3.2)

where \( p_f \) is the value of \( p_f(r) \) deep inside the metal.

Looking at equation (3.1) in the vacuum at a large distance from the metal, where both \( n_0(r) \) and \( p_f(r) \) vanish, and also in the asymptotic region inside the metal we get

\[ -e\Phi_0(\infty) = \frac{p_f^2}{2m} - e\Phi_0(-\infty) \]  (3.3)

which when substituted in equation (3.2) gives \( \psi_e = 0 \). Thus the work function of any physical system in the Thomas-Fermi

The limitations of the Thomas-Fermi theory are (Pines and Nozières 1966):

(i) It is justified only when the inhomogeneities in the system correspond to distances which are long compared to the interparticle spacing; otherwise the assumption of a local relationship between Fermi momentum and electron density is not valid.

(ii) The relation which connects Fermi energy to electron density is appropriate for non-interacting electrons.

The refinements to the Thomas-Fermi method have been carried out by Hohenberg and Kohn (1964) who have presented a more general formalism of an inhomogeneous electron gas, and we discuss it in the next Section to calculate the work function.

3.3 Density-Functional Formalism

It has been shown by Hohenberg and Kohn (1964) that the ground state energy, \( H \), of an inhomogeneous electron gas can be written as a unique functional of the density. For an electron gas of slowly varying density, \( n_0(r) \), this functional may be expressed as (Smith 1969)

\[
H = -e \int \frac{n_0(r)n_+(r')}{|r-r'|} d^3r'dr + \frac{e^2}{2} \int \frac{n_0(r)n_0(r')}{|r-r'|} d^3rd^3r' + x_K \int \frac{n_0^{5/3}}{n_0^{2/3}} d^3r \\
- x_A \int n_0^{4/3} d^3r - 0.056e^2 \int \frac{n_0^{4/3}}{0.079 + a_0n_0^{1/3}} d^3r + \frac{\hbar^2}{72m} \int \frac{(vn_0)^2}{n_0} d^3r 
\]

(3.4)
where $a_0$ is the Bohr radius, $n_+(r)$ is the charge density of the positive background, and $\chi_K$ and $\chi_A$ are defined in equation (1.8). The first two terms in equation (3.4) are due to the electrostatic interaction, whereas the next three terms represent, respectively, the kinetic, exchange and correlation energies of a homogeneous electron gas of density $n_0$. The last term is an inhomogeneity term.

The work function, $\psi_e$, of a metal may be defined as (Bardeen 1936, Smith 1969)

$$\psi_e = -\left(\frac{3H}{3N}\right)_{N=N_+}$$

(3.5)

where $N$ and $N_+$ are the total number of electrons and ions in the metal, respectively. In order to calculate $\psi_e$ using equations (3.4) and (3.5), we apply equation (3.4) to a model of a metal surface in which positive ions are replaced by a uniform background of positive charges whose density has a constant value $n_+$ on the negative side of the XY plane and is zero elsewhere. The electron density distribution at the metal surface is to be determined self-consistently. A little manipulation gives

$$\psi_e = e\phi_0(-\infty) - \frac{5}{3} \chi_K n_0^{2/3} + \frac{4}{3} \chi_A n_0^{1/3}$$

$$+ \frac{e^2 n_0^{1/3} (0.0059 + 0.056a_0 n_0^{1/3})}{(0.079 + a_0 n_0^{1/3})^2}$$

(3.6)

where

$$\phi_0(r) = \int \frac{n_+(r') - e n_0(r')}{|r-r'|} d^3r'$$

(3.7)
and $n_0$ is the electron density deep inside the metal. 

$\phi_0(\rightarrow)$ represents the value which $\phi_0(r)$ approaches asymptotically inside the metal, and $\phi_0(r)$ is set equal to zero at large distances from the metal. The first term in equation (3.6) gives the surface contribution to the work function, while the remaining terms arise due to the bulk properties of the metal. Equation (3.6) has been employed by Smith (1969) to calculate the work function of those metals which may be amenable to the free electron model. The agreement with the experimental data has been found to be reasonably good. In order to determine the work function using equation (3.6), it is necessary to know the electron density distribution at the metal surface. Smith (1969) has obtained it in an approximately self-consistent manner by assuming a parametrized form for $n_0(r)$ and minimizing the energy functional, $H$, given in equation (3.4), subject to the condition that the total number of electrons remain fixed. The calculation has been refined by Lang and Kohn (1971) who have employed an improved form of the energy functional, $H$, and determined the electron density in a self-consistent way (Lang and Kohn 1970). They have also incorporated the discrete nature of the positive ions in their analysis.

The density-functional formalism, discussed above for a calculation of the work function, has also been found very useful in calculating surface energy (Smith 1969, Lang and Kohn 1970), image potential (Appelbaum and Hamann 1972, Lang and Kohn 1973), adhesive energy (Ferrante and Smith 1973), chemisorption energy (Ying et al 1975), effective polarizability (Meixner and Antoniewicz 1976) etc.
3.4 Charge Response Theory

In Chapter 2 we have seen that the theory of the charge response of a metal surface can be developed in many ways, but perhaps the simplest formalism, which has the essential properties of metallic electrons built in, is the hydrodynamic model of Bloch. Here we employ this model to estimate the free electron contribution to the work function of metals. When an external electron is brought from infinity to the surface of a metal at 0°K, the negative of the change in the energy of the system (metal and external electron) is equal to the work function. Here we show that the contribution to this work function from the free electrons in the metal can be calculated in terms of the induced charge due to the additional electron at the metal surface (Mehrotra and Mahanty 1978b).

We consider a free electron model of a metal surface in which positive ions are replaced by a uniform positive background filling the half-space \( Z < 0 \) (Bardeen 1936, Smith 1969). The equilibrium electron density, \( n_0 \), at the metal surface is assumed to form a step-function (Heinrichs 1975a,b, Mahanty and Paranjape 1977). An external charge source of strength \( q \) and frequency \( \omega \) at a point \( \mathbf{r}_0 \) produces induced charge \( -e n_1(\mathbf{r},t) \) in the metal, \( n_1 \) being the deviation from the equilibrium electron density \( n_0 \). This charge deviation is worked out in Section 2.2 by using the basic hydrodynamic equations (1.10) in conjunction with equations (1.11) and (2.4), and in the time-independent form can be expressed as (Mahanty and Paranjape 1977)

\[
\begin{align*}
n_1(\mathbf{r}) &= \frac{q}{e} \frac{\omega^2}{(2\pi)^2} \int \frac{\exp\{-K|Z_0|\gamma|Z| + iK.(\mathbf{R}-\mathbf{R}_0)\}}{\beta^2 \gamma - \omega^2/(\gamma+K)} \, d^2K \quad \text{for} \quad Z < 0 \\
&= 0 \quad \text{for} \quad Z > 0
\end{align*}
\]
where
\[ \gamma^2 = K^2 + \frac{(\omega_p^2 - \omega^2)}{\beta^2} \quad ; \quad \omega_p^2 = 2\omega_s^2 = 4\pi n_0 e^2/m \quad . \quad (3.9) \]

Here \( R \) and \( Z \) are the components of \( \mathbf{r} \) along and perpendicular to the surface, respectively, and \( K \) is a two-dimensional wave vector parallel to the surface. The parameter \( \beta^2 \) is a measure of the pressure force arising out of the density deviation in the metal. It has been shown in Section 1.3.2 that the value of \( \beta^2 \) may be taken to be either \((1/3)v_F^2\) or \((3/5)v_F^2\), depending on the frequency range we want to describe, \( v_F \) being the Fermi velocity. The former value of \( \beta^2 \) is valid in the low frequency range and gives Thomas-Fermi result for the bulk dielectric response function, whereas the latter leads to the RPA result for bulk plasmon dispersion to the order \( k^2 \). As the present analysis is carried out in the static limit, we here take \( \beta^2 = (1/3)v_F^2 \).

Equation (3.8) can be used to calculate the change in the energy of the system due to the presence of an additional electron at the metal surface. The electrostatic energy, \( U \), of the system consisting of an external electron at the metal surface and the charge distribution arising out of it for \( \omega = 0 \) and \( r_0 = 0 \) is given by

\[ U = \frac{e^2}{2} \left\{ \frac{n_1(r)n_1(r')}{|r-r'|} \ d^3r d^3r' + e^2 \int \frac{n_1(r)}{|r|} \ d^3r \right\} \quad (3.10) \]

The presence of an additional electron at the metal surface alters the electron density of the metal from \( n_0 \) to \( n_0 + n_1 + 1/V \), where \( V \) is the total volume of the metal, ultimately set equal to \( \infty \). This produces a change in the
kinetic energy of the system which, in the static limit of \( \omega = 0 \), may be evaluated in the Thomas-Fermi approximation and is given by

\[
\Delta T = \chi_K \int \left\{ (n_0 + n_1 + 1/V)^{5/3} - n_0^{5/3} \right\} \, d^3r
\]

\[
= \frac{5}{9} \chi_K n_0^{-1/3} \int n_1^2 \, d^3r \quad (3.11)
\]

where only the first three terms of the binomial series of the first term in the integrand in the first line of equation (3.11) are retained, \( V \) is set equal to \( \infty \), and \( \chi_K \) is defined in equation (1.8).

The use of the Thomas-Fermi approximation in equation (3.11) is motivated by the fact that the hydrodynamic model parameter \( \beta^2 \) in the static limit is chosen to give the Thomas-Fermi result for the bulk dielectric response function.

In the static limit of \( \omega = 0 \), the integrals in equations (3.10) and (3.11) become elementary and can be put in the form

\[
U = 2e^2 \omega_s^4 \int \frac{dK}{\zeta(\zeta + \beta K)^3} - 2e^2 \omega_s^2 \int \frac{dK}{(\zeta + \beta K)^2} \quad (3.12)
\]

\[
\Delta T = \frac{5\chi_K n_0^{-1/3} \omega_s^4}{9\pi \beta} \int \frac{K \, dK}{\zeta(\zeta + \beta K)^2} \quad (3.13)
\]

where \( \zeta^2 = \omega_p^2 + \beta^2 K^2 \). As the hydrodynamic model deals with the macroscopic quantities such as density, drift velocity, the wavelengths involved are long and thus a cut-off in the \( K \)-integrations in equations (3.12) and (3.13) should be introduced. This is essential as the model breaks down beyond the upper limit of the
cut-off in the momentum space. A proper choice of the cut-off is rather difficult to make due to intrinsic uncertainty in the theoretical value for it as is also mentioned in Section 1.4. However, here in a somewhat arbitrary manner, we may choose a cut-off at $K_c = \omega_p / v_F$. This is a natural cut-off beyond which the bulk plasmons are unstable against decay into particle-hole excitation (Heinrichs 1973b). Another possible cut-off which may be adopted is at $K_c = \omega_p / \sqrt{2} v_F$ as suggested by Schmit and Lucas (1972). Using this choice, Schmit and Lucas (1972) have calculated plasmon contribution to the surface energy of metals and obtained a good agreement with the experimental data. Although these choices are not fully satisfactory on the theoretical grounds (Heinrichs 1973b, Jonson and Srinivasan 1973), we here employ them as the possible cut-offs. It may be argued that these choices refer to the high frequency range, whereas the present analysis is carried out in the static limit. However, even in the static case there is a need for a cut-off which is of the same order of magnitude as the above choices (Pines and Nozières 1966).

Using equations (3.12) and (3.13), the contribution of the free electrons in a metal to its work function, $\psi_e$, is thus given by

$$\psi_e = -(U + \Delta T)$$

$$= \frac{e^2}{2} \left( \frac{\omega_p}{\beta} \right) \int_0^u \frac{du}{(u^2 + (1 + u^2)^{1/2})^2}$$

(3.14)

where $u_c$ is equal to $1/\sqrt{3}$ or $1/\sqrt{6}$ depending upon whether $K_c = \omega_p / v_F$ or $\omega_p / \sqrt{2} v_F$, respectively. If we denote the
numerical value of the integral in equation (3.14) by \( \mu \),
then for \( \beta^2 = (1/3)v_F^2 \), which is the static limit as mentioned
in connection with equation (3.8), equation (3.14) becomes

\[ \psi_e = \frac{3\mu}{(18\pi)^{1/3}} \frac{e^2}{a_0^{\sqrt{s}}} \]  \hspace{1cm} (3.15)

Here \( a_0 \) is the Bohr radius and \( r_s \) is the usual electron
density parameter defined by \( n_0 = 3/4\pi r_s^3 a_0^3 \). The integral in
equation (3.14) is easily calculated numerically and the value
of \( \mu \) is found to be 0.346 or 0.280 depending upon whether
\( u_c = 1/\sqrt{3} \) or \( 1/\sqrt{6} \), respectively. For \( u_c \to \infty \), the value of \( \mu \)
is \( 2/3 \). Equation (3.15) shows that the free electron contri­
bution to the work function of metals scales as \( 1/\sqrt{r_s} \).

In Table 3.1 we give the values of \( \psi_e \) obtained from
equation (3.15) for \( u_c \) equal to \( 1/\sqrt{3} \) as well as \( 1/\sqrt{6} \).
We have computed for those metals which were considered by
Smith (1969). For comparison, we give Smith's (1969) results
for some of the metals, and for the remaining the improved self­
consistent values of Lang and Kohn (1971) in the uniform­
background model. It is observed that the agreement with other
theoretical calculations is reasonable considering the
simplicity of the approach followed here. In fact for \( u_c = 1/\sqrt{6} \)
our results agree surprisingly well with those of Lang and Kohn
(1971). For instance, the agreement is exact for Mg, but in
general the discrepancy is less than 4%, except for Al where the
value differs by about 7%. For the remaining metals, our results
for \( u_c = 1/\sqrt{6} \) agree with those of Smith (1969) within 5-25%.
However, when \( u_c \) is chosen to be \( 1/\sqrt{3} \), the agreement is not so
good, we notice a difference of 20-35% with Lang and Kohn's (1971)
results and a discrepancy of 30-55% with Smith's (1969) values.

To compare our results with experimental data we give the values quoted by Lang and Kohn (1971) as they are the best to compare with the results of jellium model (Lang and Kohn 1971). For other metals we list the values given by Rivière (1969) where they are available and by Fomenko (1966) in the remaining cases. Excluding noble metals, where the calculated values are seen to be 15-35% too low, we observe that our results for $u_c = 1/\sqrt{6}$ differ from the experimental data quoted by Lang and Kohn (1971) by less than 20%. However, for $u_c = 1/\sqrt{3}$ the disagreement is as large as 45% for some of the alkali metals. Our results for $u_c = 1/\sqrt{6}$ differ from the values given by Rivière (1969) by less than 15%, whereas the discrepancy is upto 40% for $u_c = 1/\sqrt{3}$. For $u_c = 1/\sqrt{6}$ the difference with Fomenko's (1966) values is found to be less than 20%, while for $u_c = 1/\sqrt{3}$ the discrepancy is within 15-45%.

The agreement with previous theories as well as experimental data is better for $u_c = 1/\sqrt{6}$, suggesting this choice as more appropriate in the present formulation. Although the cut-off at $K_c = \omega_p/\sqrt{2} v_F$ is criticized by Heinrichs (1973b) and Jonson and Srinivasan (1973) for the surface energy calculations of Schmit and Lucas (1972), they have not given a rigorous explanation for choosing $K_c = \omega_p/v_F$ as the cut-off for a semi-infinite system and have also pointed out the intrinsic uncertainty in the choice of $K_c$. In the present estimate the values are somewhat sensitive to the assumed range of values of the cut-off $K_c$, but are finite even when $K_c \to \infty$; however, that is an unrealistic limit. The discrepancy between our calculated
results and the experimental values, considering that we are making an estimate of only the contribution of free electrons to the work function, is not unreasonable.

3.5 Conclusion

In this Chapter we have estimated the free electron contribution to the work function of metals using the linearized hydrodynamic model. It is shown to be inversely proportional to $\sqrt{r_s}$. The numerical values obtained for various metals show reasonable agreement with experimental results, as also with previous theoretical predictions based on the density-functional approach, despite the simplicity of the model used here. There is a theoretical uncertainty in the value of the cut-off in the momentum space, but within the range of that uncertainty, the hydrodynamic model gives a reasonable explanation of the work function of metals.

The only parameter which governs the surface charge response in the hydrodynamic model is $r_s$, which gives $\omega_p$ and also $\beta$. In metals having a complicated band structure so that the jellium model is not a good description of electrons in them, the hydrodynamic model parameter would deal with the effective number of free electrons. However, in the present estimate the number of conduction electrons per atom is taken to be the group number as it describes many physical properties adequately (Smith 1969).
Table 3.1. Comparison of the work functions for $u_c$ equal to $1/\sqrt{3}$ and $1/\sqrt{6}$. Values with superscripts a, b and c are taken from Lang and Kohn (1971), Rivière (1969) and Smith (1969), respectively. $r_s$ values are computed from the electron densities given by Smith (1969).

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<th>Experimental</th>
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CHAPTER 4

PHYSISORPTION ON METAL SURFACES

4.1 General Considerations

So far we have been concerned with the interaction of charged particles with metal surfaces. The need for a proper understanding of the interaction between an atom (or a molecule) and a metal surface is fundamental to physisorption. The examples of physisorption are adsorption of inert gas atoms on metals where a strong interaction is not possible due to the closed-shell nature of the adsorbate atoms. A review article by Wojciechowski (1972) deals with the theory of adsorption on metal surfaces. A physisorbed atom may be considered as being bound to the metal surface under the combined action of two forces:

(i) van der Waals interaction which represents the long-range attractive part and arises due to the correlation between the charge fluctuation in the metal surface and in the interacting atom or molecule.

(ii) a short-range repulsive part which arises from the overlap of the electronic wavefunctions of the atom and the metal surface.

The literature on van der Waals interaction of an atom with a flat metal surface is extensive and goes back to more than forty years, when Lennard-Jones (1932) carried out a calculation using the method of images. He treated the metal
as a perfect conductor and the atom as a quantum mechanical system which is perturbed by the potential due to the classical images of the constituent charges. The resulting interaction energy, $E_I$, has been found to be

$$E_I = -\frac{e^2}{12Z^3} <d^2>$$

(4.1)

where $Z$ is the distance of the atom from the metal surface and $<d^2>$ is the mean-square displacement of electrons in the atom. Bardeen (1940) has presented a quantum mechanical formulation of the problem and pointed out that the result obtained by Lennard-Jones (1932) should be an upper limit to the interaction energy. Margenau and Pollard (1941) have formulated the problem in terms of induced dipole moments on small volume elements of the metal and obtained the result which closely resembles that of Bardeen (1940).

The van der Waals interaction of an atom with a semi-infinite body may be obtained by pairwise summation of the interaction energy between two atoms which may be derived from an expression for the force between two semi-infinite media calculated by Lifshitz (1956). The resulting interaction energy is found to be proportional to $Z^{-3}$. The procedure is, however, not accurate due to the many-particle character of the van der Waals forces which means that if we have an assembly of atoms then the energy of their interaction is not exactly equal to the sum of the energies of the interaction between isolated atoms.

The van der Waals interaction of an atom with a solid surface has also been a subject of study by Mavroyannis (1963).
and McLachlan (1964). Mavroyannis (1963) has explicitly evaluated numerical values of interaction energies of rare gas atoms with a few metals. McLachlan (1964) has treated the solid as a continuous dielectric medium and used the theory of electrical images to derive the van der Waals forces at the surface of a solid. The theory gives the attraction between a single atom and the surface, between two atoms which are both close to the surface, and between two bodies separated by a gap. The excitation spectrum and the ground-state energy for the interaction of an atom with a metal surface has recently been discussed by Mavroyannis and Hutchinson (1977) from a microscopic point of view.

Mukhopadhyay and Mahanty (1975) have derived a formula for the van der Waals interaction of an atom with a metal surface by treating the polarization of the metal in the linear response theory and regarding the metallic system as a semi-infinite electron gas. Their result for the interaction energy is reducible to a form similar to that given by Bardeen (1940). More recently, Mahanty and Paranjape (1977) have investigated the effect of spatial dispersion on the van der Waals interaction of an atom with a metal surface in the hydrodynamic approximation. We shall discuss this method in Section 4.3.

The repulsive contribution to the interaction energy for helium atom physisorbed on various metals has been evaluated by Kleiman and Landman (1973 a,b) using density-functional method. They have taken the repulsive part to originate from the change in the electronic kinetic energy of the atom-metal system. By adding it to the attractive van der Waals interaction energy, they could find both the physisorption energy
and the equilibrium distance of the ad-atom as a function of the electron density. The values of the adsorption energies have been found to be mainly governed by the van der Waals interaction energy evaluated at an appropriate distance. Their results show that the equilibrium position of the adsorbed atom increases monotonically with increasing electron density, and is not related simply to the atomic radii of the adsorbed atom and metallic atoms as has been assumed by Mavroyannis (1963). The repulsive part of the helium-metal physisorption potential has also been calculated by Zaremba and Kohn (1977) in the Hartree-Fock approximation. By combining it with the previous result for the van der Waals interaction (Zaremba and Kohn 1976), binding energies and equilibrium positions of helium atom adsorbed on simple and noble metals have been determined by them.

The experimental study of the van der Waals interaction of an atom with a metal surface has been performed by atomic beam deflection technique. The deflection of a beam of caesium atoms by a gold surface has been observed by Raskin and Kusch (1969) and the results are shown to agree in form and magnitude with those predicted from theoretical potential. However, their measurements are not sufficiently accurate to make a critical assessment for the various theoretical formulae available for the interaction energy. Shih et al (1974) have studied the interaction potential between a molecule having permanent dipole moment and a conducting surface.

The above discussion is confined to planar surfaces. The geometrical effect of the surface curvature on the attractive part of physisorption energy has been studied by Schmeits and
Lucas (1975, 1977). They have calculated the van der Waals interaction of an atom with a metallic surface having planar, spherical or cylindrical shape. The interaction energy of a neon atom adsorbed on solid aluminium has been plotted as a function of radius of curvature of the surface for a full sphere, a full cylinder, a cylindrical pore, and a spherical pore (Schmeits and Lucas 1977). The numerical values have also been obtained for an argon atom physisorbed on a silver sphere or on a spherical cavity in solid silver (Schmeits and Lucas 1975). It has been found that the interaction energy becomes weaker with respect to the plane surface for the sphere, whereas it is enhanced if the atom is in the cavity. The distance of separation of the physisorbed atom from the surface has been taken to be an average of nearest-neighbour distances in the respective solids of ad-atoms and solid atoms.

When the geometry of the surface of a solid is not planar, it becomes difficult to evaluate the van der Waals interaction of an atom with the surface. Recently, Cole and Schmeits (1978) have presented a simple approximate treatment for physical adsorption on curved surfaces. Their analysis is based on the assumption that the interaction between an atom and a non-planar solid surface can be estimated in the continuum limit by pairwise summation of the interaction between the external atom and the atoms constituting the solid, provided the interaction constant between the interacting atoms is such that it yields known result for the planar surface. The explicit results have been given for the spherical and cylindrical geometries and it has been found that the forms of the approximate potentials are more compact and convenient than the
usual expressions (Schmeits and Lucas 1977).

Here we are only concerned with the attractive or van der Waals part of the physisorption energy. The analysis is carried out by using the hydrodynamic model of the electron gas. The mathematical formulation of the problem is set up in Section 4.2. The response of planar and spherical metal surfaces to an external oscillating charge source is discussed in Sections 4.3-4.5. The results are employed to evaluate the van der Waals interaction of an atom with both planar and spherical surfaces. The dispersion formulae for surface plasma oscillations follow as a direct consequence of the analysis.

4.2 Mathematical Formulation

We have seen in the previous Section that the van der Waals interaction of an atom with a metal surface plays an important role in physisorption and can be evaluated from various points of view. Here we analyse the problem by using the dispersion self-energy formalism as it has been found very useful due to its directness (Mahanty and Ninham 1973a, Mukhopadhyay and Mahanty 1975, Mahanty and Ninham 1976). The dispersion self-energy of an atom near a metal surface may be defined as the difference in the zero-point energy of the electromagnetic field modes in the presence of the atom and the metal surface and in the presence of the metal surface alone. This difference gives the van der Waals interaction energy, $E_I$, of the atom with the metal surface. The force field on the atom due to the surface is the negative gradient of $E_I$. 
For convenience we neglect the spatial extension of the atom. The effect of the size of the atom on the interaction energy with a planar interface between two dielectric media has been considered by Mahanty and Ninham (1973a). The retardation effects are also disregarded here, as is reasonable for comparatively short distances between the atom and the metal surface. Mahanty et al. (1978) have recently evaluated the retarded van der Waals interaction of a point atom with a metal surface using the hydrodynamic model of the electron gas.

If the atom is located at a point \( \mathbf{r}_0 \), and \( \alpha(\omega) \) is its polarizability at frequency \( \omega \) then the electric field, \( \mathbf{E}(\mathbf{r},\omega) \), due to the instantaneous polarization on the atom is given by the relation

\[
\mathbf{E}(\mathbf{r},\omega) = \alpha(\omega) \mathbf{G}(\mathbf{r},\mathbf{r}_0;\omega) \mathbf{E}(\mathbf{r}_0,\omega)
\]  

(4.2)

where the dyadic \( \mathbf{G}(\mathbf{r},\mathbf{r}_0;\omega) \) defines the electric field at \( \mathbf{r} \) due to a unit dipole source at \( \mathbf{r}_0 \) oscillating with frequency \( \omega \), and is determined by the metal surface. In terms of the potential, \( \mathbf{G}(\mathbf{r},\mathbf{r}_0;\omega) \), at a point \( \mathbf{r} \) due to a unit oscillating charge source at a point \( \mathbf{r}_0 \), \( \mathbf{G}(\mathbf{r},\mathbf{r}_0;\omega) \) can be constructed as

\[
\mathbf{G}(\mathbf{r},\mathbf{r}_0;\omega) = -\nabla_{\mathbf{r}} \nabla_{\mathbf{r}_0} \mathbf{G}(\mathbf{r},\mathbf{r}_0;\omega) .
\]  

(4.3)

Using equation (4.2), the secular equation for the perturbed frequencies of the electric field can be written as

\[
D(\omega) \equiv \left| I - \alpha(\omega) \mathbf{G}(\mathbf{r},\mathbf{r};\omega) \right| = 0
\]  

(4.4)
where, for simplicity of notation, we have replaced \( r_0 \) by \( r \) and thus the atom is now taken at the point \( r \). The zeros of \( D(\omega) \) give the frequencies of the electric field modes as perturbed by the presence of the atom and the metal surface, whereas the poles correspond to the frequencies of the electric field modes in the presence of the metal surface alone (Mukhopadhyay and Mahanty 1975).

The change, \( E_s \), in the zero-point energy of the field, which is the dispersion self-energy of the atom at 0°K, is thus given by (Mahanty and Ninham 1976)

\[
E_s = \frac{1}{2\pi i} \oint \frac{\hbar \omega}{2} \frac{d}{d\omega} \left[ \ln D(\omega) \right] d\omega
= \frac{\hbar}{4\pi} \int_{-\infty}^{\infty} \ln[D(i\xi)] \, d\xi
= -\frac{\hbar}{2\pi} \int_{0}^{\infty} \alpha(i\xi) \, \text{Tr} \frac{G(r, r, i\xi)}{\ln D(\omega)} \, d\xi
\]

(4.5)

where the contour in the first integral encloses the positive real axis in the complex \( \omega \)-plane. An integration by parts and then a change of the variable to \( \omega = i\xi \) leads to a more useful form of \( E_s \) which is given in the second integral. The third integral is obtained by substituting the expression for \( D(\omega) \), given in equation (4.4), and expanding the logarithm in a series in powers of the polarizability of the atom and retaining only the leading order term.

It may be mentioned that the quantity \( G(r, r_0; \omega) \) and hence \( \text{Tr} \frac{G(r, r; i\xi)}{\ln D(\omega)} \) consist of two parts. The first part, \( G_D(r, r_0; \omega) \), is a direct contribution due to the source and does
not depend upon the position of the atom relative to the surface. For a point atom, this gives a divergence in the corresponding expression for $\text{Tr}_G(r,r;\imath \xi)$ and hence equation (4.5) leads to a divergent result for the self-energy of the atom. This divergence is unphysical and may be removed by introducing the finite size of the atom (Mahanty and Ninham 1976). In any case, such a term is not of any interest in calculating the van der Waals interaction energy, $E_I$, of the atom with the metal surface and hence may be dropped from the analysis. The other contribution, $G_I(r,r_0;\omega)$, to $G(r,r_0;\omega)$ comes from the charges induced in the metal by the source and yields the desired interaction energy, which may thus be expressed as

$$E_I = -\frac{\hbar}{2\pi} \int_0^{\infty} \alpha(\imath \xi) \text{Tr}_G(r,r;\imath \xi) d\xi \quad (4.6)$$

Equation (4.6) constitutes the basis of our analysis.

The polarizability that appears in equation (4.6) depends in a complicated way on the interaction between the atom and its surrounding medium. However, to facilitate the integration in equation (4.6), it will be presumed that the atom has a dominant absorption frequency at $\omega_0$, so that

$$\alpha(\omega) = \frac{\alpha_0 \omega_0^2}{\omega_0^2 - \omega^2} \quad (4.7)$$

where $\alpha_0$ is the static polarizability of the atom.
4.3 Interaction with a Flat Surface

The interaction of an external oscillating charge source with a flat metal surface has been studied in Section 2.2. The quantity of interest in evaluating the van der Waals interaction of an atom with a metal surface is \( G_I(\Sigma, r_0; \omega) \) and may be obtained from the expression for the potential \( \phi \), given in equation (2.5) for \( Z > 0 \), when \( q \) is set equal to one and the part of \( \phi \) which is directly due to the charge source is removed. Thus

\[
G_I(\Sigma, r_0; \omega) = -\omega_s^2 \int_0^\infty \frac{J_0(K|R-R_0|) \exp(-K(Z+Z_0))}{\beta^2\gamma(\gamma+K) - \omega_s^2} \, dK. \quad (4.8)
\]

The cut-off in the \( K \)-integration is ignored here as it is insignificant if the source is not very close to the surface.

It may be recalled that in deriving equation (4.8), the equilibrium electron density profile at the surface is taken to form a step-function and the positive ions are replaced by a uniform positive background filling the half-space \( Z \geq 0 \).

Using equations (4.3) and (4.6)-(4.8), the van der Waals interaction energy, \( E_I \), of an atom with the metal surface can be expressed as (Mahanty and Paranjape 1977)

\[
E_I = -\frac{\hbar \alpha_0 \omega_0^2 \omega_s^2}{2\pi} \int_0^\infty d\xi \int_0^\infty dK \frac{K^2 \exp(-2KZ)}{(\omega_0^2 + \xi^2)\{\beta^2\gamma(\gamma+K) - \omega_s^2\}_{\omega=i\xi}} \quad (4.9)
\]

where

\[
I_1 = \frac{\omega_s}{\omega_0 + \omega_s}
\]
\[
I_2 = \frac{3\beta \omega_0 \omega_S^2}{Z} \int_0^\infty \frac{(\omega_0^2 + \xi^2)^{1/2}}{(\omega_0^2 + \xi^2) (\omega_S^2 + \xi^2)^2} \, d\xi
\]
\[
I_3 = \frac{3\beta^2 (3\omega_0^2 + 9\omega_0 \omega_S + 8\omega_S^2)}{8\omega_S (\omega_0 + \omega_S)^3} \frac{1}{Z^2}
\]

and the second line of equation (4.9) is obtained by expanding the algebraic part of the integrand in the first line in a Taylor series in powers of \( K \) and retaining only the first three terms. The expansion explicitly gives the effect of spatial dispersion on the van der Waals interaction energy. The inclusion of second term in equation (4.9) leads to a weakening in the conventional inverse-cube dependence \( (Z^{-3}) \) of the interaction energy, which agrees with the result of Kleiman and Landman (1974) but not with that of Zaremba and Kohn (1976). The disagreement with the conclusion of Zaremba and Kohn (1976) may be due to the sharp discontinuity in the equilibrium electron density at the metal surface in the present case. A similar discrepancy has also been mentioned in Section 2.2 for a charge source situated outside a metal surface.

4.3.1 Surface Plasma Oscillations

The bulk plasma oscillations have been considered in Section 1.3.2. When a surface is created, surface plasmons appear. Mathematically the phenomenon arises due to the fact that the density fluctuations in the metal have to satisfy certain boundary conditions at the surface. The surface plasmons are sensitive to the electron density at the surface as has recently been discussed by Boardman \textit{et al} (1975). The surface
plasmons have been found to contribute to the image potential (Ritchie 1972), surface energy (Schmit and Lucas 1972, Heinrichs 1973b), and the van der Waals interaction between two metal surfaces (Heinrichs 1975a). The review articles by Economon and Ngai (1974) and Raether (1977) deal with the surface plasmons in detail.

The hydrodynamic model of the electron gas offers a good explanation of the surface plasmon dispersion. The poles in the integrand in equation (4.8) basically correspond to the surface plasmon dispersion which is thus given by

\[ \beta^2 \gamma (\gamma + K) - \omega_s^2 = 0 \]  

(4.11)

Equation (4.11) can easily be solved for \( \omega \) to give the well-known result (Heinrichs 1973a, 1975a)

\[ \omega = \frac{1}{2} \left[ \left( 2 \omega_p^2 + \beta^2 K^2 \right)^{1/2} + \beta K \right] . \]  

(4.12)

For \( K = 0 \), equation (4.12) gives \( \omega = \omega_s = \omega_p/\sqrt{2} \), which is the surface plasmon frequency, and may also be obtained by using the image result of classical electrostatics, given in equation (2.6). Boardman et al (1974) have shown that for small wave vectors a surface plasmon mode always occurs at the frequency \( \omega_s \), irrespective of the nature of the electron density profile at the surface.

The dependence of the surface plasmon frequency on the wave vector, \( K \), is of special interest because of its sensitivity to the electronic structure of the metal surface. For a step-
function profile at the surface, equation (4.12) shows that this dependence increases monotonically with the wave vector. Bennett (1970) has found that if the equilibrium electron density at the metal surface falls linearly to zero, then the surface plasmon frequency first decreases and then increases with further increase in the wave vector. The positive background in his analysis has also been taken to form a linear profile at the metal surface. In agreement with the result of Bennett (1970), Egiluz et al (1975) have also shown that the slope of surface plasmon dispersion at K = 0 changes sign if the diffuseness of the electron density profile at the surface increases from zero. The effect of retardation on the surface plasmons in metals has recently been considered by Egiluz and Quinn (1976) who have also allowed for a smoothly varying electron density profile at the surface. Boardman et al (1975) have obtained a dispersion formula for the surface plasma oscillations using a double step-function model of the metal surface. This contains two adjustable parameters so that they could obtain a good agreement with the experimental results of Kunz (1966). Using high energy electron transmission technique, Kunz (1966) has found that the dispersion curve shows a small dip followed by an increase in the frequency when K is further increased (Boardman et al 1975). More recently Krane and Raether (1976) have measured the surface plasmon dispersion in aluminium and indium by energy-loss experiments with 50-KeV electrons. Their results are accounted very well by Forstmann and Stenschke (1978) who have used a double step-function model of the metal surface and also included the effect of retardation.
An early attempt to obtain approximate surface plasmon dispersion in a metal foil with an abrupt change of the electron density at the bounding surfaces has been made by Ritchie (1963). His result for a thick foil agrees with equation (4.12) if only the linear term in \( K \) is retained. Equation (4.12) is also implicit in the analysis of Ritchie and Marusak (1966) who have given it in terms of the bulk dielectric function of the electron gas. A review of some aspects of surface plasmon in solids has been compiled by Ritchie (1973). Heinrichs (1973c) has presented an alternative treatment for the surface plasmon dispersion which consists of replacing the dielectric response function in the constitutive relation connecting the displacement field to the electric field by its asymptotic expression in the bulk region. The treatment is referred to as a dielectric approximation and leads to a linear term in \( K \) in the dispersion curve which is one-half of its value in the specular case. The method is found to be superior to the step-density approximation.

The above discussion is mainly confined to the determination of surface plasmon dispersion using hydrodynamic model of the electron gas. Newns (1970) has employed a time-dependent Hartree approximation to calculate surface plasmon dispersion. The RPA has been extensively used in the calculation of surface plasmon dispersion (Feibelman 1968, 1973; Harris and Griffin 1971; Beck and Celli 1972; Inglesfield and Wikborg 1974) and it has been found that if the potential barrier at the surface is represented by a finite step potential then the agreement with the experimental results is good (Beck and Celli 1972). Using RPA, Feibelman (1971) has shown that the infinite wavelength surface plasmon frequency is \( \omega_s \), irrespective of the electron
density profile at the surface.

4.4 Response of a Metallic Sphere

The behaviour of the aggregates of metal atoms as catalysts is well known (Anderson 1975). Although such aggregates are not necessarily spherical, it is of interest to study the response of a metallic sphere to external charged and neutral particles. The van der Waals interaction between macroscopic particles is of some significance in dyeing and washing processes as is discussed by Langbein (1971, 1974). A study of the interaction with spherical surfaces has also aesthetic importance. The van der Waals interaction of an atom with a metallic sphere has been of some theoretical interest in recent years (Schmeits and Lucas 1975, 1977; Cole and Schmeits 1978). The effect of curvature on the plasmon-mediated interaction between physically adsorbed atoms has recently been studied by Schmeits and Lucas (1978).

Here we employ the hydrodynamic model of the electron gas to calculate the response of a metal sphere to an external oscillating charge source, and use the result to find the van der Waals interaction of an atom with the sphere. The formalism directly leads to the dispersion relation for plasma oscillations in the metallic sphere which has been of considerable interest (Boardman and Paranjape 1977, Ruppin 1978).

We consider a metal sphere of radius $a$ with its centre as the origin. An external oscillating charge source of strength $q$ and frequency $\omega$, situated at a point $r_0$, induces density fluctuation, $n_1$, in the metal sphere. If the equilibrium electron
density of the sphere falls off abruptly from its bulk value $n_1$ to 0 at the surface of the sphere, then by using the basic hydrodynamic equations (1.10) in conjunction with equation (1.11), the equation satisfied by $n_1$ in the time-independent form can be expressed as

\[(\nabla^2 - \lambda^2)n_1 = 0 \quad r < a\]  (4.13)

where $\lambda^2$ is defined in equation (1.13). In the vacuum, i.e. for $r > a$, $n_1$ can be set equal to zero. Equation (4.13) can easily be solved for $n_1$ to give

\[n_1 = \sum_{\ell m} C_{\ell m} \left(\frac{\pi}{2\lambda r}\right)^{\ell/2} I_{\ell+1/2}(\lambda r) Y_{\ell m}(\theta, \phi)\]  (4.14)

where $I_{\ell+1/2}(\lambda r)$ are the modified spherical Bessel functions of the first kind (Abramowitz and Stegun 1965) and $Y_{\ell m}(\theta, \phi)$ are the spherical harmonics. The coefficient $C_{\ell m}$ is to be determined by using the specular boundary condition which, by using the first of equations (1.10) in conjunction with equation (1.11), can be expressed as

\[E_0 \frac{\partial \phi}{\partial r} \bigg|_{r=a} - m^2 \frac{\partial^2 n_1}{\partial r^2} \bigg|_{r=a} = 0\]  (4.15)

where $\phi$ is the potential due to the oscillating charge source and is given by Poisson's equation in the set of equations (1.10). Using equations (4.14) and (4.15), and the boundary conditions that $\phi$ and its normal derivative across the surface are continuous (Heinrichs 1973d) we get
\[
C_{\ell m} = -\frac{q}{\varepsilon} \left(\frac{2\lambda a}{\pi}\right)^{1/2} \left(\frac{\ell \omega^2}{D_{\ell}}\right) \frac{a^{\ell-1}}{r_0^{\ell+1}} Y_{\ell m}(\theta, \phi) \tag{4.16}
\]

where

\[
D_{\ell} = \omega^2 (\ell+1) I_{\ell+3/2}(\lambda a) - (\omega^2 - \omega^2 P) \ell I_{\ell-1/2}(\lambda a) \quad . \tag{4.17}
\]

Equations (4.14) and (4.16) determine the response of the metal sphere to an external oscillating charge source.

### 4.4.1 Plasmon Frequencies

The above analysis can be used to find the plasmon frequencies of a metal sphere. The zeros of \( D_{\ell} \), defined in equation (4.17), give the dispersion formula for plasma oscillations in the sphere. In the local approximation, \( \beta = 0 \), and thus the modified spherical Bessel functions in equation (4.17) may be replaced by their asymptotic forms to give the well-known result for the eigenfrequencies of the surface modes (Lucas 1973)

\[
\omega^2 = \frac{\ell \omega^2 P}{2\ell+1} \tag{4.18}
\]

The dispersion formula, given in equation (4.17) when \( D_{\ell} \) is equated to zero, agrees with the recent result of Ruppin (1978), and shows that the frequencies of plasma oscillations move to higher values as the diameter of the particle decreases (Ruppin 1978). Ruppin (1978) has also included the effect of diffuseness of the equilibrium electron density by means of a linear profile. It has been found that both diffuseness and spatial dispersion can cause significant shifts of the plasmon
frequencies. The shifts are, however, in opposite directions, so that the combined influence of both the effects is relatively small.

The surface plasma oscillations in small metallic particles have been detected by Fujimoto and Komaki (1968) from energy loss spectrum of transmitted electrons. Kreibig and Zacharias (1970) have investigated surface plasma losses in small Ag and Au particles embedded in a medium with dielectric constant \( \varepsilon_a = 2.37 \) by using 51-KeV electrons. They have noted that the maximum in the transition probability shifts to modes with higher \( \ell \) with increase in the radius of the particle. The problem of the optical absorption by small metal particles has also been of considerable interest (Ganière et al 1975). The incident light polarizes the electron gas in the metal particle, and produces oscillations with the frequency of the light. When this frequency approaches a natural frequency of the electron gas in the particle, i.e. the surface plasmon frequency, a resonant absorption occurs. Ganière et al (1975) have given the measured positions of the peaks in the absorption spectra of small silver particles, and observed that they moved to lower frequencies (i.e. longer wavelength) as the particle diameter is decreased below 100 Å. They could not explain this behaviour by using simple theoretical arguments, and have concluded that there exists some size effect which may be responsible for this phenomenon.

Ascarelli and Cini (1976) have employed a hydrodynamic model to explain the "red shift" of the surface plasmon resonance absorption by fine metal particles with decrease in the size of
the particles. The phenomenon is explained in terms of the diffuseness of the metal particle surface. They have noticed that the diffuseness in the sharp surface can be introduced very simply if the usual boundary conditions are applied at a point just outside the surface. Thus the density distribution is not confined to the region where the unperturbed density equals the bulk value, but is allowed to spread. The approach introduces a 'surface width' and gives the negative surface plasmon dispersion for a planar surface at low values of the wave vectors, as expected at a diffuse interface (cf. Section 4.3.1). The same idea, when applied at a spherical surface with reasonable 'surface width', gives a 'red shift' of surface plasmon frequencies that agrees fairly well with the experimental data of Ganière et al (1975).

A detailed theoretical study of the surface plasmon modes of a metal sphere embedded in a dielectric medium has been made by Boardman and Paranjape (1977) who have considered the effects of retardation, spatial dispersion and surface structure in their formalism. The inclusion of retardation becomes important for particle sizes which are of the order of 1000 Å. The spatial dispersion is found to exert a significant influence for small spheres, which is similar to the large dispersion for small wavelengths for a semi-infinite system. The surface structure has been included by means of a double step-function profile. The effect of structure weakens as the radius of the sphere increases, i.e. the role of inhomogeneity is less significant in the retardation than in the electrostatic regime. However, the effect of structure becomes stronger as $\lambda$ increases which is expected, because for $\lambda \gg 1$, the field solutions are
less sensitive to the curvature of the surface and the effect of structure for a planar surface is found to be large (Boardman et al 1976). Their results are consistent with the experimental data of Ganière et al (1975) if the surface structure is adjusted appropriately.

The optical absorption of ultrafine metal spheres has recently been studied by Granqvist and Hunderi (1978). Their calculations show that the wavelength of the observed dipole plasma peak can either increase or decrease on going to smaller diameters depending on the size of the non-metallic core and its dielectric constant. The theoretical results are found to be in reasonable agreement with the experimental data.

4.4.2 Interaction Energy

The present formalism can also be used to calculate the van der Waals interaction of an atom with the metallic sphere. Using equations (4.14) and (4.15) in Poisson's equation, given in equations (1.10), the potential, $\phi$, due to the oscillating charge source can be worked out. For $r > a$, we obtain

$$\phi = \frac{q_0^2}{a} \sum_{\ell=1}^{\infty} \frac{\ell I_{\ell+3/2}(\lambda a)}{D_\ell} \left(\frac{a^2}{rr_0}\right)^{\ell} P_\ell(\cos \Omega) + \frac{q}{|r-r_0|} \quad r > a$$

(4.19)

where $\Omega$ is the angle between the vectors $\mathbf{r}$ and $\mathbf{r}_0$, and $D_\ell$ is given by equation (4.17). Equation (4.19) is exact within the framework adopted here and gives the effect of spatial dispersion on the induced potential due to the oscillating charge source. In the absence of spatial dispersion, the modified spherical Bessel functions in equation (4.19) may be replaced by their asymptotic forms to give the standard result of classical
electrostatics (Jackson 1962) provided the quantity 
\[ \varepsilon_0 = 1 - \left( \frac{\omega_p}{\omega} \right)^2 \] is taken as the local dielectric constant of the medium inside the sphere.

The van der Waals interaction energy, \( E_I \), of an atom with the metallic sphere can now be written with the help of equations (4.3), (4.6), (4.7) and (4.19) as

\[
E_I = \frac{\hbar \alpha_0 \omega_0^2}{2 \pi a^3} \sum_{\ell=1}^{\infty} \frac{\ell(\ell+1)(2\ell+1)}{\left( \frac{a}{R} \right)^{2\ell+4}} \int_0^{\infty} \frac{d\xi}{(\omega_0^2 + \xi^2)} \left\{ \frac{I_{\ell+3/2}(\lambda a)}{D_\ell} \right\}_{\omega=\xi}.
\]

If the effect of spatial dispersion is neglected then equation (4.20) reduces to

\[
E_I = -\frac{\hbar \alpha_0 \omega_p}{4a^3} \sum_{\ell=1}^{\infty} \frac{(\ell+1)(2\ell+1)}{\left( \frac{\omega_p}{\omega_0} \right) + \left( \frac{(2\ell+1)}{\ell} \right)^2} \left( \frac{a}{R} \right)^{2\ell+4}.
\]

Equations (4.20) and (4.21) give the attractive part of physisorption energy on the metallic sphere. Recently Schmeits and Lucas (1977) have employed a quantum mechanical formulation to obtain equation (4.21). This equation is also implicit in their earlier work where the result is expressed in terms of the dynamic polarizability \( \alpha(\omega) \) of the atom and the dynamic dielectric response function \( \varepsilon(\omega) \) of the solid (Schmeits and Lucas 1975). It is clear from the analysis of Cole and Schmeits (1978) that the form of equation (4.21) for a sphere of sufficiently large radius is similar to that for a flat surface. Using equation (4.21), the physisorption energy, for a neon atom adsorbed on a solid aluminium sphere, as a function of the radius of the sphere has been plotted by Schmeits and Lucas (1977), and it has been found that the interaction becomes weaker with respect
to the result for a planar surface.

4.5 Interaction involving a Void

Voids are formed in metals by neutron irradiation and have been a subject of extensive study in recent years (Ferrell et al 1976, Jena et al 1976, Maksimenko et al 1977). Apart from their intrinsic scientific interest, they are also of technological importance (Lucas 1973). The amount of surface area introduced into irradiated samples, due to the formation of voids, can be very large as compared with the area of the external boundaries. Lucas (1973) has calculated that part of the surface energy of an isolated void in a metal, which is due to the existence of surface plasmon characteristic of the spherical boundary of the void. The interaction between two voids is also calculated by him as it is important in explaining physically observable array of voids in certain materials. His analysis is based on the assumption of a local dielectric response function. The dispersion energy between two spherical cavities in a dielectric has recently been determined by Ronveaux et al (1975).

The van der Waals interaction of an atom in a void with the spherical boundary has been of some theoretical interest in the local approximation (Schmeits and Lucas 1975, 1977; Cole and Schmeits 1978). Here we introduce the effect of spatial dispersion to calculate it by using the hydrodynamic model of the electron gas. The analysis also gives interaction of a charged particle with the void, and surface plasmon dispersion which is characteristic of the void geometry.
We consider an isolated spherical void of radius $a$ in a metal, and take the centre of the void as the origin. An oscillating charge source of strength $q$ and frequency $\omega$, located at a point $r_0$ in the void, produces density deviation $n_1$ in the metallic region. If the equilibrium electron density, $n_0$, of the metal at the boundary of the void forms a step-function then, as we have seen in the previous Section, the equation satisfied by $n_1$ for $r > a$ becomes

$$(\nabla^2 - \omega^2) n_1 = 0 \quad r > a \quad (4.22)$$

Inside the void $n_1$ can be set equal to zero. The solution of equation (4.22) may be expressed as

$$n_1 = \sum_{\ell m} c_{\ell m}^{(v)} \left[ \frac{\pi}{2 \lambda r} \right]^{1/2} K_{\ell + 1/2}(\lambda r) Y_{\ell m}(\theta, \phi) , \quad r > a \quad (4.23)$$

where $K_{\ell + 1/2}(\lambda r)$ are the modified spherical Bessel functions of the third kind (Abramowitz and Stegun 1965), and $c_{\ell m}^{(v)}$ is an arbitrary coefficient which is to be determined by using the boundary condition that the normal component of current at the surface of the void must be zero. The condition is given by equation (4.15) and, when used in conjunction with the second of equations (1.10) and equation (4.23) leads to the following result

$$c_{\ell m}^{(v)} = -\frac{q}{\epsilon} \left( \frac{2\lambda a}{\pi} \right)^{1/2} \frac{(\ell + 1) \lambda \omega^2 r_0^\ell}{D_\ell^{(v)}} \frac{P_0}{a + \frac{2}{\ell + 2}} Y_{\ell m}^*(\theta_0, \phi_0) \quad (4.24)$$

where

$$D_\ell^{(v)} = \ell \omega^2 K_{\ell - 1/2}(\lambda a) + (\ell + 1)(\lambda^2 - \omega^2) K_{\ell + 3/2}(\lambda a) . \quad (4.25)$$
The frequencies of plasmon modes of oscillations around a void may be obtained from the zeros of $D_{\ell}^{(v)}$. When there is no spatial dispersion, the modified spherical Bessel functions may be replaced by their asymptotic forms (Abramowitz and Stegun 1965) to give the well-known relation for the eigen-frequencies of the surface modes (Lucas 1973)

$$\omega^2 = \frac{(\ell+1)\omega_p^2}{2\ell+1}. \tag{4.26}$$

Equation (4.25) when $D_{\ell}^{(v)}$ is equated to zero, or equation (4.26) shows that the $\ell=0$ mode always occurs at the frequency $\omega_p$, which is the frequency of the bulk plasmon. Nevertheless, it represents a surface mode since the density fluctuation associated with it decays away from the surface. The mode corresponds to a radially symmetric oscillation of the electron gas. Equation (4.25) also shows that the $\ell$th mode is $(2\ell+1)$-fold degenerate.

In principle, there should be an upper bound, $\ell_h$, for the value of $\ell$. By combining equations (4.23) and (4.24), the sum over $m$ can easily be performed and the expression for $n_1$ may be expressed in terms of $Y_{\ell_0}(\Omega)$, $\Omega$ being the angle between the vectors $\vec{r}$ and $\vec{r}_0$. The value of $\ell_h$ can thus be determined by demanding that the number of fluctuations of $Y_{\ell_0}(\Omega)$ should not exceed the number of conduction electrons along a great circle of the surface of the void (Lucas 1973). However, we shall not explicitly introduce the cut-off in $\ell$ in our formalism as it is not very important if the oscillating charge source is not very close to the surface.

An exact expression for the potential, $\phi$, due to the
oscillating charge source inside the void may be worked out with
the help of equations (4.23), (4.24) and Poisson's equation,
given in equations (1.10). For \( r < a \), we get

\[
\phi = \frac{q\omega^2}{a} \sum_{\ell=0}^{\infty} \frac{(\ell+1)K_{\ell-\frac{1}{2}}(\lambda a)}{D_{\ell}^{(v)}} \left( \frac{rr_0}{a^2} \right)^{\ell} P_{\ell}(\cos \Omega) + \frac{q}{|S-S_0|}, \quad r < a
\]

(4.27)

where \( D_{\ell}^{(v)} \) is defined in equation (4.25). In the absence of
spatial dispersion, the modified spherical Bessel functions in
equation (4.27) may be replaced by their asymptotic forms to
give the usual result of classical electrostatic (Jackson 1962)
provided the dielectric constant of the metallic medium is taken
to be \( \varepsilon_0 = 1 - (\omega_p/\omega)^2 \).

The van der Waals interaction energy, \( E_I \), of an atom
in the void with the surface may be calculated by using equations
(4.3), (4.6), (4.7) and (4.27). After some algebra, we get

\[
E_I = \frac{\hbar a_0^2 \omega^2}{2\pi a^3} \sum_{\ell=1}^{\infty} \frac{\ell(\ell+1)(2\ell+1)\left(\frac{r}{a}\right)^{2\ell-2}}{\int_0^\infty \frac{d\xi}{(\omega_0^2+\xi^2)^{1/2}} \left[ \frac{K_{\ell-\frac{1}{2}}(\lambda a)}{D_{\ell}^{(v)}} \right]_{\omega=\xi}}
\]

\( \omega=\xi \)

(4.28)

In the local approximation, the above equation reduces to

\[
E_I = -\frac{\hbar a_0^2 \omega^2}{4a^3} \sum_{\ell=1}^{\infty} \frac{\ell(2\ell+1)}{(\omega_p/\omega_0) + (2\ell+1)/(\ell+1)} \left( \frac{r}{a} \right)^{2\ell-2}
\]

(4.29)

which agrees with the recent result of Schmeits and Lucas (1977)
whose analysis is based on a quantum mechanical formulation.
Equation (4.29) has been employed by Schmeits and Lucas (1977)
to show graphically the dependence of physisorption energy, for
a neon atom adsorbed on a spherical cavity in solid aluminium, as a function of radius of the cavity. They have found that the interaction is enhanced with respect to the result for a planar surface, and approaches it asymptotically for large radius of the cavity.

The systems with more complicated geometries have recently been investigated by Moussiaux et al (1977) in the local approximation. Maksimenko et al (1977) have used the RPA to study surface plasma oscillations in various geometries.
CHAPTER 5

INTERACTION NEAR BIMETALLIC JUNCTIONS

5.1 Introduction

In Chapter 4 we have studied the van der Waals interaction of a molecule with a metal-vacuum interface. The interaction has been found to be of considerable interest. Here we present similar calculations for bimetallic junctions in the hydrodynamic model of the electron gas. The general metal-metal interface is a slightly more complicated problem than the corresponding metal-vacuum interface. The problems concerning bimetallic junctions are, therefore, of some interest from a theoretical point of view as they represent the next step in complexity with respect to the surface problems. The importance of research on interfaces has recently been emphasised by Somorjai et al (1978). They have pointed out that the efforts to make a transition from surface science to a science of interface can reveal more useful information.

There are several aspects of bimetallic junctions which have been studied in recent years. The examples are the density of states and specific heat (Yaniv 1978), the interface and adhesive energies (Rouhani and Schuttler 1973, Ferrante and Smith 1973, Mehrotra et al 1976, Muscat and Allan 1977), the interface plasma oscillations (Stern and Ferrell 1960, Miller and Axelrod 1965, Forstmann and Stenschke 1978) and the electron density distribution at the interface (Bennett and Duke 1967, Rouhani and Schuttler 1973, Ferrante and Smith 1973, Mehrotra et al 1976, Muscat and Allan 1977). Of these, the last two are of
An extensive study of the density oscillations and response to an external field in systems with a non-uniform electron density has been made by Mukhopadhyay and Lundqvist (1975). As an application of their formalism to inhomogeneous systems, they have discussed plasma oscillations in bimetallic junctions with planar as well as spherical interfaces. The case of a thin metallic shell has also been considered by them and the frequencies of the plasmon modes have been determined. The dispersion of plasmons at a bimetallic junction has recently been studied by Forstmann and Stenschke (1978). The calculations have been performed by a proper combination of electrodynamics with the hydrodynamic approximation using appropriate boundary conditions at the metal-metal interface (Forstmann and Stenschke 1977).

The calculation of the electron density distribution at a metal-metal interface is of fundamental importance (Bennett and Duke 1967). A knowledge of the electron density distribution is useful in calculating adhesive energy (Rouhani and Schuttler 1973, Ferrante and Smith 1973, Mehrotra et al 1976, Muscat and Allan 1977). When the two metals are separated by a distance which is greater than the interatomic distance then the force between them is mainly due to the van der Waals interaction (Lifshitz 1956, Heinrichs 1975a, Inglesfield 1976). This force may be interpreted as if it arises from the change in the zero-point energy of surface plasmons when the metals are brought from infinity to a finite separation (Van Kampen et al 1968, Heinrichs 1975a). The electronic structure of the metal surfaces in such calculations is not very significant and may be approximated as a step-function (Heinrichs 1975a,b). However, when the metals are brought into
microscopic contact, the interaction involved is essentially different and is caused by a sharing of electrons between them. It is this distribution of electrons which is responsible for the adhesive bond between the two metals (Rouhani and Schuttler 1973, Ferrante and Smith 1973, Mehrotra et al 1976, Muscat and Allan 1977).

An approximately self-consistent calculation of the electron density distribution at a metal-vacuum interface has been performed by Smith (1969) using the density-functional formalism. Ferrante and Smith (1973) have assumed that the electron density at the metal-metal interface may be taken as a superposition of the electron densities of the separate metal-vacuum interfaces. They have used this approach to calculate the adhesive energy at the bimetallic interface. Mehrotra et al (1976) have determined the electron density distribution at the interface by assuming that there is a transfer of electrons from the higher density metal to the lower one. A similar calculation has been performed by Rouhani and Schuttler (1973). Swingler and Inkson (1977) have investigated the charge density profile near the bimetal interface by using an approach which is a simple extension of the Thomas-Fermi theory. Their results for the force between two metals agree with the exact results of Heinrichs and Kumar (1976). Heinrichs and Kumar (1976) have derived an exact expression for the force between two metals in the jellium model, when the separation between them vanishes, and expressed the result in terms of the bulk properties of the metal. A good agreement with the exact results of Heinrichs and Kumar (1976) has also been found by Smith and Ferrante (1976).
for their earlier analysis (Ferrante and Smith 1973). The interface energy of two free-electron-like metals has recently been calculated by Muscat and Allan (1977) who have obtained it as a by-product from their analysis of the electron density distribution and the potential at the interface.

The above discussion shows that the self-consistent calculations lead to a smooth variation of the electron density at the bimetallic interface. However, for simplicity, a step-function form of the electron density distribution at the interface will be assumed here. Within the framework of a hydrodynamic description of the electron gas, the crudeness arising due to a sharp cut-off for the density at the interface may not be regarded as too serious (Heinrichs 1975a,b). The model contains no information about the way the interface is formed, but assumes the existence of such an interface from the outset. The motivation for a sharp-interface model has arisen due to its success for a metal-vacuum interface in both semiclassical (Heinrichs 1975a) and quantum mechanical treatments (Beck and Celli 1970, Beck et al 1970). In both of these treatments the surface is idealized as a perfectly reflecting well-defined boundary, from which the electrons are scattered specularly. A simple alternative to the sharp-surface model has been suggested by Heinrichs (1973c,d) who has assumed that the dielectric kernel in the general constitutive relation may be replaced by its asymptotic form, in a similar spirit as the equilibrium density profile is replaced by the bulk electron density in the usual treatments.

The approach of this Chapter has recently been developed
by Mehrotra and Mahanty (1978c) and is a simple extension of the metal-vacuum interface discussed in Chapter 4. The analysis is based on the assumption that the electrons are bound on either side of the interface which scatters them specularly (Heinrichs 1975a). The results for the induced potentials due to an oscillating charge source near a bimetallic junction are given for planar as well as spherical interfaces, and are employed to evaluate the van der Waals interaction of a molecule or other impurity embedded in one of the metals with the interface. The dispersion formulae for interface plasma oscillations are discussed for both planar and spherical geometries. The boundary conditions which are used here are different from those of Forstmann and Stenschke (1978) as they have allowed a passage of current across the interface.

5.2 General Formalism

An oscillating charge source of strength $q$ and frequency $\omega$ at a point $r_0$ in a jellium induces a density deviation $n_1(r,t)$ which is superposed on the equilibrium density $n_0(r)$ of the electrons. The density deviation $n_1$ may be calculated from the set of equations (1.10) and (1.11). For a bimetallic junction with an abrupt change of the equilibrium density from $n_{01}$ to $n_{02}$ at the interface, the equation satisfied by $n_1$ in the time-independent form may be expressed as

\[
(\nabla^2 - \lambda_1^2)n_1 = 0 \quad \text{region 1}
\]

\[
(\nabla^2 - \lambda_2^2)n_1 = -\frac{q}{e} \left(\frac{\omega^2}{\beta_2^2}\right)^2 \delta(r-r_0) \quad \text{region 2}
\]
where
\[ \lambda_i^2 = \left( \frac{\omega_i^2 - \omega^2}{\Pi_i} \right) / \beta_i^2 \quad ; \quad i = 1, 2 \quad (5.2) \]

\( \omega_i \) are the bulk plasmon frequencies of the isolated metals, and the oscillating charge source is taken to be in the region 2. The parameters \( \beta_i^2 \) are \((1/3)\nu_i^2\) in the low frequency range whereas a comparison with the RPA result for bulk plasmon dispersion indicates that at high frequencies they may be replaced by \((3/5)\nu_i^2\), \( \nu_i \) being the Fermi velocities in the two metals when treated as separate systems. The potential, \( \phi(\mathbf{r}) \), due to the oscillating charge source may be calculated from Poisson's equation

\[ \nabla^2 \phi = 4\pi n_0 - 4\pi q \delta(\mathbf{r} - \mathbf{r}_0) \quad (5.3) \]

by using the boundary conditions that \( \phi \) and its normal derivative are continuous across the interface (Heinrichs 1973d).

The specular boundary conditions, which are employed to solve equation (5.1) are that the normal components of the currents must vanish at the interface on either side (Mehrotra and Mahanty 1978c), i.e.

\[ en_{0i} \left( \frac{\partial \phi}{\partial \mathbf{p}} \right)_i - m\beta_i^2 \left( \frac{\partial n_1}{\partial \mathbf{p}} \right)_i = 0 \quad ; \quad i = 1, 2 \quad (5.4) \]

where \( \partial / \partial \mathbf{p} \) is the normal space derivative at the interface. Equations (5.1), (5.3) and (5.4) provide the full screened potential throughout the entire space.

A quantity of interest in the present formalism is
$G_I(r, r_0; \omega)$ with $r$ and $r_0$ on the same side of the interface. It may be obtained from $\phi$ when $q$ is set equal to one and the part of $\phi$ which is due to the direct screened potential of the charge is removed. The van der Waals interaction energy, $E_I$, of a molecule, having polarizability $a(\omega)$, with the interface is obtained in equation (4.6) and is given by (Mahanty and Ninham 1976)

$$E_I = -\frac{\hbar}{2\pi} \int_0^\infty d\xi a(i\xi) Tr G_I(r, r; i\xi)$$

(5.5)

where

$$G_I(r, r_0; \omega) = -V_r V_{r_0} G_I(r, r_0; \omega).$$

(5.6)

To facilitate the integration in equation (5.5) the molecule will be treated as an oscillator of characteristic absorption frequency $\omega_0$ and static polarizability $a_0$, so that equation (4.7) for $a(a)$ may be used.

5.3 Response of a Planar Interface

The general formalism outlined in Section 5.2 can be used to study the response of a planar interface. Let regions 1 and 2 be the half-spaces $Z < 0$ and $Z > 0$ respectively, so that the solution of equation (5.1) may be put in the form

$$n_1 = \left(\frac{1}{2\pi}\right)^2 \int d^2K C_1(K) \exp(iK \cdot \vec{r} + \gamma_1 Z) \quad Z < 0$$

$$= \left(\frac{1}{2\pi}\right)^2 \int d^2K C_2(K) \exp(iK \cdot \vec{r} - \gamma_2 Z)$$

$$+ \frac{q^2 \omega^2 p_2}{4\pi \varepsilon \beta^2} \exp(-\gamma_2 |r-r_0|) \quad Z > 0$$

(5.7)
where \( \mathbf{R} \) is the component of \( \mathbf{r} \) along the interface, and the quantities \( \gamma_i \) are equal to \( (K^2 + \lambda_i^2)^{1/2} \). The coefficients \( C_i(K) \) are determined by using the boundary conditions given by equation (5.4) in conjunction with equation (5.3). The induced potential \( G_1(\mathbf{r}, \mathbf{r}_0; \omega) \) may then be calculated with the help of equation (5.3), and for large \( Z_0, Z(>0) \) we obtain

\[
G_1(\mathbf{r}, \mathbf{r}_0; \omega) = \frac{\omega^2}{\omega_p^2 - \omega^2} \int dK ((\gamma_2 + K)D(K, \omega))^{-1} \left\{ \gamma_1(\gamma_1 + K) \beta_i^2 \omega_i^2 \right. \\
\left. - \gamma_2(\gamma_2 - K) \beta_2^2 \omega_2^2 \right\} (\gamma_2 + K)J_0(K |\mathbf{R} - \mathbf{R}_0|) \exp(-K|Z + Z_0|) \\
\] (5.8)

where

\[
D(K, \omega) = \frac{\omega^2}{\omega_p^2} - \Pi \left\{ \omega_i \beta_i^2 \gamma_i(\gamma_i + K) \right\} \\
\] (5.9)

and

\[
\omega_i^2 = \frac{\omega_p^2}{2} ; \; i = 1, 2 . \\
\] (5.10)

The use of the image theory of classical electrostatics for non dispersive media gives (Jackson 1962)

\[
G_1(\mathbf{r}, \mathbf{r}_0; \omega) = -\frac{1}{\varepsilon_2} \left( \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right) \frac{1}{|\mathbf{r} - \mathbf{r}_0_{im}|} \\
\] (5.11)

where \( \mathbf{r}_0_{im} = (R_0, -Z_0) \) and \( \varepsilon_i(\omega) = 1 - (\omega_{p_i}/\omega)^2 \). Equation (5.11) may be recovered from equation (5.8) by expanding the algebraic part of the integrand in powers of \( K \) and retaining only the leading order term.
The form of $D(K,\omega)$ given in equation (5.9) is also true for imaginary $\gamma_i$, but in this case acceptable solutions of equation (5.1) are outgoing waves at large distances from the interface (Economou and Ngai 1974). The zeros of $D(K,\omega)$ correspond to the dispersion formula for the interface plasmon modes and in the limit of $K = 0$ yield the familiar relation (Stern and Ferrell 1960, Inkson 1971, Anderson 1974)

$$\omega^2 = \omega^2_{S_1} + \omega^2_{S_2}. \quad (5.12)$$

The possibility of interface plasma oscillations, at frequency given by equation (5.12), in double films composed of two different metals has been first pointed out by Stern and Ferrell (1960) using a classical argument. They have also given a simple quantitative explanation for a change in the surface plasma frequency of a clean metal surface when it is covered with a layer of a dielectric. An experimental detection of the interface plasma oscillations in a bimetallic junction has been made by Miller and Axelrod (1965). For a metal-metal interface composed of thin films of Bi and Mg, they have measured characteristic electron energy loss spectra and have found a new loss which is consistent with equation (5.12). However, the corresponding loss for Al-Mg film could not be reproduced by them as the interface was not well defined in this case.

In general, it is difficult to solve equation (5.9) for $\omega$ when $D(K,\omega)$ is equated to zero. However, for $n_{02} = 0$ equation (5.8) reduces to equation (4.8) for the metal-vacuum interface (Mahanty and Paranjape 1977) and the resulting dispersion formula can easily be solved for $\omega$ to give the well-known
relation (Heinrichs 1975a)

\[ \omega = \frac{1}{2} \left[ (2\omega_p^2 + \beta_1^2 k^2)^{\frac{1}{2}} + \beta_1 k \right] \]  

(5.13)

which is discussed in Section 4.3.1.

Using equations (5.5), (5.6), (5.8) and (4.7), the van der Waals interaction energy, \( E_I \), of a molecule in region 2 with the interface can be written in the absence of spatial dispersion as

\[
E_I = -\frac{\hbar \omega_0 \omega_0^2}{8Z^3 (\omega_0^2 - \omega_0^2)(\omega_0^2 + \omega_0^2 - \omega_0^2)} \left\{ (\omega_0^2 S_1 + \omega_0^2 S_2)^{\frac{1}{2}} (\omega_0^2 - \omega_0^2 S_2) 
+ \omega_0 (\omega_0^2 S_2 - \omega_0^2 S_1) + \omega_0 (\omega_0^2 S_1 + \omega_0^2 S_2 - \omega_0^2) \right\} .
\]

(5.14)

The interaction energy, given by equation (5.14), is attractive or repulsive depending on whether \( \omega_0^2 S_1 > \omega_0^2 S_2 \) or \( \omega_0^2 S_1 < \omega_0^2 S_2 \). The effect of spatial dispersion on the interaction energy may be studied in a systematic way by following a procedure which is similar to that of Section 4.3. However, the expressions involved are rather lengthy and will not be given here.

The \( Z^{-3} \) dependence of the interaction energy for a molecule near the interface of two dielectric media is well known in the literature (Israelachvili 1972, Mahanty and Ninham 1973a). Israelachvili (1972) has employed the method of images of classical electrostatics to calculate the van der Waals interaction of an atom with the interface between two dielectrics. In agreement with the fact that the image force on a real charge near an interface can either be attractive or repulsive, he has
mentioned that the van der Waals interaction of the atom with the interface may also be either attractive or repulsive. His analysis is, however, not rigorous as it is based on the assumption of additivity. Subsequently Mahanty and Ninham (1973a) have employed the concept of dispersion self-energy to elucidate the nature of the van der Waals interaction of an atom with an interface separating two dielectric media. The size of the atom has been explicitly considered by them. For an atom of sufficiently small size at a somewhat large distance from the interface, they have reproduced the familiar $z^{-3}$ dependence of the interaction energy.

5.4 Spherical Interface between Metals

Let us now consider a more difficult interface, one that is spherical rather than flat. Although highly idealized, the present analysis provides further understanding of metallic interfaces. The interface is defined by taking the space within a sphere of radius $a$ as region 1 and the outer space as region 2. Using equation (5.1) the density fluctuations in the two components may be written as

$$n_1 = \sum_{\ell m} C_{\ell m}^{(1)} \left( \frac{\pi}{2\lambda_1 r} \right)^{\frac{1}{2}} I_{\ell+\frac{1}{2}}(\lambda_1 r) Y_{\ell m}(\theta, \phi) \quad r < a$$

$$= \sum_{\ell m} C_{\ell m}^{(2)} \left( \frac{\pi}{2\lambda_2 r} \right)^{\frac{1}{2}} K_{\ell+\frac{1}{2}}(\lambda_2 r) Y_{\ell m}(\theta, \phi) \quad (5.15)$$

$$+ \frac{q u^2}{p_2} \frac{\exp(-\lambda_2 |r-r_0|)}{4\pi e \sigma^2 \rho^2} \quad r > a$$

where $\lambda_1^2$ are given by equation (5.2). The last term in equation (5.15) for $r > a$ arises due to the presence of a
δ-function source in this region of equation (5.1). The coefficients $C_{\ell m}^{(i)}$ are evaluated with the help of equations (5.4) and (5.3), and it is observed that the poles in $C_{\ell m}^{(i)}$ are given by the relation

$$D_\ell = \ell(\ell+1)\omega_1^2 \frac{\omega_2^2}{P_1 P_2} \lambda_{\ell+3/2}(\lambda_1 a)K_{\ell-1}^{(2)}(\lambda_2 a)$$

$$- \left\{ (\ell+1)\frac{\omega_1^2}{P_1} I_{\ell+3/2}(\lambda_1 a) - \ell(\frac{\omega_1^2}{P_1} - \omega_2^2) I_{\ell-1/2}(\lambda_1 a) \right\}$$

$$\left\{ \ell\frac{\omega_1^2}{P_1} K_{\ell-1/2}(\lambda_2 a) - (\ell+1)(\omega_2^2 - \omega_1^2) K_{\ell+3/2}(\lambda_2 a) \right\} = 0 .$$

(5.16)

The general form of equation (5.16) remains valid even for complex $\lambda_1$, but in this case the solution of equation (5.1) is to be expressed in terms of outgoing waves for $r \to \infty$ (Economou and Ngai 1974). On replacing the modified spherical Bessel functions in equation (5.16) by their asymptotic forms, we obtain the well-known result for the eigenfrequencies of the interfacial modes (Mukhopadhyay and Lundqvist 1975)

$$\omega^2 = \frac{\ell\omega_1^2}{P_1} + (\ell+1)\frac{\omega_2^2}{P_2} \frac{\omega_2^2}{(2\ell+1)} .$$

(5.17)

Equation (5.17) may also be obtained by using classical electrostatics (Jackson 1962) provided the dielectric constants of the two components are replaced by $\varepsilon_1(\omega) = 1-\omega_1^2/\omega^2$. As $\ell \to \infty$, equation (5.17) reduces to equation (5.12) which is the plane interface result. This arises due to the fact that for large values of $\ell$, the density fluctuations do not sense the curvature of the interface (Boardman and Paranjape 1977).
For a metallic sphere in vacuum and a metal having a spherical void, the dispersion formulae for plasma oscillations can be obtained from equation (5.16) by equating the first and the last factors in the second term of $D_\lambda$ to zero, respectively. The former agrees with the recent result of Ruppin (1978), whereas the latter in the absence of spatial dispersion reduces to a familiar relation (Lucas 1973) obtainable from equation (5.17) by setting $\omega_{p_1}$ equal to zero. The dispersion formulae for the plasma oscillations in a metallic sphere and a metal having a spherical void are discussed in Sections 4.4.1 and 4.5 respectively.

Using equations (5.3), (5.4) and (5.15), the induced potential $G_I(\vec{r}, \vec{r}_0; \omega)$ can be worked out exactly in terms of the modified spherical Bessel functions. The final result is rather tedious and will not be reproduced here. However, for an interface of large radius and $r_0, r \gg a$ we obtain in the leading order

$$G_I(\vec{r}, \vec{r}_0; \omega) = \frac{\omega^2(\omega_0^2 - \omega^2)}{a(\omega^2 - \omega_0^2)} \sum_{l=1}^{\infty} \frac{l}{(2l+1)\omega^2 - l\omega_0^2} \frac{1}{P_0} \frac{P_{l+1}(\cos \Omega)}{P_l(\cos \Omega)}$$

(5.18)

where $\Omega$ is the angle between the vectors $\vec{r}$ and $\vec{r}_0$.

Equation (5.18) agrees with the corresponding result of classical electrostatics for non dispersive media (Jackson 1962), and may be employed to write the van der Waals interaction energy, $E_I$, of the molecule with the interface, given in equation (5.5), as
Equation (5.19) shows that, for $r > a$, the interaction energy varies as $r^{-6}$ in the leading order. This dependence is also apparent in the analysis of Israelachvili (1972) when applied to calculate the van der Waals interaction of an atom with a spherical interface between two dielectrics.

The case for a molecule well within the inner space of an interface of large radius can be studied by adopting the same procedure. The expression for the density deviation $n_1$ due to an inner oscillating charge source may be written with the help of equation (5.15) by interchanging the region $r > a$ with $r < a$, the suffix $1$ with $2$, and $I_{l+\frac{1}{2}}$ with $K_{l+\frac{1}{2}}$. Using equations (5.3), (5.4), and this expression for $n_1$, the induced potential $G_I(r, r_0; \omega)$ is calculated exactly in terms of the modified spherical Bessel functions. The exact result is somewhat tedious, but in the local approximation it agrees with the result of classical electrostatics (Jackson 1962) provided the dielectric constants of the constituent media are replaced by $\varepsilon_i(\omega) = 1 - \omega^2_{P_1}/\omega^2$. The local result for $G_I(r, r_0; \omega)$ may be obtained from equation (5.18) by interchanging $\omega_{P_1}$ with $\omega_{P_2}$, $l$ with $(l+1)$, replacing $a^2/rr_0$ by $rr_0/a^2$, and retaining
\( P_2(\cos \theta) \) as such. The expression is employed to calculate the van der Waals interaction energy of a molecule with the interface using equations (5.5), (5.6) and (4.7), and it is found that the final result is obtainable from equation (5.19) by interchanging \( \omega_{p_1} \) with \( \omega_{p_2} \), \( \ell \) with \( (\ell+1) \), and replacing \((a/r)^{2\ell+4}\) by \((r/a)^{2\ell-2}\).

5.5 Conclusion

We have presented a simple hydrodynamic treatment for the van der Waals interaction of a molecule with a bimetallic interface. The effect of a realistic profile for \( n_0 \) is ignored here, and only that aspect of spatial dispersion is considered which arises due to the nonlocality of the dielectric response of the individual components through the pressure terms containing \( \beta_i \). In principle, there should be cut-offs in \( K \)-integrations for the planar case and sums over \( \ell \) for the spherical case, but they are disregarded here due to their insignificant role at large distances from the interface. A proper profile for \( n_0 \) will alter the results for the plasmon dispersion and the van der Waals interaction near the interface where the cut-offs in \( K \) and \( \ell \) also become important.

The expressions for the induced potentials given in equations (5.8) and (5.18) are of some interest and may be employed to calculate the force on charged particles near the interface of two media. Despite the simplicity of the approach followed here, our results for the attractive parts of the physisorption energies in non dispersive metal-vacuum systems reduce to those of Schmeits and Lucas (1977) whose analysis is based on
a quantum mechanical formulation. The results for the plasmon dispersion given in equation (5.9), when \( D(K,\omega) \) is equated to zero, and in equation (5.16) are new to our knowledge.
6.1 Introduction

The analysis of Chapters 2-5 has been carried out by assuming that there is an abrupt change in the equilibrium electron density at the interface. In spite of its simplicity, the model has enabled us to examine in detail the effect of a boundary on the dynamical behaviour of an electron gas. It gives a closed-form solution for the density response in inhomogeneous systems. For this reason its conclusions have some significance, for example, in problems involving electrostatic and van der Waals interactions near the interface. The effect of nonlocality has also been examined quite simply within this model. The model is equivalent to the infinite-barrier model which is extensively studied in recent years (Griffin et al 1974, Harris and Griffin 1975, Inglesfield and Wikborg 1975). The electrons from such a barrier reflect specularly like classical particles. This provides a boundary condition which has been used throughout our analysis in Chapters 2-5.

The use of a sharp model for a metal surface in the previous Chapter is one of the limitations of the calculations. The model is unrealistic as the electronic charge is not allowed to spill out the surface. As stated in Chapter 4, Bennett (1970) has considered the effect of charge density profiles for both positive backgrounds and electrons by assuming them to be linear. A linear profile has also been used by Ruppin (1978) in the
calculation of the plasmon frequencies of small metal spheres. A double-step model for planar (Boardman et al 1975, Forstmann and Stenschke 1978) as well as spherical (Boardman and Paranjape 1977) metal surfaces has also been studied as mentioned in Chapter 4. The effect of surface diffuseness on the plasmon dispersion has been discussed in Sections 4.3.1 and 4.4.1.

In general, it is difficult to analyse the problem with an arbitrary density profile at the interface analytically. In this Chapter a simple iteration method for solving the equation for density response near a diffuse interface is discussed in the hydrodynamic model. The analysis is carried out in the special case when the bulk electron densities of the constituent metals differ only slightly. The induced potential due to an oscillating charge source near the interface is calculated and is used to evaluate the dispersion force field on an atomic system (an atom or a molecule) near the interface. It is found that the diffuseness of the interface removes the divergence in this force field at very small separation from the interface as has been obtained in equation (4.9) for a sharp surface if the cut-off in the K-integration is ignored there. The formalism is also employed to study spherical interfaces with a sharp cut-off in the equilibrium electron density at the interface. The results for both planar and spherical interfaces are shown to be consistent with earlier calculations if the density difference between the two constituent metals is small. The approach of this Chapter is due to Mehrotra and Mahanty (1978a).
6.2 Formulation

An oscillating charge source near the interface of two metals produces an induced potential which can be used to study the force fields on charged particles in the static limit, as also the dispersion force field on an atomic system using the dispersion force field formalism (Mahanty and Ninham 1976). This potential is due to the induced density fluctuations \( n_1(\mathbf{r}, t) \) superposed on the equilibrium density \( n_0(\mathbf{r}) \) of the electrons. Using equations (1.10), the equation satisfied by \( n_1 \) in the time-independent form, when the charge source is at a point \( \mathbf{r}_0 \) and is of strength \( q \) and frequency \( \omega \), can be put in the form

\[
\begin{align*}
n_0 P(n_0) \nabla^2 n_1^1 + m(\omega^2 - \omega^2_P) n_1^1 &= -4\pi q e n_0 P(n_0) \delta(\mathbf{r} - \mathbf{r}_0) \\
&\quad + P(n_0) \nabla n_0 \cdot \nabla (e\phi - n_1^1) 
\end{align*}
\]

(6.1)

where

\[
n_1^1 = P(n_0) n_1 \quad ; \quad \omega^2_P = 4\pi n_0 e^2/m
\]

and the potential \( \phi \) is given by Poisson's equation

\[
\nabla^2 \phi = 4\pi e n_1 - 4\pi q \delta(\mathbf{r} - \mathbf{r}_0) \quad .
\]

(6.2)

The particular form of \( P(n_0) \) used here is due to the kinetic and exchange energies of the electron gas and is given in equation (1.7). Equations (6.1) and (6.2) form a set of coupled differential equations for \( n_1 \) and \( \phi \). In general, it is difficult to solve them for a diffuse interface. However, if the difference in the bulk electron densities of the two constituent metals is small then we may approximate equation (6.1) as
\[ n_A P(n_A) \nabla^2 n_1' + m(\omega^2 - \omega_A^2) n_1' = -4\pi q e n_A P(n_A) \delta(\mathbf{r} - \mathbf{r}_0) \]
\[ + P(n_A) \nabla n_0 \cdot \nabla (e^\phi - n_1') \quad (6.3) \]

with \( n_1' = P(n_A) n_1 \). \( n_A \) is the average electron number density of the bimetallic system and \( \omega_A^2 = 4\pi n_A e^2 / m \). Here we have replaced \( n_0 \) by \( n_A \) everywhere except in the gradient term on the right-hand side which gives the effect due to inhomogeneity. \( P(n_0) \) is a slowly varying function of the density and hence it is replaced by \( P(n_A) \) everywhere. The approximation made in equation (6.3) is valid only when the difference in the bulk electron densities of the two constituent metals is small and hence in this limit the general behaviour of the solution can be studied in a very simple way with the help of equations (6.2) and (6.3). Using the Green's function

\[ G(\mathbf{r}, \mathbf{r}') = \frac{1}{4\pi n_A P(n_A)} \exp(-\lambda_A |\mathbf{r} - \mathbf{r}'|) \quad (6.4) \]

where

\[ \lambda_A^2 = m(\omega_A^2 - \omega^2) / n_A P(n_A) \]

equation (6.3) can be converted into the integral equation

\[ n_1 = \frac{q e}{P(n_A)} \frac{\exp(-\lambda_A |\mathbf{r} - \mathbf{r}_0|)}{|\mathbf{r} - \mathbf{r}_0|} + \int d^3 r' G(\mathbf{r}, \mathbf{r}') \nabla n_0 \cdot \nabla (e^\phi - P(n_A) n_1). \quad (6.5) \]

We shall consider the solution of equation (6.5) obtained by iterating once, starting with the zeroth order solution.
and taking $n = (n_{01} - n_{02})/2 \ll n_A$ as the iteration parameter, $n_{01}$ and $n_{02}$ being the bulk electron densities for the two metals. By substituting the resulting first order solution for $n_1$ in equation (6.2) we can write down an expression for the potential, $\phi$, due to the oscillating charge source which would give $G_I(r,r_0;\omega)$ a quantity of our interest, when $q$ is set equal to one and the part of $\phi$ associated with the homogeneous medium of density $n_A$, i.e. $\phi(0)$ is removed.

The interaction energy, $E_I$, of the atomic system, having polarizability $\alpha(\omega)$, with the interface is derived in Section 4.2 and is given by (Mahanty and Ninham 1976)

$$E_I = -\frac{\hbar}{2\pi} \int_0^\infty d\xi \alpha(i\xi) \text{Tr} G_I(r,r_0;i\xi)$$

(6.7)

where

$$G_I(r,r_0;\omega) = -\nabla_r \nabla_{r_0} G_I(r,r_0;\omega).$$

(6.8)

The dispersion force field on the atomic system is the negative gradient of $E_I$. To facilitate the integration in equation (6.7) we shall treat the atomic system as a harmonic oscillator of characteristic absorption frequency $\omega_0$ and static polarizability $\alpha_0$ so that equation (4.7) for $\alpha(\omega)$ may be used.

6.3 Planar Interface

The formalism developed in Section 6.2 may be used to study the response of a planar bimetallic interface. At a
bimetallic interface we expect a transfer of electrons from the higher density metal to the lower one. The equilibrium electron density at the interface may thus be approximated as (Mehrotra et al. 1976)

\[ n_0 = n_A - \eta \text{Sgn}(Z) (1 - \exp(-b|Z|)) \]  

(6.9)

where \( Z \) is the distance from the interface and \( b \) is a parameter which characterizes the diffuseness of the interface. The parameter \( b \) may be determined by minimizing the energy functional for the bimetallic system with respect to \( b \) (Smith 1969, Mehrotra et al. 1976). The variations in the electron density distribution through the parameter \( b \) satisfy the condition for the conservation of total number of electrons in the bimetallic system. The particular form of \( n_0 \), given in equation (6.9), has been found useful for a metal-vacuum interface in the calculation of the work functions and surface energies (Smith 1969). A similar electronic distribution has also been considered by Rouhani and Schüttler (1973) for calculating the adhesive energies of various metallic pairs.

Using the form of \( n_0 \) given by equation (6.9) in equation (6.5) of the last Section and performing the calculations as indicated there we obtain

\[
G_I(x,x_0,\omega) = -\frac{\eta e^2 b \omega^2}{m(\omega_A^2 - \omega^2)^2} \int d^2k \, dZ' \, \text{Sgn}(Z'-Z_0) \exp\left(iK.(R-R_0)-b|Z'|\right) 
\]

\[
\left[ \exp\left(-K|Z'-Z_0|\right) - \exp\left(-\gamma_A|Z'-Z_0|\right) \right] 
\]

(6.10)
where \( \mathbf{r} = (R, Z) \), \( \mathbf{r}_0 = (R_0, Z_0) \) and \( \gamma_A^2 = k_A^2 + \lambda_A^2 \). With the help of equations (6.7), (6.8), (6.10) and (4.7), the dispersion force field on the atomic system at a sufficiently large distance from the interface can be written as

\[
F_z = -\frac{3E_I}{2Z} = -\frac{3\hbar \pi \eta e^2 \alpha_0 \omega_0^2}{4\omega_p A (\omega_p + \omega_0)^2} \frac{1}{Z^4} \left( 1 + \frac{20}{b^2 Z^2} + \ldots \right) \quad (6.11)
\]

where we have neglected terms which are exponentially small. Equation (6.11) does not contain the effect of spatial dispersion and is valid on either side of the interface.

In the asymptotic region of large \( Z \), the dispersion force field, given in equation (6.11), does not depend on the profile parameter \( b \). The correction to the force field, arising out of the profile, makes the interaction stronger than the asymptotic result. An increase in the absolute value of the interaction energy with respect to the asymptotic limit has also been obtained by Zaremba and Kohn (1976) for a metal-vacuum interface.

In the special case when \( b \to \infty \) the profile defined by equation (6.9) becomes a step-function and equation (6.11) reduces to

\[
F_z = -\frac{3\hbar \pi \eta e^2 \alpha_0 \omega_0^2}{4\omega_p A (\omega_p + \omega_0)^2} \frac{1}{Z^4} \quad (6.12)
\]

The \( 1/Z^4 \) dependence of the dispersion force is well known in the literature (Israelachvili 1972, Mahanty and Ninham 1973a). For \( \eta \ll \eta_A \), equation (6.12) agrees with the image result of Israelachvili (1972) provided spatially non-dispersive dielectric
functions for the two components are used. An expression similar to equation (6.12) has also been obtained by Mahanty and Ninham (1973a) for the dispersion force on an atom near an interface between two dielectrics.

From equations (6.8) and (6.10) it may be seen that in the limit when \( Z \to 0 \), \( \frac{\partial}{\partial Z} \text{Tr} G_{\alpha \beta}(r, r; \omega) \) does not diverge and the expression for the force field remains finite provided \( b \) is finite. However, as expected, this is not the case when \( b \to \infty \), i.e. when the profile approaches a step-function. A divergence in the force field on an atom at a very small separation from a sharp metal surface is apparent in the analysis of Mahanty and Paranjape (1977) if a cut-off in the \( K \)-integration is ignored there.

6.4 Spherical Interface

We now consider a spherical interface between metals and assume that the equilibrium electron density at the interface forms a step-function so that it can be expressed as

\[
n_0 = n_A - \eta \text{Sgn}(r-a)
\]

(6.13)

where \( a \) is the radius of the interface. The density of electrons inside the interface is \( n_{01} \), whereas outside it is \( n_{02} \). By performing the calculations as indicated in Section 6.2 for sufficiently large \( a \) and \( r, r_0 \gg a \), we obtain

\[
G_1(r, r_0; \omega) = \frac{8 \pi n e^2 \omega^2}{m a (\omega^2 - \omega_0^2)^2} \sum_{\ell=1}^\infty \left( \frac{\ell}{2\ell+1} \right) \left( \frac{a^2}{rr_0} \right)^{\ell+1} P_\ell(\cos \Omega)
\]

(6.14)

where \( \Omega \) is the angle between the vectors \( r \) and \( r_0 \), and
we have dropped exponentially decaying terms arising from the products of modified spherical Bessel functions of the first and third kinds (Abramowitz and Stegun 1965). The approximation involved in writing equation (6.14) is equivalent to the neglect of spatial dispersion which arises through the pressure term containing \( P(n_0) \).

The force field on the atomic system near the interface can be calculated by using equations (6.7), (6.8), (6.14) and (4.7). To leading order in \( 1/r \) we get

\[
F_r \equiv -\frac{3E_r}{3r} = -\frac{12\pi\eta^2 a^2 \alpha_0 \omega_0^2}{m^A P(\omega^A + \omega_0)^2} \frac{1}{r^7}. \tag{6.15}
\]

For \( \eta < n_A \) this agrees with the result of Israelachvili (1972) provided the dielectric constants of the two media in his approach are replaced by the local dielectric response functions. In order to obtain equation (6.15), only the first term in equation (6.14) is retained. The higher order terms are not evaluated here, as a detailed analysis of this problem has been presented in Section 5.4 by using suitable boundary conditions.

6.5 Conclusion

We have presented a hydrodynamic treatment to obtain the nature of dispersion force fields in weakly inhomogeneous media. The effect of spatial dispersion does not appear explicitly in the asymptotic expressions for the force fields given in equations (6.11) and (6.15). Despite the one-iteration solution for \( n_1 \) used here, the essential features of the phenomenon are there in this simple description. A feature of the
method developed here is that by making the operator on the left-hand side of equation (6.1) homogeneous we could solve the coupled set of differential equations (6.1) and (6.2) without using any boundary conditions. Alternatives to the approximation made in equation (6.3) are to replace \( n_0 \) by \( n_{01} \) or \( n_{02} \) which are also justified as the major contribution in the iterative process used here comes from the gradient term containing \( \phi \).
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A NOTE ON BOUNDARY CONDITIONS

(Appended to Ph.D. thesis entitled 'Collective Response of Electrons and Surface Properties of Metals' by R. Mehrotra)

The analysis presented in this thesis is based on the assumption that the normal component of the drift velocity at the surface of a metal is zero. This is equivalent to the infinite-barrier model of the metal surface and has been extensively used in the literature (Griffin et al. 1974; Harris and Griffin 1975; Inglesfield and Wikborg 1975; Heinrichs 1975a). The advantages and shortcomings of the model are discussed in Sections 5.1 and 6.1. As mentioned on pp.66-67, it has been found by Ascarelli and Cini (1976) that the diffuseness of the equilibrium surface in the model can be introduced very simply by applying this boundary condition for the vanishing of the normal component of the current at a point just outside the surface. This leads to better results for the surface plasmon frequencies for planar as well as spherical surfaces when compared with the experimental data (Ascarelli and Cini 1976).

The infinite-barrier model of the metal surface discussed above is equivalent to assuming that the metal boundary acts as a rigid wall. The model does not allow for modes such as ripples at the metal surface. These modes will arise at the free surface of a fluid. However, in the jellium model of the metal, the electrons are supposed to move in a uniform positive background which is regarded as rigid. A further simplification is made here by assuming that the electron density at the metal surface forms a step-function and thus the electrons at the surface are assumed to be reflected specularly (Heinrichs 1975a).
The experimental results for surface plasma oscillations obtained from low energy electron diffraction and high energy electron loss spectroscopy (Krane and Raether 1976) are in reasonable agreement with those obtained by using sharp model of the metal surface (cf. Chapter 4). On the other hand, the ripple-like modes of the electron fluid on the surface of a metal, which would arise by relaxing the boundary condition used here, are not observed experimentally nor known in the literature (Heinrichs 1975a).

The boundary condition used here at the surface of a metal is different from that used in the case of many electron atoms (Monaghan 1973) or in the case of water waves (Landau and Lifshitz 1959). The appropriate boundary condition for the oscillations of electrons in a many-electron atom is that the rate of change of the density, \( n \), of the electrons, following the motion, vanishes at the boundary (Monaghan 1973), i.e.

\[
\frac{dn}{dt} = \nabla n + \mathbf{v} \cdot \nabla n = 0
\]  

(A1)

In the other case, i.e. for water waves, the boundary condition is that the pressure should be continuous across the surface (Landau and Lifshitz 1959). The actual surface in this case is determined by looking for the surface on which this pressure difference is zero (Ledoux and Walraven 1958). Thus if \( P \) is the pressure in the water, and \( P_0 \) is the atmospheric pressure, then the surface is given by (Lamb 1945; Ledoux and Walraven 1958)

\[
\frac{\partial}{\partial t} (P - P_0) + \mathbf{v} \cdot \nabla (P - P_0) = 0
\]

(A2)
The boundary conditions given in equations (A1) and (A2) are useful for the oscillation modes of a fluid with free surface. However, because of the aforesaid rigidity of the metal surface we have used the infinite-barrier model. The success of this model in both semiclassical (Heinrichs 1975a) and quantum mechanical (Beck and Celli 1970; Beck et al. 1970) treatments has been the main reason for confining the analysis here to the boundary condition of vanishing of the normal component of the current at the metal surface.

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