Role of Collective Modes in some Surface Properties of Metals

by

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PREFACE

Excluding Chapter 1, which simply represents my collation, from many sources, of the basic concepts involved in this thesis, most of the material presented is my original contribution to the subject. The work was done in close collaboration with my supervisor, Dr J. Mahanty, and in part with Professor B.V. Paranjape who, while a visitor to the Department early in 1977, introduced me to the usefulness of the hydrodynamic model.

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In addition to the personal gratitude I hope I have expressed, it is with the sincerest warmth that I will remember the following people for having contributed so much during the course of this work.

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My wife, Angela, for her love, patience and strength, especially during the past three years, for her most satisfying arrangement and typing of this thesis, and for our children, with whom comes that special sense of worth and purpose.
The theory of the solid state for unbounded bulk samples has, since the advent of quantum mechanics, reached a high degree of sophistication, and the knowledge of the properties of a wide range of solids is adequate for their extensive technological and industrial use. However, the theoretical explanation of many well known phenomena in terms of the electronic properties of solids is far from complete, mainly because of the inherent mathematical difficulties incurred when the ubiquitous surface is introduced. Many properties associated with metal surfaces and interfaces, and of their interaction with external configurations of charges and polarisable molecules and atoms can be understood in terms of the characteristic collective oscillations (bulk and surface plasmons) of their valence or conduction electrons. The use of Bloch's hydrodynamic formalism has facilitated considerable understanding of the properties associated with metal surfaces, to which this thesis makes some further contribution.

In Chapter 1, the hydrodynamic model is defined within the context of the many-body solid-state problem, and the collective oscillations are introduced with a derivation of the hydrodynamic dispersion relations for the surface and bulk plasmons. Throughout, the step-function model for the surface is used and the well known effect of a more realistic density profile on the surface plasmon dispersion frequencies is indicated in this chapter.
Chapter 1 also contains a brief discussion on the necessity, within the hydrodynamic model, of the phenomenological introduction of an upper cutoff in the wavenumber for both bulk and surface plasmons.

The finiteness of the velocity of light is a fact of life, and while it may be neglected for interactions over very short distances, retardation is important for dispersion interactions over larger separation distances. In addition, the effect of the transversality of electromagnetic fields has a dramatic effect on the small wavenumber (or momentum) surface plasmons which, while basically of longitudinal nature, also take on a transverse character in this region. Retardation effects are considered in Chapter 2, where the hydrodynamic equation of motion is solved in conjunction with the full set of Maxwell's equations for the general case of a charge source situated between two separated metal half-spaces. This leads, in the appropriate limits, to an evaluation of the retarded dispersion interactions between two identical metals and of a charge (and hence a simple molecule) with a metal surface. The general retarded dispersion relations for the symmetric and antisymmetric surface plasmon branches in the coupled two-metal system are derived and the universal effect of retardation in reducing the van der Waals interactions by increasing their dependence on the inverse separation distance by a power, is clearly indicated in terms of its effect on the surface plasmon dispersion frequencies. The effects of retardation can always be generalised qualitatively, and for simplicity
the remaining chapters deal only with the nonretarded limit.

Following a discussion of the role of vdW forces in physisorption, and the question of an appropriate reference plane for their measurement, the explicit contributions from bulk and surface plasmons to the vdW interaction of a molecule with a metal surface are given in the normal mode analysis of Chapter 3. The normal mode analysis is also used to derive the nonretarded dispersion relations for the surface plasmon branches for two identical coupled metal half-spaces, thus demonstrating the role of bulk plasmons in their interaction. The fact that all bulk contributions vanish in the local or spatially nondispersive approximation is the reason for the common inferral that such interactions are of purely surface plasmon origin.

Of considerable interest for the practical use of metals is the understanding of the electronic properties of a bimetallic interface. A derivation of the boundary conditions which relax the infinite surface barriers at a bimetallic junction is outlined in Chapter 4. The collective modes of the bimetallic system are derived with these relaxed boundary conditions (giving the interface plasmon) and the effect of cleaving and separating the two metals is then considered. This leads to the derivation of the generalisations of the upper (symmetric) and lower (antisymmetric) surface plasmon branches well known for identical metals. In addition, a novel character of the electron response, namely the image plasmon, is predicted.
It is also argued that, while both the infinite barrier (vanishing normal current) and relaxed (continuous current) boundary conditions lead to an 'interface' mode with the expected infinite-wavelength (or zero-wavenumber) behaviour, it is the latter which describes the commonly observed interface mode and hence that this long-established phenomenon has been misunderstood.

The final Chapter 5 deals with the force on an external charge which is moving with constant velocity parallel to a metal surface. Throughout this chapter, the contributions from both bulk and surface plasmons to this dynamical interaction are given in terms of the normal mode decomposition of Chapter 3. The fact that the force components normal and parallel to the particle's motion derive from 'surface' plasmons with phase velocity greater and less than the velocity of the particle, respectively, has been interpreted on the basis of excitation of virtual and real 'surface' plasmons. While complementing this, the origin of the force components is given a much clearer physical basis in terms of the nature (and in fact symmetry properties) of the induced density, which may be written as the sum of a symmetric and an antisymmetric part, again associated with plasmons of 'fast' and 'slow' phase velocity, respectively, relative to the velocity of the external charge.

References have been kept as specific as possible throughout, and naturally many more general texts and reviews, as well as key publications in closely related fields not discussed here, have been omitted. Since these
have played important roles in helping coordinate and place in context many of the ideas here, the following are also given recognition: Pines (1956, 1961, 1964), Nozières and Pines (1958), Kadanoff and Baym (1962), Feinberg and Sucher (1970), Feibelman et al (1972), Wooten (1972), Ziman (1972), Sucher (1973), Mahan (1974), Raether (1977) and Madelung (1978).

Most of the work described in Chapters 2 to 4 has either been published or accepted for publication in the following papers:

Mahanty J., Summerside P. and Paranjape B.V. 1978  


The following manuscript, covering the material presented in Chapter 5 has been submitted to J. Phys. F: Metal Phys. :

Mahanty J. and Summerside P. 1979  Force on a Moving Charge Near a Metal Surface: Effect of Spatial Dispersion.
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1.1 INTRODUCTORY REMARKS

Physically, the many-body problem in solid state physics is well defined, the aim being to describe the properties of a large number of mutually interacting particles. Computationally, the problem is insoluble, but the long-range order occurring in most solids lends itself to a hierarchy of models capable of giving insight into various aspects of the solid-state problem with varying degrees of quantitativeness, and of qualitative clarity. This hierarchy takes two forms, in that it is often possible to a first approximation to isolate different physical phenomena, such as on the basis of the concept of elementary excitations, and then introduce an appropriate succession of secondary approximations. Elementary excitations may be differentiated as single particle excitations and collective excitations, including phonons, plasmons, magnons and broadly speaking, polaritons and excitons. Of interest here are the plasmons, which describe the collective oscillations of
the valence electrons in metals.

In this work the hydrodynamic model will be used to study the role of plasmons in the description of the dielectric response of the metallic electrons in various systems involving metal surfaces. The hydrodynamic model was first used by Bloch (1933) to describe a many-electron atom in the study of the scattering and stopping of fast moving ions by atomic media. Here, it is used to describe the valence or conduction electrons in a macroscopic metal. While different applications of the model require distinct boundary conditions, its essential features follow from a derivation from the Boltzmann equation, given in §1.3.1. For studies of the interaction between a metal and an external field source it is then used to derive the well known hydrodynamic dielectric response function $\epsilon_{\text{HD}}(\mathbf{k},\omega)$. This helps to correctly place the hydrodynamic model in context within the general many-body problem and in §§1.2 the model is first approached 'from above' by considering the various approximations commonly used to render the solid-state problem tractable and then reducing the general dielectric function to the equivalent of $\epsilon_{\text{HD}}(\mathbf{k},\omega)$.

With the introduction of a surface to the electron gas, the question of appropriate boundary conditions arises. These are discussed in §1.4.1. Surface plasmons are then introduced within the planar step-function model of the surface in §1.4.2, and the effect of a more realistic surface profile is discussed in §1.4.3. While there exists a natural upper limit to the wavenumber for which collective oscillations are well defined, and beyond which plasmons are strongly damped by single particle excitations, this cutoff must be introduced in a
phenomenological manner within the hydrodynamic model. The commonly used cutoff for bulk plasmons is introduced in §1.2.1 and the appropriate choice for surface plasmons is discussed in §1.4.4. Other fundamental questions concerning the model and collective modes in general are discussed in relevant sections of later chapters. Thus the effect of retardation is included in Chapter 2, the question of an appropriate reference plane from which to measure interactions with a metal surface is discussed in Chapter 3 and the boundary conditions for a bimetallic interface and a metal surface are considered in detail in Chapter 4.

1.2 REDUCTION OF THE MANY-BODY PROBLEM FOR THE STUDY OF ELECTRONIC PROPERTIES OF METALS

1.2.1 Approximating the Hamiltonian

The general many-body Hamiltonian may be written, in the absence of external fields, as

$$H = H_{el} + H_{ion} + H_{el-ion}$$  \hspace{1cm} (1.1)

where $H_{el}$ and $H_{ion}$ include both kinetic and interaction terms which, for the Coulomb interacting electrons may be written

$$H_{el} = \sum_i \frac{p_i^2}{2m} + \frac{e^2}{\sum_{ij} \frac{1}{|r_i - r_j|}} \hspace{1cm} (1.2)$$

Since the Schrödinger equation is insoluble with the general
Hamiltonian (1.1), in the spirit of the adiabatic or Born-Oppenheimer approximation, the electronic and ionic properties of a solid may be studied independently by neglecting appropriate terms in equation (1.1). The very nature of free-electron-like metals leads to a further simplification in the study of their electronic properties by including in $\mathbf{H}_{el}$ only the valence electrons and essentially neglecting the core electrons which are then contained in the ionic terms. This is not reasonable in, say, transition metals in which the $d$ orbitals are not sufficiently localised for the core-core and core-valence interactions to be neglected.

While neglecting ionic properties, charge neutrality must be maintained by at least assuming the ions to be present in their equilibrium positions. The obvious next approximation is then to average the positive charge background into some constant space charge density $\rho_+^*$. This defines the popular jellium model which will be adopted here.

The problem still requires approximations concerning the electron-electron interactions which, in the reduction to a one-electron theory, are partially accounted for by averaging the field due to all other electrons. This then defines the Hartree model which, with the inclusion of spin, is corrected by the quantum mechanical exchange term of the Hartree-Fock approximation.

In the free-electron approximation the ground state is defined by a filled Fermi sphere in momentum space, with radius $k_F$ given by $k_F^3 = 3\pi^2 n$, $k_F$ being the Fermi wavenumber and $n$ the electron concentration. The excited states correspond to single or multiparticle excitations of electrons to states
outside $k_F$, resulting in the creation of electron-hole pairs. When these excitation energies are small compared to the Fermi energy $\varepsilon_F$, they are conveniently described using the concept of quasiparticles which likewise obey Fermi statistics. The free-electron approximation, by its nature is most applicable to the study of conduction electrons in simple monovalent metals and low carrier concentration semiconductors, but proves very useful in explaining many phenomena in non-ideal systems by the introduction of an effective mass $m^*$.

The inclusion of the Coulomb interaction as in equation (1.2) introduces, in addition to the single particle excitations, the collective excitations of the electron gas, these being quantised as plasmons. More specifically, the collective excitations are associated with the screening of the long range Coulomb interaction as, through their mutual repulsion, each electron tends to create a region of relatively positive charge in its vicinity. This is distinct from the purely quantum mechanical exchange hole arising from the Pauli exclusion of electrons with like spin. The collective oscillations are classical in origin and may be described to a first approximation in terms of a system of simple harmonic oscillators.

This distinction leads to the description of the single and collective excitations in terms of different canonical coordinates (Bohm and Pines 1953, Pines 1953 and their introductory papers, Bohm and Pines 1951, Pines and Bohm 1952) which may be conveniently handled within the occupation number representation (second quantisation). The collective oscillations associated with the long range part of the Coulomb
interaction are then usually separated in the electronic
Hamiltonian for the jellium model by introducing a cutoff \( k_c \)
in the Fourier components of the Coulomb potential. Into the
long range part \( (k < k_c) \) are introduced the collective
oscillator coordinates describing the plasmons and the
resulting Hamiltonian may be written (before second
quantisation) as

\[
H = \sum_i \frac{p_i^2}{2m} + \frac{2\pi e^2}{\Omega} \sum_{ij} \sum_{k > k_c} \frac{\exp[i \mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)]}{k^2} - \frac{m_0^2}{2} \sum_{k > k_c} \frac{1}{k^2} \\
+ \frac{\hbar}{4} \sum_{k < k_c} \left( \mathbf{P}_k^* \mathbf{P}_k + \mathbf{Q}_k^* \mathbf{Q}_k \right) - \frac{m_0^2}{k^2} \\
+ \frac{2e}{m} \sqrt{\frac{\pi}{\Omega}} \sum_{k < k_c} \sum_i \mathbf{Q}_k \frac{\mathbf{P}_k}{k} \left( \mathbf{P}^*_i - \frac{m_0^2}{2} \right) \exp(i \mathbf{k} \cdot \mathbf{r}_i) \\
+ \frac{2\pi e^2}{m \Omega} \sum_{k, k' < k_F \neq k, k'} \mathbf{Q}_k \mathbf{Q}_k' \sum_i \exp[i (\mathbf{k} + \mathbf{k}' \cdot \mathbf{r}_i) . \mathbf{r}_i] . \tag{1.3}
\]

Here, the collective coordinates \( \mathbf{Q}_k \) and \( \mathbf{P}_k \) are introduced as
the Fourier transforms of the vector potential and electric
field arising from the electrons' mutual Coulomb potential,

\[
\dot{\mathbf{A}}(\mathbf{r}_j) = 2 \sqrt{\frac{\pi}{\Omega}} \sum_k \frac{\mathbf{k}}{k} \mathbf{Q}_k \exp(i \mathbf{k} \cdot \mathbf{r}_j) \\
\dot{\mathbf{E}}(\mathbf{r}_j) = -\frac{\delta \mathbf{A}(\mathbf{r}_j)}{\delta t} = -2 \sqrt{\frac{\pi}{\Omega}} \sum_k \frac{\mathbf{k}}{k} \mathbf{P}_k^* \exp(i \mathbf{k} \cdot \mathbf{r}_j)
\]

where \( \dot{\mathbf{Q}}_k = \mathbf{P}_k^* \) and \( \dot{\mathbf{Q}}_k^* (\mathbf{P}_k^*) = -\mathbf{Q}_k (-\mathbf{P}_k) \). It is easily verified
from Poisson's equation \( \nabla \cdot \mathbf{E} = 4\pi \rho \), with the charge density also
expanded in a Fourier series, that
\[ P_k = \frac{2ie}{k} \sqrt{\frac{\pi}{\Omega}} \sum_j \exp(i\mathbf{k} \cdot \mathbf{r}_j) \]

Thus \( P_k \) (through \( P_k^* \)) is closely related to the Fourier component of the electron density \( \rho_k = \sum \exp(-i\mathbf{k} \cdot \mathbf{r}_j) \).

The first three terms in equation (1.3) give the electronic kinetic energy, and the short range (or screened) interaction between electrons, and between the electrons and the positive background respectively. The fourth term describes the plasma oscillations and the fifth the interaction between plasmons and single electrons. Neglect of the final plasmon-plasmon term amounts to the common random phase approximation (RPA), so named because the neglect of the last term is justified on the assumption that the electrons are statistically distributed, rendering the sum over \( \mathbf{r}_j \) vanishingly small.

A central feature of the approximation (1.3) is the introduction of the limit \( k_c \) for short and long range interactions. Physically, there must be a natural upper limit \( k_c \) for plasmons since beyond \( k_c \) the wavelength assumes atomic dimensions, for which a collective oscillation is meaningless. Indeed for all wavenumbers \( k > k_c \) there is an increasing probability that the plasmons will decay into single particle or pair excitations. A commonly used estimate for \( k_c \) is given by equating the maximum energy of a pair excitation \( E_{\text{max}}(k) = (\hbar^2/2m)(k^2 + 2kk_p) \) with the plasmon energy \( E_{\text{pl}}(k) = \hbar \omega_p(k) \). For small \( k \) this gives \( k_c = \omega_p/v_p \) (Ferrell 1956, 1957).

1.2.2 The Dielectric Function

The study of all properties of the electron gas necessarily involves the introduction of an external
perturbation which ideally, should not alter the unperturbed properties of the system. The linear response of the electron gas may then be described in terms of a frequency- and wavenumber-dependent dielectric function $\varepsilon(\vec{k}, \omega)$ relating the total or local potential with the external and induced potentials, thus,

$$\varphi_{\text{tot}}(\vec{k}, t) = \varphi_{\text{ind}}(\vec{k}, t) + \varphi_{\text{ext}}(\vec{k}, t)$$

$$= \varphi_{\text{ext}}(\vec{k}, t) / \varepsilon(\vec{k}, \omega)$$

$$= \varphi_{\text{ind}}(\vec{k}, t) / [1 - \varepsilon(\vec{k}, \omega)] , \quad (1.4)$$

where the potentials are understood to be harmonic; $\varphi(\vec{k}, t) \equiv \varphi(\vec{k}) \exp(i\omega t)$. Common useful approximations for $\varepsilon(\vec{k}, \omega)$ may be obtained from the self-consistent field (SCF) approximation (Ehrenreich and Cohen 1959) in which the induced density is calculated self-consistently with the total potential. In the Liouville equation of motion for the density operator

$$i\hbar \frac{\partial \rho_{\text{op}}}{\partial t} = [H, \rho_{\text{op}}] , \quad (1.5)$$

the Hamiltonian is given by

$$H = H_0 + \varphi_{\text{tot}}(\vec{r}, t) , \quad (1.6)$$

where $H_0$ is a suitably approximated Hamiltonian such as equation (1.3) for the unperturbed electron gas. After Fourier analysing, the equation for the induced density matrix elements becomes
\begin{equation}
\langle q+k|\rho^\prime_{op}|q\rangle = \frac{f(E_{q+k}) - f(E_q)}{E_{q+k} - E_q - \hbar\omega - i\hbar \eta} \varphi_{tot}(\vec{k},t) \tag{1.7}
\end{equation}

where \(\rho_{op} = \rho^+_{op} + \rho^-_{op}\), \(f(E_q)\) is the Fermi-Dirac distribution function for the eigenvalue of state \(|q\rangle\) and a factor \(\exp(\eta t)\), \(\eta \rightarrow 0\), has been introduced into the external potential both to ensure causality and to phenomenologically damp the perturbation.

The charge density within the medium is now obtained from the definition

\begin{equation}
n = \text{Tr}[\rho_{op} \delta(\vec{r} - \vec{r})] \tag{1.8}
\end{equation}

Using plane wave basis states, appropriate for a free electron gas, and letting \(n = n_o + n_1\), the induced density fluctuation becomes

\begin{equation}
n_1 = \frac{1}{\Omega} \sum_{\vec{q},\vec{k}} \exp(i\vec{k}.\vec{r}) \langle \vec{q} + \vec{k}|\rho^\prime_{op}|\vec{q}\rangle \tag{1.9}
\end{equation}

Then from Poisson's equation for \(\varphi_{ind}\) and equation (1.7),

\begin{equation}
\varphi_{ind}(\vec{k},t) = \frac{4\pi e^2}{k^2 \Omega} \varphi_{tot}(\vec{k},t) \sum_{\vec{q}} \frac{f(E_{q+k}) - f(E_q)}{E_{q+k} - E_q - \hbar\omega - i\hbar \eta} \tag{1.10}
\end{equation}

which, from equation (1.4), defines the Lindhard (1954) dielectric function for a free electron gas,

\begin{equation}
\epsilon(\vec{k},\omega) = 1 - \lim_{\eta \rightarrow 0} \frac{4\pi e^2}{k^2 \Omega} \sum_{\vec{q}} \frac{f(E_{q+k}) - f(E_q)}{E_{q+k} - E_q - \hbar\omega - i\hbar \eta} \tag{1.11}
\end{equation}

This may be generalised using Bloch functions to include the
periodicity of the positive background lattice (Adler 1962, Wiser 1963). Contributions from both interband and intraband transitions are contained implicitly in equation (1.11) and are indicated by labelling the initial and final states as $\varepsilon_{q+\vec{k},l'}$ and $\varepsilon_{q,l}$ where the band indices $l$ and $l'$ may take on any appropriate value, including of course $l=l'$. The main interest here lies in a further reduction of $\varepsilon(\vec{k},\omega)$ appropriate for simple metals, in which interband transitions may be neglected. Dropping $\eta$ for now, the principal, real part of $\varepsilon(\vec{k},\omega)$ may be written

$$\varepsilon(\vec{k},\omega) = 1 - \frac{4\pi e^2}{k^2 \Omega} \sum_{q,l} f(\varepsilon_{q,l}) \left[ \frac{\Delta_{q,\vec{q}-\vec{k},l} + \hbar \omega}{\Delta_{q,\vec{q}-\vec{k},l}^2 - (\hbar \omega)^2} - \frac{\Delta_{q+\vec{k},\vec{q},l} + \hbar \omega}{\Delta_{q+\vec{k},\vec{q},l}^2 - (\hbar \omega)^2} \right] \quad (1.12)$$

where $\Delta_{q+\vec{k},\vec{q},l} = \varepsilon_{q+\vec{k},l} - \varepsilon_{q,l}$.

a) Local (loc) Approximation: In the finite-frequency, long-wavelength range, to a first approximation the squares of the energy differences may be neglected with the assumption $\Delta^2 \ll (\hbar \omega)^2$ and a small $k$ expansion for the $\varepsilon_{q+\vec{k},\vec{q}}$ then gives

$$\varepsilon(\vec{k},\omega) = 1 - \frac{e}{\pi \hbar \omega} \sum_l \int d^3 q \, f(\varepsilon_{q,l}) \frac{\partial^2 \varepsilon_{q,l}}{\partial q^2 \mu} \quad (1.13)$$

where $\mu$ defines the direction of propagation $\vec{k}$. In simple monovalent metals only a single (valence) band is important and the summation over $l$ is dropped. With the introduction of a constant effective mass $m^*=\hbar^2 (\alpha^2 \varepsilon / \partial q^2)^{-1}$, the remaining integral is simply one of the Fermi-Dirac distribution over the
volume of the Brillouin zone, resulting in

$$\varepsilon_{loc}(\omega) = 1 - \frac{\omega^2}{\omega_p^2}/\omega^2$$

(1.14)

where $\omega_p^2 = 4\pi e^2 n_o/m$, $n_o \equiv N/\Omega$ being the electron density.

b) Hydrodynamic (HD) Approximation: Retaining the $\lambda^2$ terms in equation (1.12) as the first order terms in a small $k$ expansion, similarly gives

$$\varepsilon_{HD}(\omega) = 1 - \frac{\omega^2}{\omega_p^2}/(\omega^2 - \lambda^2 k^2 \langle q^2 \rangle/m^2)
= 1 - \frac{\omega^2}{\omega^2 - \beta^2 k^2}$$

(1.15)

where $\langle q^2 \rangle = (3/5)k_F^2$ and

$$\beta^2 = (3/5)\nu_F^2$$

(1.16)

c) Thomas-Fermi (TF) Approximation: In the static limit ($\omega = 0$) the small $k$ behaviour of the real dielectric function is

$$\varepsilon_{TF}(\omega) = 1 + \frac{\lambda_{TF}^2}{\lambda^2}$$

(1.17)

where the Thomas-Fermi screening length $\lambda_{TF}^{-1}$ is defined by

$$\lambda_{TF} = \frac{\sqrt{3} \omega_p}{\nu_F} = \frac{\omega_p}{\beta}$$

(1.18)

with

$$\beta^2 = (1/3)\nu_F^2$$

(1.19)
d) Random Phase (RPA) and Hartree-Fock (HF) Approximations: While the above forms for ε will serve to illustrate the nature of the hydrodynamic approximation, for completeness the more general explicit form of equation (1.11) may be quoted as (Lindhard 1954)

\[
\varepsilon_{\text{RPA}}(\vec{k},\omega) = 1 + \frac{\lambda_{TF}^2}{k^2} \left\{ \frac{k_F}{4k} \left[ \left( 1 - \frac{(\omega - \hbar k^2/2m)^2}{k^2 \nu_F^2} \right) \ln \left| \frac{\omega - kv_F - \hbar k^2/2m}{\omega + kv_F + \hbar k^2/2m} \right| \right] \right. \\
+ \left. \left( 1 - \frac{(\omega + \hbar k^2/2m)^2}{k^2 \nu_F^2} \right) \ln \left| \frac{\omega + kv_F + \hbar k^2/2m}{\omega - kv_F - \hbar k^2/2m} \right| \right\} 
\]

(1.20)

for which the static generalisation of the Thomas-Fermi approximation is

\[
\varepsilon_{\text{RPA}}(\vec{k}) = 1 + \frac{\lambda_{TF}^2}{k^2} \left\{ \frac{k_F}{4k} \left[ \left( 1 - \frac{x^2}{4} \right) \ln \left| \frac{1+x}{1-x} \right| \right] \right. \\
+ \left. \left( 1 - \frac{x^2}{4} \right) \ln \left| \frac{1+x}{1-x} \right| \right\} 
\]

(1.21)

where \( x = k/2k_F \). The RPA is often referred to as the time-dependent Hartree-Fock approximation. Its generalisation of the HF model may be seen by writing the RPA dielectric function in terms of the free-electron polarisability as

\[
\varepsilon_{\text{RPA}}(\vec{k},\omega) = 1 + 4\pi\alpha(\vec{k},\omega) 
\]

(1.22)

The dielectric function characterising the HF approximation is given by

\[
\varepsilon_{\text{HF}}^{-1}(\vec{k},\omega) = 1 - 4\pi\alpha(\vec{k},\omega) 
\]

(1.23)

corresponding to only the leading term in the expansion of \( \varepsilon_{\text{RPA}}^{-1}(\vec{k},\omega) \).
1.3 THE BLOCH HYDRODYNAMIC MODEL

1.3.1 Hydrodynamic Equation of Motion

The Bloch hydrodynamic equation of motion follows simply from the Boltzmann (or Vlasov) equation

\[
\frac{df(r,p,t)}{dt} = \frac{\partial f}{\partial t} + \vec{v}_{r} \cdot \vec{\nabla}_{r} f + \vec{v}_{p} \cdot \vec{\nabla}_{p} f = -\frac{f - f_{0}}{\tau} . \quad (1.24)
\]

As in equations (1.11)-(1.12), the explicit damping mechanism will be dropped by letting the excitation lifetime \( \tau = \infty \). It may be reintroduced phenomenologically at any stage both to expedite the mathematics and facilitate physical understanding.

The electron density is defined, as usual, as

\[
n(r,t) = \int \frac{d^{3}p}{(2\pi)^{3}} f(r,p,t) \quad (1.25)
\]

and in keeping with the realm of linear response theory, all quantities are expanded in terms of infinitesimal fluctuations as

\[
n = n_{o} + n_{1} + \ldots .
\]

\[
f = f_{o} + f_{1} + \ldots \quad \text{etc. ,} \quad (1.26)
\]

where \( n_{o} \) and \( f_{o} \) are the equilibrium particle density and Fermi-Dirac distribution respectively. The zero and first moments of equation (1.24) give, respectively, the equation of continuity

\[
\frac{\partial n_{1}}{\partial t} = -n_{o} \vec{v}_{1} \cdot \vec{v}_{1} \quad (1.27)
\]
and the linearised hydrodynamic equation (Wakano, 1961)

\[ m \frac{\partial \dot{\mathbf{v}}_1}{\partial t} = \mathbf{F} - \mathbf{\nabla} \left( \int_0^n \frac{dp(n')}{n'} \right) \]  

(1.28)

for the first order density fluctuations \( n_1 \) of the electron gas. The last term in equation (1.28) derives with the assumption of an isotropic pressure tensor. An additional assumption must be made to close equations (1.27) and (1.28). While the pressure density \( p(n) \) may in general include contributions from exchange, the approximation employed by Bloch was that of the ground state or degenerate Fermi gas,

\[ p(n) = n^{5/3} \left( \frac{3\pi^2}{2} \right)^{2/3} \frac{n^2}{5m} \]  

(1.29)

This leads to the first order quantity

\[ P_1(n_1) \equiv \left( \int_0^n \frac{dp(n')}{n'} \right) = \beta^2 m \frac{n_1}{n_0} \]  

(1.30)

where \( \beta^2 = (1/3) v_F^2 \) as in equation (1.19) for the Thomas-Fermi approximation. However, with hindsight, this only gives the correct behaviour of the RPA dielectric response for small wavenumbers in the static or low frequency limit. For the finite plasmon frequency range \( (\omega_p \sim 10^{15} \text{ sec}^{-1}) \) considered here, the assumption that the right hand side of equation (1.30) is proportional to \( n_1 \) will still be maintained, but with proportionality constant \( \beta^2 = (3/5) v_F^2 \) (equation (1.16)). The dielectric function derived below in the Bloch model will then be equivalent to equation (1.15) and give the correct RPA behaviour to order \( k^2 \). Finally, the forces considered here will
be of electromagnetic origin and in equation (1.28), to first order, \( \mathbf{F} \) may be written in terms of the total electric field. Thus the linearised hydrodynamic equation becomes

\[
\frac{\partial \mathbf{v}}{\partial t} = -en_0 \mathbf{E} - m\beta^2 \mathbf{v} + \frac{\partial \rho}{\partial t}, \quad (1.31)
\]

where the subscripts have been dropped from the implicitly first order quantities \( \mathbf{v}, \mathbf{E} \) and \( n \). Equation (1.31) forms the basis of all work presented here.

1.3.2 Hydrodynamic Dielectric Function

For an infinite homogeneous system \( (n_0 = \text{const}) \), equation (1.31) may be written for each Fourier component as

\[
i\omega n_0 \mathbf{v}(k, \omega) = en_0 \mathbf{E}(k, \omega) + im\beta^2 n(k, \omega)
\]

with the equation of continuity (1.27) becoming

\[
\omega n = n_0 \mathbf{k} \cdot \mathbf{v}
\]

and where the following Fourier transform convention is adopted throughout,

\[
G(\mathbf{r}, t) = \int \frac{d^3k}{(2\pi)^3} \frac{d\omega}{2\pi} \exp[i(k \cdot \mathbf{r} - \omega t)] G(k, \omega), \quad (1.34)
\]

\[
G(k, \omega) = \int d^3r \int dt \exp[-i(k \cdot \mathbf{r} - \omega t)] G(\mathbf{r}, t).
\]

In the electrostatic limit the response of the metallic electrons to the external field \( \mathbf{E}_{\text{ext}} = -\nabla \varphi_{\text{ext}} \) is longitudinal.
The divergence of equation (1.32) may then be taken, giving

\[(\omega^2 - \beta^2 \kappa^2)n = -\frac{\epsilon_n \omega}{m} \kappa^2 (\varphi_I + \varphi_{ext}) \quad . \quad (1.35)\]

Since the induced potential \(\varphi_I\) and induced density fluctuations are related through Poisson's equation

\[\kappa^2 \varphi_I = -4\pi \epsilon n \quad , \quad (1.36)\]

it simply follows, from equation (1.4) that

\[\varepsilon_{HD}(\kappa, \omega) = 1 - \frac{\omega^2}{\omega^2 - \beta^2 \kappa^2} \quad . \quad (1.37)\]

With the above empirical choice of the parameter \(\beta\), this corresponds identically with equation (1.15). The Bloch hydrodynamic model is thus one which accounts both for the dynamical response of the electrons to an external source and phenomenologically for the screening of the electrons' Coulomb potential. The latter phenomenon, associated with the non-local spatial response of the electrons due to their finite 'average' velocity \(\beta\), is equivalently referred to as spatial dispersion.

Equation (1.37) is derived principally to establish the equivalence of the hydrodynamic equation of motion with the dielectric function or linear response formalism, and throughout, the equation of motion (1.31) will be solved directly. This leads to a more direct understanding of the various physical concepts involved, in terms of the induced densities, potentials etc. The derivation of equation (1.37) is a reminder that
\(\varepsilon_{\text{HD}} \equiv \varepsilon_{\text{HD}}^L\) is the longitudinal dielectric function. The corresponding transverse function \(\varepsilon_{\text{HD}}^T\) requires that equation (1.31) be solved in conjunction with the full set of Maxwell's equations. This will be done in Chapter 2, while the derivation for the general SCF or RPA dielectric function is given by Adler (1962). It will be merely noted here that

\[
\varepsilon_{\text{HD}}^T = 1 - \frac{\omega^2}{\frac{p}{2}}.
\] (1.38)

That this corresponds to the local approximation (equation (1.14)), for which \(\varepsilon_{\text{loc}}^L \equiv \varepsilon_{\text{loc}}^T\), is simply a statement of the vanishing shear modulus of the electron gas (Kittel 1971).

1.3.3 Infinite Homogeneous Electron Gas: Bulk Plasmons

The wave equation for the electric field, which in an infinite medium may be taken to have the spatial dependence \(\exp(i\hat{k} \cdot \hat{r})\), reduces to

\[
\hat{k} \times (\hat{k} \times \hat{E}) - \varepsilon(\hat{k},\omega) \frac{\omega^2}{c^2} \hat{E} = 0.
\] (1.39)

The eigenvalue conditions for self-sustaining longitudinal (\(\hat{k} \parallel \hat{E}\)) and transverse (\(\hat{k} \perp \hat{E}\)) modes are, respectively

\[
\varepsilon^L(\hat{k},\omega) = 0
\] (1.40)

and

\[
\omega^2 \varepsilon^T(\omega) = c^2 k^2.
\] (1.41)
With the hydrodynamic functions (1.37) and (1.38) these give the well known frequencies for the longitudinal bulk plasma and transverse electromagnetic oscillations inside the metal,

\[ \omega_L^2 = \omega_p^2 + \beta^2 k^2 \]  

and

\[ \omega_T^2 = \omega_p^2 + \sigma^2 k^2 \]  

1.4 BOUNDED ELECTRON GAS: SURFACE PLASMONS

1.4.1 Boundary Conditions

With the introduction of a surface, the choice of appropriate boundary conditions requires a brief review not only of the model, but also of its application; the latter particularly, because of the many varied uses of the hydrodynamic model in different physical systems. In a recent application of Bloch's formulation by Monaghan (1973, 1974) for the study of collective excitations in a many-electron atom, the equilibrium surface of the electron cloud is first determined from the equation of hydrostatic equilibrium with the boundary condition that the normalised density vary from unity at the centre to zero at the surface \( r = r_0 \). Monaghan then considers both radial (\( \ell = 0 \)) and nonradial (\( \ell = 1 \), dipole) modes of collective excitation, requiring only that the excitations be stable. For the radial modes this corresponds, as in the theory of pulsating
stars, to the requirement that the displacement of a spherical shell from its equilibrium radius remain finite. For the dipole modes the velocity potential, defined by \( \dot{\psi} = \nabla \psi \), is zero at the centre and finite everywhere else. In particular, the requirement that \( \psi \) be finite at the surface is sufficient to satisfy the boundary condition (Monaghan 1973) that the Lagrangian variation of the density vanish at the surface,

\[
\frac{\partial n}{\partial t} + \dot{\psi} \cdot \nabla n = 0 .
\]  

(1.44)

In the more standard use of the hydrodynamic model for classical fluids (eg. Lamb 1945, Landau and Lifshitz 1959) the characteristic surface excitations (ripples) are transverse waves. In this context, gravitational forces and surface tension play central roles of varying relative importance and the equilibrium surface is defined by the cancellation of the internal and external pressures \( P \) and \( P_o \). The boundary condition may then be given as (Lamb 1945)

\[
\frac{\partial}{\partial t} (P-P_o) + \dot{\psi} \cdot \nabla (P-P_o) = 0 .
\]  

(1.45)

It may be noted that if the classical fluid is replaced by a degenerate Fermi gas with \( P \approx n \) (cf equation (1.30)) and with gravitational forces playing a negligible role, then equations (1.44) and (1.45) are identical.

The above uses of the hydrodynamic model have the common feature of a 'free' surface. The equilibrium surface is first parametrised and the uniform boundary conditions are then used to describe fluctuations involving a
distortion of the surface (eg. radial stellar oscillations, transverse ripples, radial and dipole excitations of the many-electron atom).

In the present work the model is used to describe compressional or longitudinal oscillations at the surface of an electron gas having metallic densities. For the jellium model, the surface is naturally defined in relation to the edge of the positive background which, in both quantum and classical treatments, is customarily taken as a step-function. A realistic equilibrium configuration for the electron gas, which must conserve charge neutrality, will have a smoothly varying surface profile with characteristic Friedel-like oscillations into the metal. For mathematical simplicity the model of the surface in which the electron gas, too, is a step-function, exactly overlaying the positive background, will be used here. As is commonly done, this will also be loosely referred to as the infinite barrier or classical infinite barrier (CIBM) model. The nature of the error this introduces into the surface plasmon dispersion curves is well known and will be indicated below (§1.4.3).

Within this framework there is still a choice (and in general a mixture) of boundary conditions, corresponding to either specular or diffuse reflection of electrons at the surface (Pippard 1947, Reuter and Sondheimer 1948). The former corresponds to scattering of the electrons by the 'surface' barrier, with reversal of the normal ($z$) component of their velocity and the latter to scattering with complete loss of the electron's drift velocity. By 'surface' here is meant the skin depth region. The diffuse reflection is then understood in
terms of the electron suffering many collisions within the surface region so that it loses knowledge of its original velocity and finally emerges, governed only by Fermi statistics. If $p$ is the fraction of electrons which are specularly reflected the Wigner distribution function $f = f_0 + f_1^{(1,2)}$, where the superscripts (1) and (2) denote before and after surface reflection, may be expressed as (Reuter and Sondheimer 1948)

$$f_0 + f_1^{(2)}(v_x, v_y, v_z, z=0) = p[f_0 + f_1^{(1)}(v_x, v_y, -v_z, z=0)] + (1 - p)f_0 . \tag{1.46}$$

Since the difficulty of solving the Boltzmann equation for the general case $0 < p < 1$ reduces it to a numerical problem, the cases $p = 0$ and $p = 1$ are usually considered (Reuter and Sondheimer 1948) and the solutions fitted independently to experimental data (eg. Chambers 1952). However, the conclusion, from the best fit, that one type of surface reflection is dominant is not necessarily conclusive in view of the more general approximations made for the dielectric or conductivity function. In general the two extremes ($p = 0,1$) show the same qualitative behaviour and do not greatly influence results (Reuter and Sondheimer 1948, Kleiman and Landman 1974). For these reasons the simplifying assumption of specular reflection ($p = 1$) will be made throughout this work. In the hydrodynamic equation (1.31) this will be equivalent to the boundary condition that

$$v_z \big|_{z=0^-} = 0$$

or, with the harmonic time dependence $\exp(\iota \omega t)$,
where throughout, the metal will be taken to occupy the negative z half-space, with the x-y plane as its surface. A more rigorous derivation of this boundary condition by Forstmann and Stenschke (1977) will be outlined in Chapter 4, where in fact the assumption of specular reflection will be relaxed by the removal of the infinite barrier at a bimetallic interface.

1.4.2 Surface Plasmons

Ritchie (1957) predicted that fast charged particles passing through a metal foil could suffer energy losses less than the characteristic bulk plasma loss $\hbar \omega_p$. Such an energy loss, now well verified both theoretically and experimentally, is due to the excitation of longitudinal surface waves, for which Ritchie gave the condition leading to the dispersion relation for the surface plasmon frequencies in the foil.

Ritchie's prediction of surface plasmons was of fundamental importance, not just because of its contribution to the theory of the electron gas, but because it prompted the search and ultimate discovery of other types of surface excitations (including surface phonons and polaritons) beginning with the work of Fuchs and Kliewer (1965, Kliewer and Fuchs 1966a,b) on the optical modes of vibration of an ionic crystal slab.

As an introduction, the dispersion relations for the surface plasmons are considered briefly in the spatially non-dispersive limit. In the planar geometry considered here, the transverse spatial dependence of all quantities is taken as
exp(ik·p) where \( \vec{k} = (k_x, k_y) \) and \( \vec{p} = (x, y) \). In the local limit, with \( \varepsilon(\omega) \) given by equation (1.14) inside the metal and \( \varepsilon = 1 \) outside, matching of the solutions of the wave equation

\[
\left[ \frac{d^2}{dz^2} - \kappa^2 + \varepsilon(\omega) \frac{\omega^2}{\sigma^2} \right] \hat{E}(z) = 0 \quad (1.48)
\]

across the surface results in the eigenvalue equation for the surface modes,

\[
\left( \frac{\sigma k}{\omega} \right)^2 = \frac{\varepsilon(\omega)}{1 + \varepsilon(\omega)} \quad (1.49)
\]

As before, the longitudinal bulk modes are given by the condition \( \varepsilon(\omega) = 0 \) or \( \omega = \omega_p \). Equation (1.49) is easily solved for the corresponding surface modes, with the result

\[
\omega^2 = \omega_s^2 + \sigma^2 \kappa^2 - (\omega_s^2 + \sigma^2 \kappa^2)^{\frac{1}{2}} \quad , (1.50)
\]

while in the electrostatic or nonretarded limit \( (\sigma \to \infty) \) the poles of equation (1.49), given by

\[
l + \varepsilon(\omega) = 0 \quad , (1.51)
\]

lead to the result

\[
\omega = \omega_s \equiv \frac{\omega_p}{\sqrt{2}} \quad , (1.52)
\]

which is also the asymptotic (large \( \kappa \)) limit of equation (1.50).

The local results, equations (1.50) and (1.52), are
significantly modified with the inclusion of spatial dispersion. A useful derivation of the nonretarded surface plasmon frequencies for a metal half-space, which introduces the commonly used concept of an 'effective surface dielectric function' is given by Ritchie and Marusak (1966). The potential due to an induced charge density $Q_n(\mathbf{r},t)$ may be written, in Fourier representation,

$$
\varphi(\mathbf{r},t) = 4\pi Q \int \frac{d^3k}{(2\pi)^3} \frac{d\omega}{2\pi} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \frac{n(\mathbf{k},\omega)}{k^2 \varepsilon(\mathbf{k},\omega)}.
$$

They define a surface sheet charge density by

$$
n(\mathbf{r},t) = n^S(\mathbf{r},t) \delta(z),
$$

for which

$$
\varphi^S(\mathbf{r},t) = \int \frac{d^2k}{(2\pi)^2} \frac{d\omega}{2\pi} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \varphi^S(\mathbf{k},s,\omega),
$$

where

$$
\varphi^S(\mathbf{k},s,\omega) = 2Q \int_{-\infty}^{\infty} dk_3 \exp(ik_3 s) \frac{\rho^S(\mathbf{k},\omega)}{k^2 \varepsilon(\mathbf{k},\omega)}.
$$

This is matched with the bounded solution of Laplace's equation in the vacuum,

$$
\varphi_o(\mathbf{r},t) = \int \frac{d^2k}{(2\pi)^2} \frac{d\omega}{2\pi} \exp[i(\mathbf{k} \cdot \mathbf{r} - \omega t)] \varphi_o(\mathbf{k},s,\omega),
$$

where

$$
\varphi_o(\mathbf{k},s,\omega) = \text{const.} \exp(\kappa s),
$$

to give the eigenvalue condition.
\[ 1 + \frac{\kappa}{\pi} \int_{-\infty}^{\infty} \frac{dk_3}{k^2 \varepsilon(k, \omega)} = 0 \quad (1.59) \]

The nature of the derivation of equation (1.59) and its similarity with equation (1.51) lead to the definition of a 'surface dielectric function'

\[ \varepsilon^S(k, \omega) = \frac{\kappa}{\pi} \int_{-\infty}^{\infty} \frac{dk_3}{k^2 \varepsilon(k, \omega)} \quad (1.60) \]

For the hydrodynamic dielectric function (1.37), this gives (Heinrichs 1973a)

\[ \varepsilon_{\text{HD}}^S(k, \omega) = \frac{\omega^2 - \omega_p^2}{\omega^2 - \kappa \omega_p^2 / \gamma} \quad (1.61) \]

where \( \gamma = [\kappa^2 + (\omega_p^2 - \omega^2) / \beta^2]^{1/2} \). The well known solution of equation (1.59) for the surface plasmon frequencies in the hydrodynamic model is

\[ \omega_s^2(\kappa) = \frac{1}{2} [\omega_p^2 + \beta^2 \kappa^2 + \beta \kappa (2 \omega_p^2 + \beta^2 \kappa^2)] \quad (1.62) \]

A similar analysis leads to the retarded generalisation for the surface plasmon branch, satisfying the equation (Crowell and Ritchie 1970)

\[ \omega^2 \gamma(\nu + \lambda) = \omega_p^2 (\gamma \lambda + \kappa^2) \quad (1.63) \]

where \( \nu = [\kappa^2 + (\omega_p^2 - \omega^2) / \sigma^2]^{1/2} \) and \( \lambda = (\kappa^2 - \omega^2 / \sigma^2)^{1/2} \). An alternative derivation of this result is given in Chapter 2. The nonretarded and retarded surface plasmon curves satisfying
equations (1.62) and (1.63) are plotted in figure 1.1.

1.4.3 Effect of a Surface Density Profile

The surface plasmon curves in figure 1.1 were obtained using a step-function model for the surface and differ from typical experimental curves which show an initial dip in the region $\omega_p/c < \kappa \ll k_F$ (figure 1.2). That this discrepancy is due to the unrealistic model of the surface is verified by the various parametrisations of the surface which have been used to reproduce the experimental behaviour (Bennett 1970, Eguiluz and Quinn 1975, 1976, Eguiluz et al 1975, Boardman et al 1975, 1976). While all of these methods are very useful qualitatively, only a fully self-consistent calculation of the electron density profile as attempted by Appelbaum and Hamann (1972) or within the density functional method by various workers (Smith 1969, Lang 1969, Lang and Kohn 1970, 1971, 1973) can hope to be quantitative. Unfortunately however, these self-consistent calculations do not address the question of surface plasmon dispersion.

A common feature of the simpler models is that, while the experimental curves can be reproduced quite well by variation of the parameters, they also predict a number of other modes corresponding to higher multipole excitations (Eguiluz et al 1975). The fact that these modes have not been observed may point to a fairly obvious lack of consistency of these models in not properly accounting for the variation with density of the various constants (eg. $\omega_p$, $v_F$) in the sense that in each step is chosen a value of $\omega_p$ appropriate for an infinite sample of the same density (ie. through the local relation $\omega_p^2 = 4\pi e^2 n_o(x)/m$).
Caption for Figure 1.1

Retarded (R) and nonretarded (N) surface plasmon dispersion curves for a single metal half-space. The effect of retardation is dramatic in the small-κ region (figure 1.1b).
Figure 1.1 (a)
Figure 1.1 (b) small-$k$ region

\[ \omega = \frac{\omega_p}{\sqrt{2}} \]

\[ \frac{\omega}{\omega_p} \]

\[ K = 0.01 \, k_F \]

\[ \beta k / \omega_p \]
Figure 1.2

Schematic behaviour of experimental surface plasmon curve \( \omega_s(\text{exp}) \) compared to the nonretarded curve \( \omega_s \) given by equation (1.62). \( \omega_b \) is the lower bound of the bulk continuum, and arbitrary units are used.
Thus the two-step models more closely resemble a system in which a film of one metal is deposited onto the surface of another. In this case higher multipole excitations may well be possible, corresponding to an effective system of multiple or diffuse images.

Regardless of the question of these other modes, an interesting result was demonstrated by Feibelman (1971) within the RPA, that in the nonretarded limit the surface plasmon frequency \( \omega_s = \omega_p/\sqrt{2} \) at infinite wavelength is independent of the density profile. This was confirmed analytically by Boardman \textit{et al} (1974) for the hydrodynamic model. Finally, it should also be noted that within the RPA neither Feibelman (1971) nor Beck and Celli (1972) obtained the multipole modes which occur in the simpler parametrisations of the surface. Insofar as this question remains open, the simplifying assumption of the step-function model will be made throughout.

1.4.4 Cutoff Wavenumber for Surface Plasmons

As discussed in §1.2.1 for the bulk plasmons, there must be a natural upper limit \( \kappa_c \) for the existence of well-defined surface plasmons. The choice of \( \kappa_c \) has been rather a controversial issue. Recalling that the bulk cutoff may be approximated as \( \kappa_c = \omega_p/v_F \), Schmit and Lucas (1972a,b), working within the local approximation, chose for the surface plasmons,

\[
\kappa_c^{loc} = \frac{\omega_s}{v_F} = \frac{\omega_p}{\sqrt{2} v_F} . \tag{1.64}
\]

With this cutoff they obtained remarkably good agreement with
experiment for the surface energies of a number of metals. While the full explanation of this agreement still depends on the complete solution of the surface problem, it must be argued, and has often been stated (Jonson and Srinivasan 1973, Feibelman 1973, Kohn 1973, Heinrichs 1973b, 1975) that it is a result of some rather fortuitous cancellations (Harris and Jones 1974a,b, Griffin et al 1974, Harris and Griffin 1975). Despite this, it may be argued in support of Schmit and Lucas (1972a,b) that $\kappa_c^{loc}$ is indeed the most appropriate, and in fact the only consistent choice within the local approximation. This is illustrated in figure 1.3 where, in the local limit, the straight line bulk and surface plasmon curves enter the single particle spectrum at different wavenumber values. This point has been overlooked in the many criticisms of the work of Schmit and Lucas.

More widely accepted is the use of the same cutoff for both bulk and surface plasmon,

$$k_c = \kappa_c = \omega_p / \nu_F$$

(1.65)

since in general (with a realistic inclusion of spatial dispersion), the two dispersion curves converge and enter the single particle region almost simultaneously (figure 1.3). Since one of the well recognised shortcomings of the hydrodynamic model is that the bulk and surface plasmon dispersion curves do not enter the single particle region, but only approach it asymptotically (that is, it does not describe this damping mechanism for plasmons), a cutoff must be introduced phenomenologically. Where appropriate, the cutoff
Figure 1.3 Schematic diagram showing entry of bulk $\omega_b$ and surface $\omega_s$ plasmon curves into the region of single particle excitations.
value \( \omega_p/\nu_F \) will be used here. The use of such a cutoff is important in calculations of surface energy (Barton 1978b) and the van der Waals interaction between two metal half-spaces (Chapter 2). However, as pointed out by Heinrichs (1973a), the convergence of the hydrodynamic bulk and surface plasmon curves arising from the inclusion of spatial dispersion, on its own removes the zero separation divergences associated with local calculations, and the neglect of the cutoff introduces only a finite error.

1.5 CONCLUDING REMARKS: JUSTIFICATION OF THE MODEL

While the approximations involved in the hydrodynamic model may seem rather extravagant, its limitations are well known and it is possible to project, qualitatively, the results of the model into the context of a more complete theory. Thus while neglecting single particle excitations and such effects as Friedel-like oscillations associated with the natural cutoff wavenumber for collective modes, the model represents the simplest and often most illuminating method for studying the effect of the nonlocal dielectric response of the metallic electrons. It represents a significant improvement on the more commonly cited local (spatially non-dispersive) model which is much less physical in that it only correctly describes the infinite wavelength plasmons, and only gives quantitative results for interactions with a metal surface over very large distances.

The simplification afforded by the hydrodynamic model is
evident throughout. Its justification and indeed advantage is particularly evident in Chapters 4 and 5. Chapter 4 deals with the collective modes associated with a bimetallic system and in particular predicts a novel character of the electron response in two unlike metals separated by a vacuum, namely the 'image' plasmon. In Chapter 5 the force on an external charge moving parallel to a metal surface is derived. The hydrodynamic model firstly introduces, through the inclusion of spatial dispersion, the role of bulk plasmons, and secondly, clearly illustrates the exact mechanism for the force components normal to and in the direction of the particle's motion, in terms of the nature and symmetry properties of the induced density.
2.1 INTRODUCTION

The finiteness of the velocity of light is important in dispersion interactions over distances which are large compared to both the atomic dimensions of the interacting media and the wavelengths of the electromagnetic fields involved. This statement provides the justification for the neglect of retardation in virtually all quantum and semi-classical investigations of general many-body bulk properties using models more sophisticated than the hydrodynamic model. It also limits the validity of the many nonretarded calculations on interactions between systems of atoms, molecules and solids to very small separation distances.

In this chapter the effects of both retardation and spatial dispersion are investigated in the van der Waals (vdW) interaction between a molecule and a metal surface (Mahanty et al 1978) and between two metal half-spaces (Summerside and Mahanty 1979). The inclusion of spatial dispersion
removes the zero-separation divergences (Heinrichs 1973a) associated with these interactions in previous local results (Casimir and Polder 1948, Casimir 1948, Lifshitz 1956) and provides higher order correction terms to these long-standing local results for large separation distances. A wavenumber analysis of the interaction between two metals tends to clarify the origin of and mechanisms for the universal effect of retardation in increasing the dependence of the asymptotic forms of dispersion forces on the inverse separation distance by a power, compared to the nonretarded forms.

A resumé of some earlier results, by way of historical development, and some of the major limitations and approximations involved in these, serves to set the present work in context. Inherent in the present work are those approximations, mentioned in Chapter 1, used to reduce the general many-body dielectric function to the form (equation (1.37))

\[
e(k,\omega) = 1 - \frac{\omega^2}{\omega^2 - \beta^2 k^2} \quad (2.1)
\]

Early studies on interactions involving metals were a natural extension of the work on intermolecular forces which attempted to confirm and elaborate on the vdW equation of state for gases. The first notable work on the vdW interaction between two molecules was by London (Eisenshitz and London 1930, London 1930a,b) who showed, using second order perturbation theory, that the nonretarded vdW energy could be written as a sum over oscillator strengths (or
equivalently, transition probabilities or polarisabilities) as

$$E(d) = \frac{3e^4\alpha^4}{2m^2\hbar^6} \sum_{n,n'} \frac{f_{on} f_{on'}}{(E_o - E_n)(E_{o'} - E_{n'}) \left[ (E_o - E_n) + (E_{o'} - E_{n'}) \right]}$$

(2.2)

where $f_{on}$ is the oscillator strength for a dipole transition between the ground state $|0\rangle$, eigenenergy $E_o$, and the $n^{th}$ excited state $|n\rangle$, $E_n$, both molecules being assumed to be initially in their ground state. Equation (2.2) is obtained with the assumption that the molecules are small compared to their separation distance so that a multipole expansion is possible, with only the leading dipole-dipole term in the interaction Hamiltonian being retained.

The $d^{-6}$ behaviour of the London-vdW interaction had previously been obtained (Reinganum 1912) from a statistical averaging of the $d^{-3}$ dipole-dipole interactions, and in the special case of two H atoms by Wang (1927) using perturbation theory. Evaluation of the sums in equation (2.2) requires a knowledge of either the molecular wavefunctions (approximated from some appropriate set of basis functions) or the oscillator strengths of the transitions from the ground state (obtained from experimental data).

de Boer (1936) and Hamaker (1937) independently extended London's work to macroscopic bodies by assuming pairwise additivity of the London-vdW intermolecular forces. For two dielectric half-spaces this led to a $d^{-2}$ form for the interaction energy. Although their basic assumption of pairwise additivity proved to be unfounded, the semi-classical work of de Boer and Hamaker, and a little later, the quantum
approach of Bardeen (1940) established that the vdW energy of interaction between a molecule and a metal half-space behaved as $d^{-3}$.

The first major work to include retardation was that of Casimir and Polder (1946, 1948, Casimir 1948, 1949). They realised that since the vdW interaction arises from the induced polarisation of each molecule due to the instantaneous polarisation field of the other, then the interaction could be extracted from the change in energy of the electromagnetic field, caused by the presence of the molecules or bodies. Using a quantum electrodynamical approach, they obtained for the energy of interaction between two neutral molecules, a distance dependence of $d^{-7}$, while for a simple isotropic molecule in the vicinity of a metal surface, the result

$$E(d) = -\frac{3\hbar \alpha(0)}{8\pi d^4}.$$  \hspace{1cm} (2.3)

The simplicity of their result led Casimir (1948, 1949) to reformulate the problem semi-classically and for two perfectly conducting metal plates he obtained the result

$$E(d) = -\frac{\hbar \sigma \pi^2}{720d^3}.$$  \hspace{1cm} (2.4)

In all cases, the inclusion of retardation led to a remarkable increase in the power of the inverse separation distance in the vdW interaction, compared to previous nonretarded results.

Casimir and Polder treated the metals as perfect conductors, and thus neglected all many-body and dynamic effects. The results (2.3) and (2.4) were obtained from more
general formulae in the asymptotic \((d \to \infty)\) region and by assuming the molecule to have an isotropic, static polarisability. They may be considered to be reasonable first order approximations only as long as \(d >> \delta \approx 0.1\mu\), the skin depth of a typical metal.

The classic paper by Lifshitz (1956), on the macroscopic theory of dispersion forces between two homogeneous, isotropic media characterised by local dielectric functions \(\varepsilon(\omega)\), gave, in the limit of zero temperature, the expression for the attractive force between two arbitrary dielectric half-spaces,

\[
F(d) = \frac{\hbar}{2\pi^2\alpha^3} \int_0^\infty d\xi \xi^3 \int_1^\infty dp \frac{1}{p} \left\{ \frac{(s_1+p)(s_2+p)}{(s_1-p)(s_2-p)} \exp(2p\xi d/\sigma) - 1 \right\}^{-1} + \frac{(s_1+p\epsilon_1)(s_2+p\epsilon_2)}{(s_1-p\epsilon_1)(s_2-p\epsilon_2)} \exp(2p\xi d/\sigma) - 1 \right\}^{-1},
\]

where

\[
s_j = [\varepsilon_j(i\xi) - 1 + p]^{1/2}; \quad \omega = i\xi.
\]

From equation (2.5), the various static results of Casimir and Polder for perfectly conducting metals can be obtained. For example, setting \(\varepsilon_j(\omega=0) = \infty\) and changing variables to \(x(\xi) = 2p\xi d/\sigma\), the integrals are elementary and the result (2.4) is obtained. Lifshitz' approach was generalised using quantum field theory by Dzyaloshinskii et al (1961) to the case in which the interacting media are separated by some arbitrary third dielectric medium. The many applications of Lifshitz' theory, including the extensions to spatially dispersive, inhomogeneous, anisotropic and magnetic media are reviewed by
Still within the local (spatially nondispersive) approximation, van Kampen et al (1968) demonstrated that the information about nonretarded dispersion interactions, contained in the change in the electromagnetic modes from the field point of view, could be expressed in terms of the normal surface modes of the interacting media. (In Chapter 3 it will be shown that this is true only in the local approximation, and that in general the bulk modes are also important (Summerside and Mahanty 1978)). The method was subsequently generalised to include retardation (Ninham et al 1970, Gerlach 1971, Schram 1973) and Lifshitz' results could then be obtained simply by solving Maxwell's equations and applying the appropriate boundary conditions on the electromagnetic fields to obtain a secular equation for the surface modes. In essence, the roots $\omega(\kappa)$, of this secular equation, which also correspond to the poles of the Green's function for the particular problem, are then added to obtain the dispersion interaction energy. This procedure is outlined in §§2.4.4,5.

Most of the recent publications which have included retardation in the study of various interacting systems have used at best, the equivalent of the oversimplified local dielectric continuum model. These include, apart from the molecule/metal (Boyer 1972, 1973) and metal/metal (Boyer 1968) systems studied here, the image potential for both a stationary (Mahan 1972, Ritchie 1972) and moving (Tomaš and Šunjić 1975) charge, interacting thin metal films (Economou 1969), the effect of bounding surfaces on the dispersion interaction between molecules (Mahanty and Ninham 1973a), dispersion
contribution to the surface energy (Mahanty and Ninham 1973b), and of course the optical excitation of plasmons (Stern 1967, Wilems and Ritchie 1967, Otto 1968, Kretschmann 1971, Abelès 1971, 1976). With few exceptions, the inclusion of both retardation and spatial dispersion has been confined to studies of surface plasmons in single metal systems (Ritchie and Wilems 1969, Harris and Griffin 1971, Fuchs and Kliwer 1971) and the optical excitation of plasmons via their interaction with electromagnetic fields (Fedders 1968, Ritchie and Wilems 1969, Crowell and Ritchie 1970, Melnyk and Harrison 1970a,b, Agarwal et al 1971a,b, Maradudin and Mills 1973). The notable exceptions include investigations of the effect of a surface density profile on surface plasmons in single metal systems (Eguiluz and Quinn 1975, 1976, Boardman et al 1976, Forstmann and Stenschke 1978), the bimetallic interface (Forstmann and Stenschke 1978) and the more general quantum-electrodynamic/linear-response treatment by Agarwal (1975) in which the case of a spatially dispersive (metal)/spatially nondispersive (dielectric) system is considered. In addition, there have been various nonlocal extensions of Lifshitz' theory in both the nonretarded (Lushnikov and Malov 1974) and retarded limits (including the detailed review by Barash and Ginzburg 1975), and of the method of van Kampen et al (1968) (for example, Davies 1971).

Finally, of particular relevance here is the work of Chan and Richmond (1976a), formulated in terms of an arbitrary frequency- and wavenumber-dependent dielectric function. Their explicit calculation of the retarded vdW energy of interaction between two metal half-spaces is done using the
hydrodynamic dielectric function (2.1), and includes finite temperatures in the usual way by summing over the internal free energies rather than the zero point energies. Their zero temperature results would therefore be equivalent to the end results presented here. However, their emphasis is on the effect of spatial dispersion on the interaction at short distances and they give no discussion of retardation. The emphasis here, being on the retarded region, temperature effects may be neglected (Lifshitz 1956). In addition, the analysis of the plasmon dispersion curves for the interacting system presented here reveals some interesting new features as well as giving some further insight into the nature of retardation effects.

2.2 PRELIMINARY ANALYSIS

2.2.1 Fundamental Equations

The basic equations, valid for any system of plasma-like metals with external or impurity sources of charge or current, can be grouped into those characterising the metallic electron gas and those which characterise the external fields. Each of these sets yields an equation relating, say, the current density $\mathbf{j}$ and the electric field $\mathbf{E}$. These two equations can then be solved simultaneously for any configuration, using the appropriate boundary conditions.

Inside the metal the linearised hydrodynamic
The equation of motion for the electrons is (equation (1.31))

\[
\frac{mn_o}{\beta} \frac{\partial \dot{v}}{\partial t} = -en_o \dot{E} - m\beta^2 \dot{v}n
\] (2.6)

With the assumed time dependence of \(\exp(-i\omega t)\), which is implicit throughout, equation (2.6) can be differentiated with respect to time to give the first equation linking the current density and electric field,

\[
\left[\beta^2 \nabla (\nabla \cdot) + \omega^2\right] \vec{j} = \frac{i\omega e^2 n_o}{m} \dot{E}
\] (2.7)

Here, \(\vec{j}\) is introduced through the definition

\[
\vec{j} = -en_o \dot{v}
\] (2.8)

and is related to the induced density fluctuation by the equation of continuity,

\[
\nabla \cdot \vec{j} = e \frac{\partial n}{\partial t}
\] (2.9)

The external fields are governed by Maxwell's equations which are written in microscopic form as

\[
\nabla \times \dot{E} = -\frac{1}{c} \frac{\partial \dot{H}}{\partial t}
\] (2.10)

\[
\nabla \cdot \dot{E} = 4\pi \rho_{\text{total}}
\] (2.11)

\[
\nabla \times \dot{H} = \frac{1}{c} \frac{\partial \dot{E}}{\partial t} + \frac{4\pi}{c} \vec{j}_{\text{total}}
\] (2.12)

\[
\nabla \cdot \dot{H} = 0
\] (2.13)
In this form the charge and current densities, $\rho_{\text{total}}$ and $j_{\text{total}}$, may include any external configurations $\rho_{\text{ext}}$, $j_{\text{ext}}$, as well as the first order quantities $\rho = -en$, $j = e\vec{\nabla}\vec{M}$, associated with the fluctuations of the metallic electrons. They may also include any polarisation effects which are usually written explicitly as $\rho_{\text{pol}}$, $j_{\text{mag}} = e(\vec{\nabla}\times\vec{M})$ and $j_{\text{pol}} = \partial\vec{E}/\partial t$.

In the dielectric formalism (for example, Chan and Richmond 1976a) these individual terms are absorbed into the definition of the macroscopic dielectric function through the introduction of the linear electric susceptibility response function $\chi$. Thus $\partial\vec{E}/\partial t + 4\pi j_{\text{pol}} = (\partial/\partial t)(1 + 4\pi\chi)\vec{E} = \partial(e\vec{E})/\partial t = e\vec{D}/\partial t$, etc.

From equation (2.12) and the curl of equation (2.10) the second equation for $j$ and $\vec{E}$ is obtained thus,

$$\left[(\vec{\nabla}\times\vec{\nabla}) - \frac{\omega^2}{c^2}\right]\vec{E} = \frac{4\pi i\omega}{c^2}j . \tag{2.14}$$

### 2.2.2 Wave Equation for $j$ and $\vec{E}$

Combining equations (2.7) and (2.14) it is found that both $j$ and $\vec{E}$ satisfy the same wave equation,

$$\alpha^2 \vec{\nabla}(\vec{\nabla}\cdot j) - \nabla^2 j + \frac{\omega^2 - \omega_p^2}{c^2} j = 0 \tag{2.15}$$

where

$$\alpha^2 = 1 - \frac{\beta^2}{c^2} \tag{2.16}$$

and

$$\omega_p^2 = \frac{4\pi e^2 n_o}{c m} \tag{2.17}$$

defines the usual bulk plasma frequency. Equation (2.15)
represents three equations for the components of the current density \( j = [j_x(x,y,z), j_y(x,y,z), j_z(x,y,z)] \). These equations may be separated and written in matrix form as

\[
\begin{pmatrix}
\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{\omega^2 - \omega_0^2}{c^2} & -\frac{\partial}{\partial y} & -\frac{\partial}{\partial z} \\
-\frac{\partial}{\partial x} & \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{\omega^2 - \omega_0^2}{c^2} & -\frac{\partial}{\partial z} \\
-\frac{\partial}{\partial x} & -\frac{\partial}{\partial y} & \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} - \frac{\omega^2 - \omega_0^2}{c^2}
\end{pmatrix}
\begin{pmatrix}
\dot{j}_x \\
\dot{j}_y \\
\dot{j}_z
\end{pmatrix} = 0,
\tag{2.18}
\]

where the notation \( \partial^2_x \equiv \partial^2/\partial x^2 \), \( \partial^2_{xy} \equiv \partial^2/\partial x \partial y \), etc., has been used.

2.2.3 Example: Infinite Homogeneous Electron Gas

The use of equation (2.18) may be illustrated by deriving the dispersion relations for an infinite homogeneous plasma. The current density may be taken as

\[
\dot{j} = \dot{j}_0 \exp(ik \cdot \vec{r})
\tag{2.19}
\]

where \( \dot{j}_0 \) is a constant vector. There is no loss of generality by letting \( \vec{k} \) be along a particular axis, say the \( x \)-axis, so that \( k_x = k, k_y = k_z = 0 \). Then equation (2.18) becomes
The conditions for self-sustained oscillations then give the familiar relations

\[ \omega^2 = \frac{\omega^2}{\beta^2 k^2} + \omega^2, \quad (2.21) \]

for the longitudinal bulk plasma oscillations in the direction of \( \hat{k} \) and

\[ \omega^2 = \frac{\omega^2}{\beta^2 k^2} + \omega^2, \quad (2.22) \]

for the transverse electromagnetic oscillations.

### 2.2.4 Semi-infinite Electron Gas

For a homogeneous electron gas occupying the half-space \( z < 0 \), and bounded by the \( x-y \) plane, the transverse spatial dependence of all quantities may be taken as \( \exp(i\hat{k} \cdot \hat{r}) \) so that the current density takes the form

\[ \mathbf{j} = \mathbf{j}(z) \exp(i\hat{k} \cdot \hat{r}). \quad (2.23) \]

A current density is sought with vanishing \( z \)-component at the surface and which satisfies the equation of continuity (2.9). The density fluctuation \( n \) is easily obtained from
equations (2.6), (2.9) and (2.11) and satisfies the equation

\[ [d_z^2 - \kappa^2 - \frac{\omega^2}{\beta^2}] n(z) = 0 \quad , \quad (2.24) \]

where

\[ n(r) = n(z) \exp(i\mathbf{k} \cdot \mathbf{r}) \quad . \quad (2.25) \]

The solution for \( n \) which remains finite inside the metal is then

\[ n(r) = \exp(\gamma z + i\mathbf{k} \cdot \mathbf{r}) \quad ; \quad z < 0 \quad , \quad (2.26) \]

where

\[ \beta^2 \gamma^2 = \beta^2 \kappa^2 + \omega_p^2 - \omega^2 \quad . \quad (2.27) \]

With the current density (2.23), the matrix equation (2.18) becomes

\[
\begin{pmatrix}
  d_z^2 + a^2 k^2 y - \nu^2 & a^2 k x y - i a^2 k x d_z & -i a^2 k y d_z \\
  a^2 k x y & d_z^2 + a^2 k^2 y - \nu^2 & -i a^2 k y d_z \\
  -i a^2 k x d_z & -i a^2 k y d_z & \frac{\beta^2}{c^2} d_z^2 - \nu^2
\end{pmatrix}
\begin{pmatrix}
  j_x(z) \\
  j_y(z) \\
  j_z(z)
\end{pmatrix} = 0 \quad , \quad (2.28)
\]

where

\[ c^2 \nu^2 = c^2 \kappa^2 + \omega_p^2 - \omega^2 \quad . \quad (2.29) \]

The three equations in (2.28) are solved simultaneously.
with the result

\[
\mathbf{j} = -\frac{i\omega \gamma}{\gamma^2 - \kappa^2} \left\{ i\kappa \left[ \frac{\exp(\gamma z)}{\gamma} - \frac{\exp(\nu z)}{\nu^2} \right] \right. \\
+ \left. \hat{h}_3 \left[ \exp(\gamma z) - \exp(\nu z) \right] \right\} 
\]  

(2.30)

Similarly, for the half-space \( z > d \), the current density whose \( z \)-component vanishes at \( z = d \) and which satisfies the equation of continuity with

\[
n = \exp\{-\gamma(z-d) + i\kappa \cdot \mathbf{p} \} ; \quad z > d 
\]

(2.31)
is given by

\[
\mathbf{j} = -\frac{i\omega \gamma}{\gamma^2 - \kappa^2} \left\{ i\kappa \left[ \frac{\exp[-\gamma(z-d)]}{\gamma} - \frac{\exp[-\nu(z-d)]}{\nu^2} \right] \right. \\
- \left. \hat{h}_3 \left[ \exp[-\gamma(z-d)] - \exp[-\nu(z-d)] \right] \right\} 
\]

(2.32)

2.3 SOLUTION OF MAXWELL'S EQUATIONS IN FOURIER SPACE

2.3.1 General Solution

At the expense of some initial over-complications, but to avoid repetition of the calculations, the most general case is considered, of two different metals, labelled 1 and 2, occupying the half-spaces \( z < 0 \) and \( z > d \) respectively, with an oscillating point charge \( Q \exp(-i\omega t) \) situated in the vacuum between them. It is convenient to work in the Coulomb gauge in which Maxwell's equations
lead to

\[ \nabla^2 \phi = -4\pi \rho \] , \hspace{1cm} (2.33)

\[ \vec{A} = -\frac{i\omega}{c} \nabla \phi - \frac{4\pi}{c} \vec{j} \] , \hspace{1cm} (2.34)

\[ \vec{E} = \frac{i\omega}{c} \vec{A} - \nabla \phi \] . \hspace{1cm} (2.35)

In equations (2.33) and (2.34) the charge and current densities are

\[ \rho = -e n_1 - e n_2 + Q \delta(\vec{r} - \vec{r}_o) \] , \hspace{1cm} (2.36)

\[ \vec{j} = \vec{j}_1 + \vec{j}_2 \] , \hspace{1cm} (2.37)

where \( n_1, \vec{j}_1, n_2 \) and \( \vec{j}_2 \) are given by equations (2.26), (2.30), (2.31) and (2.32) respectively, with the appropriate step functions included. These individual solutions are for a particular value of \( \kappa \) and represent the Fourier components of the full electron and current densities. They are to be treated as basis functions for the normal modes corresponding to surface oscillations, and the complete electron density fluctuation in the presence of the second metal and external charge is written as a Fourier integral over them. Thus, for example,

\[ n_1(\vec{r}) = \int \frac{d^2\kappa}{(2\pi)^2} \tilde{s}_1(\kappa) \exp(\imath \kappa \cdot \vec{r} + \gamma_1 z) \theta(-z) \] . \hspace{1cm} (2.38)

Such expansions may be put in uniform 3-dimensional Fourier representation using transforms of the type
\[ \exp(\gamma z) \theta(-z) = \int \frac{dk_3}{2\pi} \frac{\exp(ik_3z)}{(k_3+i\gamma)} \quad . \quad (2.39) \]

Then equation (2.38) becomes

\[ n_1(\vec{r}) = \int \frac{d^3k}{(2\pi)^3} \exp(i\vec{k} \cdot \vec{r}) \frac{i S_1(\kappa)}{(k_3+i\gamma_1)} \quad . \quad (2.40) \]

Similarly, using the Fourier representation of the delta-function, the three terms in equation (2.36) can be combined under a single Fourier integral as

\[ \rho(\vec{r}) = -e \int \frac{d^3k}{(2\pi)^3} \exp(i\vec{k} \cdot \vec{r}) \left[ \frac{i S_1(\kappa)}{k_3+i\gamma_1} - \frac{i S_2(\kappa)}{k_3-i\gamma_2} \exp(-i\kappa \cdot \vec{x}) \right] - \frac{Q}{e} \exp(-i\vec{k} \cdot \vec{x}) \quad . \quad (2.41) \]

The full Fourier representation for the current density (2.37) is similarly,

\[ \vec{j}(\vec{r}) = \frac{\omega \gamma_1}{\gamma_2} \int \frac{d^3k}{(2\pi)^3} \exp(i\vec{k} \cdot \vec{r}) S_1(\kappa) \times \left\{ \frac{1}{\gamma_1(k_3+i\gamma_1)} - \frac{\nu_1}{\kappa^2(k_3+i\nu_1)} \right\} + \hat{\gamma}_3 \left[ \frac{1}{k_3+i\gamma_1} - \frac{1}{k_3+i\nu_1} \right] \quad . \quad (2.42) \]

\[ -\frac{\omega \gamma_2}{\gamma_2-\kappa} \int \frac{d^3k}{(2\pi)^3} \exp(i\vec{k} \cdot \vec{r}) S_2(\kappa) \times \left\{ \frac{1}{\gamma_2(k_3-i\gamma_2)} - \frac{\nu_2}{\kappa^2(k_3-i\nu_2)} \right\} - \hat{\gamma}_3 \left[ \frac{1}{k_3-i\gamma_2} - \frac{1}{k_3-i\nu_2} \right] \quad . \quad (2.42) \]

These rather complicated forms are necessary at this point for the inversion of the operators in equations (2.33) and (2.34) using the standard Green's function technique which requires \( \rho \) and \( \vec{j} \) to be defined continuously.
throughout the whole of real space. This is now straight-
forward and the solutions for \( \varphi \) and \( \hat{k} \) are substituted into
equation (2.35) for the electric field, giving

\[
\vec{E}(\vec{r}) = \int \frac{d^2 \kappa}{(2\pi)^2} \exp(i\vec{\kappa} \cdot \vec{r}) \hat{E}_\kappa(\vec{r}),
\]

(2.43)

where

\[
\hat{E}_\kappa(\vec{r}) = \frac{4\pi e i S_1(\kappa)}{\gamma_1^2 - \kappa^2} \int \frac{dk_3 \exp(ik_3 z)}{2\pi (k_3^2 + \lambda^2)} \left\{ ik_3^2 \gamma_1^2 - \gamma_1 \gamma_2 \frac{(\lambda^2 - \kappa^2)}{k_3^2 + i\gamma_1} \right\} + \hat{\gamma}_3 \left( \frac{ik_3^2 (\gamma_1^2 - \kappa^2) - \gamma_1 \gamma_2 (\lambda^2 - \kappa^2)}{k_3^2 + i\gamma_1} \right)
\]

\[
- \frac{4\pi e i S_2(\kappa)}{\gamma_2^2 - \kappa^2} \int \frac{dk_3 \exp[ik_3 (z-d)]}{2\pi (k_3^2 + \lambda^2)} \left\{ ik_3^2 \gamma_2^2 - \gamma_2 \gamma_1 \frac{(\lambda^2 - \kappa^2)}{k_3^2 + i\gamma_2} \right\} + \hat{\gamma}_3 \left( \frac{ik_3^2 (\gamma_2^2 - \kappa^2) + \gamma_2 \gamma_1 (\lambda^2 - \kappa^2)}{k_3^2 + i\gamma_2} \right)
\]

\[
- 4\pi Q \exp(-i\vec{k}_o \cdot \vec{r}) \int \frac{dk_3 \exp[ik_3 (z-z_o)]}{2\pi (k_3^2 + \lambda^2)} \frac{k_3^2 \gamma_1^2 - \gamma_1 \gamma_2 (\lambda^2 - \kappa^2)}{k_3^2 + i\gamma_1} \left( \frac{\gamma_2}{k_3^2 + i\gamma_2} \right),
\]

(2.44)

and where

\[
\lambda^2 = \kappa^2 - \omega^2/\sigma^2.
\]

(2.45)

The relations between the coefficients \( S_1(\kappa) \) and
\( S_2(\kappa) \), and the external charge are obtained as follows.
While the current and electron densities automatically
satisfy the boundary conditions by construction, the
electric field does not. Substituting \( \nu_z = 0 \) into the
\( z \)-component of the hydrodynamic equation (2.6) gives the
following conditions on the electric field at the metal surfaces,

\[-e\eta_1 E_y \bigg|_{z=0^-} = m\gamma_1 \frac{\partial \eta_1}{\partial z} \bigg|_{z=0^-}, \quad (2.46)\]

\[-e\eta_2 E_y \bigg|_{z=d^+} = m\gamma_2 \frac{\partial \eta_2}{\partial z} \bigg|_{z=d^+}. \quad (2.47)\]

These lead to the two equations for \(S_1(\kappa)\) and \(S_2(\kappa)\), in matrix form,

\[
\begin{pmatrix}
2\beta_1^2 \gamma_1 - f_1 & f_2 \frac{\omega_{p1}^2}{\omega_{p2}^2} \exp(-\lambda d) \\
\frac{\omega_{p2}^2}{\omega_{p1}^2} \exp(-\lambda d) & 2\beta_2^2 \gamma_2 - f_2
\end{pmatrix}
\begin{pmatrix}
S_1(\kappa) \\
S_2(\kappa)
\end{pmatrix}
= \begin{pmatrix}
\frac{\omega_{p1}^2 \exp(-\lambda z_0)}{\omega_{p2}^2 \exp[-\lambda(d-z_0)]} e^{i\kappa \cdot \hat{r}} \\
\frac{\omega_{p2}^2 \exp[-\lambda(d-z_0)]}{\omega_{p2}^2 \exp[-\lambda(d-z_0)]}
\end{pmatrix}
\]

where

\[f_j(\kappa, \omega) = \frac{1}{\lambda(\gamma_j^2 - \kappa^2)} \left[ \frac{\omega_{p1}(\gamma_j^2 - \kappa^2)}{\omega_{p2}^2} \right]. \quad (2.49)\]

2.3.2 Example: Single Metal Half-Space

The retarded surface plasmon dispersion relation for a single metal half-space is obtained from equation (2.48) by separating the metals to \(d = \infty\) and letting \(Q = 0\). The two independent SP dispersion relations for the uncoupled metals are then given by
or, on rearranging,

\[
\left[ \frac{\omega_p^2(\gamma \lambda + \kappa^2)}{\omega_p^2(\gamma + \lambda)} - \frac{\omega^2 \gamma (\nu + \lambda)}{(\gamma^2 - \kappa^2)^{-1}} \right] (\gamma^2 - \kappa^2)^{-1} = 0 . \quad (2.50b)
\]

This is just the result of Crowell and Ritchie (1970), except that the factor \((\gamma^2 - \kappa^2)^{-1} \equiv \beta^2 (\omega_p^2 - \omega^2)^{-1}\) is retained since \(\omega = \omega_p\) is also a non-physical solution of the remaining factor and must be avoided in a numerical solution.

In the nonretarded limit \((c \to \infty)\), equation (2.50) reduces to the form (Mahanty and Paranjape 1977)

\[
2\beta^2 \gamma (\gamma + \kappa) - \omega_p^2 = 0 , \quad (2.51)
\]

with well known solution (Ritchie and Wilems 1969)

\[
\omega^2 = \frac{1}{2} \left[ \frac{\omega_p^2}{\omega_p^2 + \beta^2 \kappa^2} + \beta \kappa (\omega_p^2 + \beta^2 \kappa^2) \right] . \quad (2.52)
\]

The local \((\beta = 0)\) retarded result (equation (1.50)) is also reproduced but is of no interest here. For general reference, the typical retarded and nonretarded SP curves have been plotted in figure 1.1 using the free electron gas parameters for Al.
2.4 TWO INTERACTING METAL HALF-SPACES

2.4.1 Surface Plasmons in the Interacting System

At this point the restriction to two identical metals is made (a) to simplify and clarify the analysis, and (b) because the validity of the result (2.48) is restricted to the region of \( \omega - \kappa \) space lying below the bulk continuum region of the less dense metal, say metal 1; that is, below the curve

\[
\omega_{b1}(\kappa) = (\omega_{p1}^2 + \beta_1^2 \kappa^2)^{1/2},
\]

since only the exponentially decaying solutions (2.26) and (2.31) for \( n \), corresponding to surface modes in both metals have been considered. For a complete picture, a separate analysis is required for the region between \( \omega_{b1}(\kappa) \) and \( \omega_{b2}(\kappa) \) in which the density fluctuations satisfying equation (2.24) are oscillatory in the less dense metal 1. This problem is considered in detail in the nonretarded limit in Chapter 4.

Setting \( Q = 0 \) in equation (2.48) gives the secular equation for the eigenfrequencies of the normal surface modes for two identical metals,

\[
D(\kappa, \omega) = \begin{vmatrix} 2\beta^2 \gamma - f(\kappa, \omega) & f(\kappa, \omega) \exp(-\lambda d) \\ f(\kappa, \omega) \exp(-\lambda d) & 2\beta^2 \gamma - f(\kappa, \omega) \end{vmatrix} = 0.
\]

The symmetry of the determinant leads to a direct
factorisation into two independent equations for the symmetric \((\omega_+,\text{upper sign})\) and antisymmetric \((\omega_-)\) modes,

\[
2\beta^2\gamma\lambda - (\gamma^2 - \kappa^2)^{-1}\left[\omega_p^2(\gamma\lambda - \kappa) + \omega^2(\nu - \lambda)\right][1 \mp \exp(-\lambda d)] = 0 .
\]

(2.55)

In the nonretarded limit this reduces to

\[
2\beta^2\gamma(\gamma + \kappa) - \omega_p^2[1 \mp \exp(-\kappa d)] = 0 ,
\]

(2.56)

with solutions (Heinrichs 1973a)

\[
\omega_{\pm N}^2 = \frac{1}{\gamma}\left\{\omega_p^2[1 \mp \exp(-\kappa d)] + \beta \left[2\omega_p^2[1 \mp \exp(-\kappa d)] + \beta^2\kappa^2\right]\right\}^{1/2} + \beta^2\kappa^2 .
\]

(2.57)

Heinrichs derived this result using the dielectric function formalism, in terms of the hydrodynamic form, equation (2.1). The equivalence of the two approaches is easily established as exemplified by these results.

The retarded and nonretarded dispersion curves given by equations (2.55) (numerically) and (2.57) are compared in figures 2.1 and 2.2, using parameters for two Al slabs. The \(\kappa\)-axis is scaled in figure 2.2 to show more clearly the effect of retardation in the small-\(\kappa\) region. It should be noted that the photon line, \(\omega = \sigma\kappa\) for the nonretarded curves is the vertical axis, and that there is no inconsistency in the group velocity for these modes apparently exceeding the velocity of light.

The splitting of the surface modes is expected and has been demonstrated in the nonretarded limit by Heinrichs (1973a) using the hydrodynamic model (equation (2.57)) and by Inglesfield and Wikborg (1975) using the
Caption for Figure 2.1

Surface plasmon dispersion curves for (a) $d = 0$ and (b) $d = 25\text{A}^\circ$. $\omega_+$ and $\omega_-$ are the symmetric and antisymmetric branches respectively, for the interacting metals, and $\omega_s$ is that for the isolated metal surface as in figure 1.1. The retarded and nonretarded curves are virtually indistinguishable except at very small $\kappa$ (see figure 2.2).

Caption for Figure 2.2

Surface plasmon dispersion curves in the small wavenumber region for (a) $d = 0$ and (b) $d = 25\text{A}^\circ$. Full lines : retarded curves, dashed lines : nonretarded curves. The $\omega_+$ branch always bends up to the line $\omega = \sigma \kappa$ at $\kappa_x = \omega_p / (\sigma^2 - \beta^2)^{1/2}$. The effect of retardation on the $\omega_+$ branch becomes increasingly significant with large $d$. 
Figure 2.1

(a) $d = 0$
\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.1}
\caption{Figure 2.1}
\end{figure}

(b) \( d = 25 \text{ Å} \)
Figure 2.2

(a) $d' = 0$
Figure 2.2

\[ \omega / \omega_p \] vs \( \beta \kappa / \omega_p \)

- \( \omega_+ \)
- \( \omega_- \)
- \( \omega = c \kappa \)
- \( \omega_s \)

(b) \( d = 25 \, \text{Å} \)
RPA. However, the latter state that this arises from the coupling only of the original surface modes, as is implied in this chapter, and by Heinrichs as well. In Chapter 3 it will be clearly demonstrated, within the nonretarded hydrodynamic approximation that bulk modes are also involved in this coupling.

2.4.2 Nature of Retardation in Surface Plasmon Dispersion

As is the case for the single SP branch of an isolated metal slab, the lower branch \( \omega_- \), for the interacting metals always remains below the photon line, \( \omega = \omega_\kappa \), but it is otherwise not too different from the nonretarded antisymmetric branch (figure 2.2). The more significant effect of retardation is seen on the upper, symmetric branch \( \omega_+ \), which is bent upwards, terminating at the intersection of the photon line with the lower bound (equation (2.53)) of the bulk continuum. This occurs at the wavenumber given by

\[
\kappa_x^2 = \omega_p^2/(\omega^2 - \beta^2),
\]

below which, no real, symmetric surface mode exists.

The behaviour of the retarded symmetric and antisymmetric branches can be attributed to a rather complicated coupling between the original retarded surface modes, which already have a transverse character through coupling with the electromagnetic field at small \( \kappa \) (for example, Fedders 1968, Ritchie 1973), and both the transverse and longitudinal bulk modes. An explicit
breakdown of this coupling would require a retarded normal mode analysis. This is difficult because of the uncertainty in the normalisation and orthogonality conditions brought about by the very coupling between transverse and longitudinal modes (Barton 1978b, Morse and Feshbach 1953).

2.4.3 Consequences of Retardation for the vdW Interaction

The effect of retardation on the surface plasmon curves (figures 2.1 and 2.2) is responsible for the shift from $d^{-2}$ to $d^{-3}$ in the leading terms of the vdW energy of interaction between two metals, in the asymptotic expansions for the nonretarded and retarded regions respectively. Retardation is insignificant at very small separation distances because the contribution from the small-$\kappa$ region is only a very small fraction of the total vdW energy. In this case a nonretarded analysis is quite adequate. For large $d$, it is well known that only small wavenumber (long wavelength) oscillations contribute significantly to the vdW interaction. But this is precisely where retardation is important. Thus as $d$ increases, the retardation-affected small-$\kappa$ contribution becomes increasingly significant and eventually dominates the interaction (table 2.2, §2.4.4).

2.4.4 vdW Interaction Energy

Following van Kampen et al (1968), the vdW interaction energy $E(d)$ can be expressed as the change in energy of the collective electron surface oscillations due to their correlation when the metals are brought from
infinity to a separation \( d \). For a harmonic oscillator at finite temperature, the energy per mode of frequency \( \omega(\kappa) \) is the internal free energy

\[
\varepsilon_\omega \equiv U = \frac{\hbar \omega}{2} \coth\left(\frac{\hbar \omega}{2k_B T}\right), \quad (2.59)
\]

or the Helmholtz free energy

\[
\varepsilon_\omega \equiv A = k_B T \ln\left[1 - \exp\left(-\frac{\hbar \omega}{k_B T}\right)\right] = \frac{\hbar \omega}{2} + k_B T \ln\left[2 \sinh\left(\frac{\hbar \omega}{2k_B T}\right)\right], \quad (2.60)
\]

depending on whether the system is taken to be at constant entropy or at constant temperature, respectively.

Lifshitz (1956, Dzyaloshinskii et al 1961) has shown that in the retarded region, \( d \gg \hbar \omega / k_B T \), temperature effects may be neglected and the free energy replaced by the zero point energy

\[
\varepsilon_\omega = \frac{\hbar \omega}{2} \quad . \quad (2.61)
\]

In general, the vdW energy can be written as

\[
E(d) = \sum_\kappa \left[\varepsilon_\omega^{(1)}(\kappa) - \varepsilon_\omega^{(0)}(\kappa)\right] \quad (2.62)
\]

where the superscripts 0 and 1 denote the uncoupled and interacting systems respectively. Replacing the sum by an integral over the continuous variable \( \kappa \), this becomes, using the zero point energies (Heinrichs 1973a),
<table>
<thead>
<tr>
<th>( d ) (( \degree ))</th>
<th>( I ) ( \text{erg/cm}^2 )</th>
<th>( % )</th>
<th>( II ) ( \text{erg/cm}^2 )</th>
<th>( % )</th>
<th>( E_{vdW} ) ( \text{erg/cm}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.63</td>
<td>0.05</td>
<td>1218.88</td>
<td>99.95</td>
<td>1219.51</td>
</tr>
<tr>
<td>5</td>
<td>0.59</td>
<td>2.1</td>
<td>28.09</td>
<td>97.9</td>
<td>28.68</td>
</tr>
<tr>
<td>10</td>
<td>0.57</td>
<td>6.8</td>
<td>7.80</td>
<td>93.2</td>
<td>8.37</td>
</tr>
<tr>
<td>25</td>
<td>0.53</td>
<td>31.3</td>
<td>1.16</td>
<td>68.7</td>
<td>1.68</td>
</tr>
<tr>
<td>35</td>
<td>0.51</td>
<td>49.0</td>
<td>0.52</td>
<td>51.0</td>
<td>1.03</td>
</tr>
<tr>
<td>50</td>
<td>0.48</td>
<td>71.0</td>
<td>0.20</td>
<td>29.0</td>
<td>0.68</td>
</tr>
</tbody>
</table>

Contribution to \( E_{vdW} \) for two interacting \( Al \) slabs from the wavenumber regions \( \kappa < \kappa_x (I) \) and \( \kappa_x < \kappa < \kappa_c (II) \).
of retardation while in region II the curves are determined largely by spatial dispersion alone. At \( d = 0 \), as expected, retardation is insignificant. This is also seen by comparing the values in table 2.1 with the nonretarded results of Heinrichs (1973b), the agreement always being within 1%. Beyond about 35°, retardation becomes the dominant factor (table 2.2).

2.4.5 Asymptotic Expansion

van Kampen et al. (1968) rederived Lifshitz' (1956) results in nonretarded form using the theorem which states that the sum of the zeros minus the sum of the poles of a meromorphic function \( D(\omega) \), within a contour in the complex plane, is given by the contour integral

\[
\frac{1}{2\pi i} \int_C d\omega \frac{d}{d\omega} [\ln D(\omega)] .
\]

(2.64)

This leads to the alternative form of equation (2.63), after the variable change \( \omega = i\xi \),

\[
E(d) = \frac{\hbar}{2\pi^2} \int_0^\infty dk \int_0^\infty d\xi \ln[1 - A(\kappa, \xi)\exp(-2\lambda d)] ,
\]

(2.65)

where

\[
A(\kappa, \xi)\exp(-2\lambda d) = \left(\frac{d_{12}}{d_{11}}\right)^2 ,
\]

(2.66)

and where \( d_{11} \) and \( d_{12} \) are the diagonal and off-diagonal elements of the matrix \( D(\kappa, \omega) \) defined by equation (2.54). On rearranging,

\[
A(\kappa, \omega) = \left[\frac{\omega_0^2(\gamma^2) + \omega_\gamma(\nu-\lambda)}{\omega_0^2(\gamma^2) - \omega_\gamma(\nu+\lambda)}\right]^2 .
\]

(2.67)
With the variable changes (Lifshitz 1956)

\[ p(\kappa) = (1 + \frac{2\kappa^2}{\xi^2})^{\frac{1}{2}}, \quad (2.68) \]

\[ x(\xi) = 2d\pi\xi/c, \quad (2.69) \]

equation (2.65) takes the form

\[ E(d) = \frac{\hbar c}{16\pi^2 d^3} \int_0^\infty dx x^2 \int_1^\infty \frac{dp}{p^2} \ln[1 - A(p,\mu)\exp(-x)], \quad (2.70) \]

where \( \mu = xc/d\omega_p \). Since the main contribution to \( E(d) \) arises from small \( x \), a Taylor expansion may be made about \( x = 0 \). To obtain this expansion, the function \( A(p,\mu) \) must be expanded for small \( \mu \), which is ensured if \( d > c/\omega_p \) (of the order of 100\( \Lambda \)\(^0 \) for typical metals). Thus

\[ A(p,\mu) = 1 - \frac{4\mu}{p^2}(\frac{\beta}{c} + 1 - \frac{\beta}{c}) + O(\mu^2), \quad (2.71) \]

for which the following asymptotic expansion is obtained,

\[ E(d) = -\frac{\hbar c\pi^2}{720d^3} [1 - 2\eta(1 + 2\frac{\beta}{c}) + O(\eta^2)], \quad (2.72) \]

where \( \eta = c/d\omega_p \).

In the limit \( \omega_p \rightarrow \infty \), corresponding to infinite conductivity, all correction terms vanish, leaving the Casimir (1948) result (2.4) for ideal conductors at \( d \rightarrow \infty \).

In the retarded region the effect of spatial dispersion is negligible since in the first correction term of equation (2.72), \( 2\beta/c \sim 10^{-3} \). This is to be expected from purely
qualitative arguments and is in contrast to the nonretarded asymptotic expansion given by Heinrichs \(1973a\) as

\[
E(d) = -\frac{\hbar \omega_p}{64\sqrt{2}\pi d^2} \left[ \frac{69}{64} - \frac{35\sqrt{2}}{4} \lambda + \frac{17703}{128} \lambda^2 - 885\sqrt{2} \lambda^3 \right. \\
\left. + \frac{13035}{2} \lambda^4 + O(\lambda^5) \right], \quad (2.73)
\]

where \(\lambda = \beta/4\omega_p d\), in which terms up to \(O(\lambda^4)\) must be included for accuracy of a few per cent for separations down to \(d = 4A^\circ\). By the nonretarded 'asymptotic' region is meant \(\lambda_o \ll d \ll c/\omega_p\), where \(\lambda_o\) is of the order of the characteristic atomic dimensions of the system.

2.4.6 Conclusion

In conclusion, the vdW interaction between metals may be summarised as follows.

(i) At very small separation distances, \(d \sim \lambda_o\), the attractive vdW interaction contributes only a small part of the overall interaction between the metals, the interaction being dominated by the repulsive forces brought about by the change in kinetic energy of the electrons near the surface. In addition, quantum effects are important as the electronic shells overlap. A semiclassical treatment, and in particular, the hydrodynamic model, is unreliable at these distances.

(ii) In the nonretarded region, \(\lambda_o < d < c/\omega_p\), the vdW interaction is dominated by the effects of spatial dispersion. Plasma oscillations of all wavelengths (down to the cutoff \(\lambda_c\)) contribute substantially to the vdW
interaction and so the effect of retardation, which is confined to very long wavelengths, is not felt. The nature of the metals is important, with the metallic parameters entering into all terms in the expansion (2.73).

(iii) In the retarded region, \( d > c/\omega_p \), retardation is the dominant factor and reduces the interaction from a \( d^{-2} \) to a \( d^{-3} \) behaviour. This effect may be considered as being due to the instantaneous mutual polarisations in the metals becoming incoherent because of the finite velocity of the electromagnetic fields. For \( d >> c/\omega_p \), to first order, the metals see each other as perfect conductors, the first term in the expansion (2.72) being independent of the metal parameters. Spatial dispersion is negligible in the correction terms. The importance of retardation can be qualitatively analysed in terms of its effect on the surface plasmon branches. This effect is dramatic for long wavelength surface plasmons which dominate the vdW interaction at large separation distances.

2.5 MOLECULE NEAR A METAL SURFACE

2.5.1 General Result

The vdW interaction for a molecule, polarisability \( \alpha(\omega) \), in the vicinity of a metal surface can be obtained from the dyadic Green's function for a unit oscillating point dipole near the metal, which in turn is obtained from the electric field associated with a point charge source. For this system, the electric field is given by equation
(2.44) without the term involving $S_2(k)$. The coefficient $S_1(k)$ is obtained from the general result (2.48) by letting $d \to \infty$, thus

$$S_1(k) = \frac{\omega^2}{e \rho} \frac{\exp(-\frac{i\kappa \cdot \rho}{\omega} - \lambda \sigma)}{D_1(k, \omega)},$$

(2.74)

where $Q$ has been set equal to $1$ and $D_1(k, \omega)$ is given by equation (2.50).

For an isotropic polarisability, the expression for the vdW interaction energy is (Mahanty and Ninham 1976)

$$E(s_o) = -\frac{\eta}{2\pi} \int_0^\infty \alpha(i\xi) \text{Tr} \hat{G}^*(\rho_o, \rho_o, i\xi) \quad (2.75)$$

The dyadic Green's function connecting the electric field at $\hat{r}$ with a unit dipole source at $\hat{r}_o$, outside the metal, is given by

$$\hat{G}^*(\rho, \rho_o; \omega) = \hat{V}_o \hat{E}_I(\rho, \rho_o; \omega),$$

(2.76)

where $\hat{E}_I$ is the interaction part of the electric field and the dyadic gradient operation is to be taken at $\hat{r}_o$. Using the explicit expressions for $S_1(k)$ (equation (2.74)) and $\hat{E}_I$ (first term of equation (2.44)), with the $k_3$ integral performed for $z > 0$, equation (2.75) becomes

$$E(s_o) = -\frac{\eta \omega^2}{\pi} \int_0^\infty \alpha(i\xi) \int_0^\infty \frac{dk \kappa \lambda}{\omega} \exp(-2\lambda s_o) F(k, \xi),$$

(2.77)

where
\[ F(\kappa, \xi) = \left[ \lambda \nu (\gamma^2 - \kappa^2) + \gamma \nu (\lambda^2 - \kappa^2) + \kappa^2 (\gamma^2 - \lambda^2) \right] \]
\[ \times \left\{ (\gamma + \lambda)(\nu + \lambda) \left[ \omega_p^2 (\gamma \lambda + \kappa^2) + \gamma \xi^2 (\nu + \lambda) \right] \right\}^{-1}. \tag{2.78} \]

With the variable changes (2.68) and (2.69) this becomes

\[ E(z_o) = -\frac{\hbar \omega^2}{16\pi^2 \varepsilon_o^4} \int_1^\infty \frac{dp}{p^2} \int_0^\infty dx \ x^3 \exp(-x) \ a(\mu) \ F(p, \mu), \tag{2.79} \]

where \( \mu = xc/2pz_o \).

2.5.2 Asymptotic Expansion

The dominance of small \( x \), through the factor \( \exp(-x) \), ensures that for reasonably large values of \( z_o \), a Taylor expansion of the integrand about \( \mu = 0 \) is possible, thus

\[ a(\mu) \ F(p, \mu) = a(0) \ F(p, 0) + \mu \left( \frac{\partial}{\partial \mu} [a(\mu) F(p, \mu)] \right)_{\mu=0} + \ldots. \tag{2.80} \]

In general, equation (2.79) may be integrated numerically, using a general form of the polarisability based on experimentally-determined oscillator strengths for the various resonant frequencies of the molecule. However, an asymptotic expansion using equation (2.80) may be obtained quite simply. For simplicity, the model polarisability

\[ a(i\xi) = \frac{a(0) \ \omega_o^2}{\omega_o^2 + \xi^2}, \quad \tag{2.81} \]

dominated by a single excitation frequency \( \omega_o \) is assumed.

The first few terms in the asymptotic expansion for \( E(z_o) \)
then become

\[
E(z_o) = - \frac{3\hbar \alpha(0)}{8 \pi z_o^4} \left[ 1 - \frac{3\sigma}{4\omega \rho z_o} (1 + \frac{\rho}{\sigma}) \right.
\]
\[
+ \frac{3\sigma^2}{2\omega \rho z_o^2} (17 + 16\frac{\rho}{\sigma} + 32\frac{\rho^2}{\sigma^2} - 10\frac{\rho}{\omega z_o^2}) \left. \right] 
\]  

(2.82)

2.5.3 Discussion

There are several points of interest here.

(i) In the limit of infinite conductivity \((\omega_p + \infty)\) only the first term in equation (2.82) remains. This is just the result of Casimir and Polder (1948) for a molecule with static polarisability \(\alpha(0)\) near a perfectly conducting metal plate (see equation (2.3)).

(ii) The first two terms in the expansion (2.82) depend only on the static polarisability of the molecule and are thus independent of the model form (2.81). For a more general form of \(\alpha(\omega)\) the oscillator strengths and excitation frequencies would only enter into the third- and higher-order terms in the retarded asymptotic expansion.

(iii) As for the two metal case, the general observation is that in the retarded region, spatial dispersion is of only very minor importance \((2\rho/c \ll 1\) in the first correction term).

(iv) A final observation concerns the comparison with the nonretarded asymptotic expansion (Mahanty and Paranjape 1977)
\[ E(z_o) = -\frac{\hbar \alpha(0)}{2\pi} \left[ \frac{\pi \omega_o \omega_s}{4(\omega_o + \omega_s)^2} - \frac{3\beta \omega_o^2 \omega_s^2}{4z_o^4} f(\omega_o, \omega_s) + O\left(\frac{\beta^2}{z_o^5}\right) \right], \]

(2.83)

where \( \omega_s = \omega_o / \sqrt{2} \) and \( f(\omega_o, \omega_s) \) is some function only of \( \omega_o \) and \( \omega_s \), and of no interest here. This expansion has been attributed to the effect of spatial dispersion in making the image of the oscillating monopole develop a diffuseness which can be represented by higher-order multipole moments. This description is borne out by the fact that in the spatially non-dispersive limit \( \beta = 0 \), the expansion (2.83) collapses to the 'point image' result (Bardeen 1940, Mukhopadhyay and Mahanty 1975)

\[ E(z_o) = -\frac{\hbar \alpha(0) \omega_o \omega_s}{8(\omega_o + \omega_s)^2 z_o^3}. \]

(2.84)

However, on taking the local limit in the retarded result (2.82), an expansion involving \( c \) still remains and hence the 'diffuse image' effect persists. This may be attributed to the incoherency of the mutual polarisations in the molecule and metal, associated with the time lag caused by the finite value of \( c \).
Normal Mode Analysis of the Image Potential and v.d.W. Interaction

3.1 INTRODUCTION

3.1.1 Preliminary Remarks

This chapter is devoted to a study of the interactions of an external stationary charge and of a neutral molecule with a metal surface, in terms of the normal plasmon modes excited in the metal by the external source. In Chapter 2 this problem was treated briefly, with the general result and asymptotic expansion being given for the retarded v.d.W interaction between a molecule and a metal surface. Here the emphasis is on the contribution of the surface and bulk collective oscillations to the v.d.W interaction. Such a study is important for the understanding of physisorption on metals and since this phenomenon necessarily involves very small separation distances, a nonretarded analysis is quite adequate.

While no attempt is being made to address the detailed problem of adsorption of atoms on metal surfaces,
a brief outline of this complex field is given in §3.1.2 to establish the important role of the vDW interaction. The quantitative value of recent applications to physisorption is also questioned.

In the study of the vDW interaction, particularly at distances involved in physisorption, the question of the reference or surface plane is often raised. In the non-self-consistent jellium model this is usually naturally chosen as the edge of the positive background. However, as highlighted in a self-consistent calculation in which the electron density extends beyond the positive background, the definition of the surface plane can greatly influence the equilibrium distances and energies involved in physisorption. This question is taken up in §3.1.3.

The classical normal mode analysis presented here, based on the hydrodynamic model, shows that the surface and bulk plasmon contributions to the image potential and to the vDW energy for a molecule near a metal surface add up to give previous results (Mahanty and Paranjape 1977) obtained by direct solution of the hydrodynamic equation for charge density fluctuations of the form \( \exp(\gamma z) \). This equivalence seems surprising but it will be shown that the response function obtained in the latter approach requires only a trivial analytic continuation to the case in which \( \gamma \) becomes complex, representing the oscillatory bulk modes. In the calculation of the vDW interaction, involving an integral over complex frequencies, this continuation is not required.

Barton (1976, 1978b), recognising that the method of Mahanty and Paranjape (1977) failed to demonstrate explicitly
the nature of the modes involved, considered the normal mode analysis quantum mechanically. His explicit results were given only in the static limit. The classical analysis here yields quite straightforwardly the general dynamic forms of the interactions for both a charge and a molecule near a metal, and these contain all previous first order dynamic approximations as well as the static results. The explicit surface and bulk contributions are given throughout, and the fact that in the local (spatially non-dispersive) limit, the bulk contributions vanish, is the reason for the common inferral, based on a local theory, that surface plasmons alone give rise to the image and vdW forces.

In general it is shown that the surface contributions are dominant in the nonretarded asymptotic forms of the interactions, always giving rise to the leading term. The net second order term, after cancellation of the surface contribution with part of the bulk term, always arises from the bulk contribution.

As a further illustration, the surface plasmon dispersion relations for the symmetric and antisymmetric modes associated with two coupled metal half-spaces are rederived, explicitly demonstrating the influence of the bulk modes in this interaction.

3.1.2 Adsorption and the Role of vdW Forces

The common distinction between physisorption and chemisorption is based on the magnitude of the binding energies involved, these being of the order $10^{-2}\text{eV}$ and lev respectively. These in turn are only a reflection of the
actual physical or chemical processes involved. The fact that an atom or molecule will reside at some equilibrium distance $d_{eq}$, from the surface, with a minimum of energy, called the adsorption energy, is a result of the cancellation of the repulsive and attractive forces on that atom or molecule.

(A) In chemisorption (eg. Newns 1969a, Wojciechowski 1971, Lyo and Gomer 1974, 1975, Gomer 1975, Williams and Lang 1977) an actual covalent or ionic bond is formed. The electron is either shared or transferred between the adatom and substrate as a result not only of the overlapping of the electron clouds due to their spatial extension, but also of the relative ionisation energies and electron affinities or electronegativities. Chemisorption will be likely for such adatoms as hydrogen, the group VII halides, the group I alkalines, and of course the all important oxygen, on various metals, and particularly on those with considerable spatially extensive electron clouds such as the transition metals, characterised by their prominent $d$-bands. A complete study of chemisorption must account for the band and orbital structure of the system and hence the LCAO-MO method (Anderson 1961, Gomer 1975) is often used, in which the Schrödinger equation is solved, using as basis functions the appropriate atomic and molecular orbital wavefunctions of the metal and adatom. Such studies do, however, suffer from considerable parametrisation with respect to the equilibrium distance, the Coulomb image attractive energy and the degree of overlap (Lyo and Gomer 1975).

The vdW forces play no role in the actual chemical
bonding associated with chemisorption; that is, in
determining the equilibrium distance and adsorption energy.
Their importance lies in their role as the long-range
attractive 'prime mover', in which capacity they may also
act to geometrically align the adatom so as to enhance
the probability of chemical bonding. That they are of little
importance in chemisorption itself is illustrated by the
fact that the alkaline metal adatoms, which have very low
first ionisation energies, actually ionise some distance
from the substrate. This, and other aspects of adsorption,
both physical and chemical, have been reviewed by
Wojciechowski (1971).

(b) Physisorption is basically much simpler in that
the overlap of electron clouds is characteristically very
small or negligible. This applies in particular to the
adsorption of inert gases such as He on simple s-p type
metals. The repulsive interaction arises mainly from the
increase in kinetic energy of the electrons in the metal
near the adatom, as a result of the quantum restrictions
placed on them in assembling the system. The attractive
forces can be divided into the short range exchange and
correlation forces associated with some degree of overlap,
and the long range vdW or dispersion forces. These will
naturally vary in relative importance, depending as the
degree of overlap varies from the case in which covalent
bonding is effective to the other extreme of no overlap.
The latter 'weak coupling' case (Kleiman and Landman 1973a,b,
1974, 1976) represents the simplest model to study and is
dominated by the vdW interaction.
While the work of Kleiman and Landman (KL) represents a valuable systematic approach to physisorption, certain criticisms are in order. Their use of the density functional (DF) method (Hohenberg and Kohn 1964, Kohn and Sham 1965) to calculate the repulsive energy must be questioned. Although they later introduced self-consistency (KL 1976), the approximation of weak coupling essentially reduced its use to a first order approximation in which self-consistency was not required. With respect to the application of the DF method to higher density metals, both simple and transition, it must be remembered that for such metals the method gave the wrong sign for surface energies (Lang and Kohn 1970) unless corrected by the inclusion of the ionic lattice. In addition, its application to the rapidly varying electron density of the single adatom must also be considered very approximate. While KL have justified these limitations within the context of the other approximations associated with 'weak coupling', and while their early results for He on various metals are in reasonable agreement with the limited available experimental data, these criticisms must certainly have a bearing on their results for heavier adatoms (KL 1976). Here, the inclusion of self-consistency increased the binding energies, but without any systematic improvement in the agreement with experimental values. It should also be pointed out that the DF method was also used by Smith et al (1973) to study hydrogen chemisorption with unsatisfactory quantitative results for the binding energies (Lyo and Gomer 1975), although giving useful information about the electron density
surface profile (Lang and Williams 1978).

Finally, in their investigation of the effects of spatial dispersion on physisorption (KL 1974), Kleiman and Landman committed the rather grave error of simply substituting a non-local dielectric function into the Lifshitz non-retarded formula. An equivalent procedure was employed by Craig (1972) in his calculation of surface energies. That this is an invalid procedure is discussed, for example, by Barash and Ginzburg (1975) and Heinrichs (1975). The proper inclusion of spatial dispersion in generalising Lifshitz' work is discussed by Barash and Ginzburg (1975, see also Lushnikov and Malov 1974). KL subsequently reverted to the local approximation (KL 1976) when they included self-consistency in the repulsive energy calculation.

The above discussion is intended to point out the complexity of the adsorption problem. The general remark must also be made, that the reliability of the vdW interaction calculated using the hydrodynamic model, let alone a local model, is questionable at the distances involved in physisorption, these being of the order of only a few angstroms. In view of this it would be futile at this stage to attempt to apply the results for the vdW interaction given here and in Chapter 2 to this problem. Instead, given the underlying importance of the vdW interaction, a detailed study of this aspect of physisorption is more appropriate.
3.1.3 The Reference Plane

The definition of the 'reference' or 'surface' plane $z = z_s$ can only be rigorously considered on a microscopic, quantum basis when the distance of a charge or a molecule from a metal surface, or between two metal surfaces may be measured in terms of the centre-centre separation of the nearest nuclei, or even the degree of overlap of the electron clouds of the interacting system. Any such definition is obviously subject to uncertainties of quantum origin as well as from approximations necessitated by the mathematics of the many-body problem. In the jellium model, whether self-consistent or not, these uncertainties are maximised to the degree that $z_s$ becomes merely a phenomenological parameter, and must be treated consistently with the model used.

Lang and Kohn (1973) have calculated the image potential self-consistently and have shown that the classical image potential, $1/4z$, (Bardeen 1940) is accurate in the nonretarded asymptotic region if $z$ is replaced by some $z_s$ which shifts the effective surface plane outside the edge of the positive background. They showed that this $z_s$ corresponds to the centre of mass of the self-consistent electron distribution, which extends beyond the jellium.

Zaremba and Kohn (1976) used an analogous procedure to define the surface plane by comparing their calculated nonretarded asymptotic expansion of the vdW energy,
\[ E(z) \approx \frac{C}{z^3} - \frac{D}{z^4} \] \hfill (3.1)

with an equivalent form

\[ E(z) \approx \frac{C}{(z - z_s)^3} \] \hfill (3.2)

Expanding the second form binomially, the second order terms coincide when

\[ z_s = \frac{D}{3C} \] \hfill (3.3)

For He on Al they obtained \( z_s = 1.04 \) a.u. and concluded that the vdW energy obtained by Kleiman and Landman (1973b) at the equilibrium separation of 7.0 a.u. would be increased by 60% with this correction. However, despite earlier criticisms of the quantitative value of the latter's work, this seems an unfair criticism. As pointed out by Kleiman and Landman, the use of the edge of the positive background for the surface plane was used consistently for the calculation of both the attractive and repulsive energies. The use of the parameter \( z_s \) would obviously likewise increase the repulsive contribution and this must be considered before such a criticism is made.

More importantly, the derivation and use of \( z_s \) itself must be questioned. Firstly, while the convergence of the expansion (3.1) is ensured by virtue of the fact that it is obtained for large \( z \), \( z_s \) is very sensitive to the values of the coefficients \( C \) and \( D \), and hence to the model
used to calculate them. Zaremba and Kohn have assumed, within the framework of linear response theory, that the coefficients will also converge. This is difficult to assess for the vdW interaction between a molecule and a metal where the value of D depends on the values of the characteristic excitation frequencies of the molecule or atom relative to the normal surface and bulk plasmon frequencies of the metal (see equation (3.81)). In particular, when an excitation frequency \( \omega_o \), of the atom, lies near the surface plasmon frequency \( \omega_s \), of the metal, Barton (1978a, b, see also Mavroyannis and Hutchinson 1977, Mavroyannis 1977, Delanaye et al 1978) has shown that a perturbation method is inadequate to treat the splitting of the spectrum about this resonance. The reference plane \( z_s \) must be re-evaluated for each type of interaction with the metal surface, whether it be a molecule, charge or another metal. In the latter cases, the convergence of the coefficients is generally well satisfied since the expansion parameter is usually of the form \( \delta = \beta/\omega_p z \), where \( \beta/\omega_p \lesssim 1\AA^2 \).

The second point relates to the use of \( z_s \) to shift the 'image' curve so as to fit a self-consistently calculated curve in the asymptotic region. (By 'image' here is meant any presumably less accurate curve.) This does not guarantee, as is its intention, an accurate correction to the image curve at distances involved in physisorption. This is obvious from figure 3.1 which shows schematically the well known behaviour of retarded and nonretarded, nonlocal and local curves for a typical vdW interaction. As discussed in Chapter 2, spatial dispersion is effective
Figure 3.1

Typical behaviour obtained for $E_{vdW}$ vs. separation distance $d$ in local-nonretarded (L-NR), local-retarded (L-R), nonlocal-nonretarded (NL-NR) and nonlocal-retarded (NL-R) levels of approximation.
at small distances where the local curves diverge together, while at large distances retardation is dominant and the retarded and nonretarded curves pair off separately. This introduces the final criticism, that if a surface plane is to be defined at all (as a parameter), then it should be obtained from the more accurate retarded asymptotic expansion which involves different coefficients C' and D' (see equations (2.72) and (2.82)).

In conclusion, the phenomenological nature of $z_s$ is such that it cannot guarantee an accurate correction to the vdW interaction obtained from approximate models, and may even be inconsistent with such a model (Kleiman and Landman 1973b). In the study of physisorption where the repulsive and attractive energies are required accurately at very small distances, only a detailed many-body calculation, taking into account the lattice structure of the metal can give quantitative results. Any non-overlapping continuum model for such interactions must be regarded with caution at small separation distances. With this in mind, it is the need for a better qualitative understanding of dispersion interactions in general that motivates the work presented here.
3.2 THE NORMAL MODE FUNCTIONS

3.2.1 Preliminary Definitions and Some Useful Results

The preliminary analysis here is identical in the long run to that of Barton (1976, 1978b) but follows a different logical progression and some definitions involve opposite signs. It is convenient to write the linearised hydrodynamic equation (1.31) in terms of the displacement vector $\xi$ of a unit volume of the electron gas from equilibrium (defined simply by $\dot{v} = \partial \xi / \partial t$) thus,

$$n_o \frac{\partial^2 \xi}{\partial t^2} = - \frac{\varepsilon n_o}{m} \dot{\xi} - \beta^2 \nabla n$$

and introduce the displacement potential $\psi$ and the electrostatic potential $\varphi$, defined by

$$\xi = - \dot{\psi}$$

$$E = - \nabla \varphi$$

These are, of course, based on the assumption that the electron displacement and electric fields are irrotational, and must be generalised with the inclusion of retardation, which brings in the full transversality of the fields. From equation (3.5), the equation of continuity, and the definition of the linearised particle current density,

$$\dot{j}_p = n_o \dot{v} = n_o \frac{\partial \xi}{\partial t}$$

it follows that
The density fluctuation is also related to the electrostatic potential through Poisson's equation, which, in the absence of any external source, is simply

\[ n = n_o \nabla^2 \psi = -n_o \nabla \cdot \mathbf{\xi} \quad . \quad \text{(3.8)} \]

The hydrodynamic equation will be most useful in the following form. Using equations (3.6) and (3.8) on the right hand side of equation (3.4) gives

\[ \frac{\partial^2 \mathbf{\xi}}{\partial t^2} + \beta^2 \nabla^2 (\nabla \cdot \mathbf{\xi}) + \frac{e}{m} \nabla \psi = 0 \quad . \quad \text{(3.10)} \]

A useful result follows from equation (3.10) after assuming the time dependence exp(\(i\omega t\)) and using equation (3.5). The first integral of the resulting equation then gives

\[ \psi = \frac{m}{e} (\omega^2 + \beta^2 \psi^2) \psi \quad . \quad \text{(3.11)} \]

Finally, the wave equations for \(n, \psi\) and \(\psi\) are derived most easily from the equation

\[ n_o \omega^2 \psi^2 - \frac{e}{m} n_o \psi^2 \psi + \beta^2 \psi^2 = 0 \quad , \quad \text{(3.12)} \]

which is obtained by taking the divergence throughout equation (3.4) and using the definitions (3.5) and (3.6).
3.2.2 Wave Equations and Boundary Conditions

Elimination of the various terms in equation (3.12) using the identities (3.8) and (3.9) is trivial and results in the following equations:

\[
\begin{align*}
(\beta^2 \nu^2 - \omega^2 p + \omega^2) n(\mathbf{r}) &= 0, \quad (3.13) \\
\nabla^2 (\beta^2 \nu^2 - \omega^2 p + \omega^2) \varphi(\mathbf{r}) &= 0, \quad (3.14) \\
\nabla^2 (\beta^2 \nu^2 - \omega^2 p + \omega^2) \psi(\mathbf{r}) &= 0. \quad (3.15)
\end{align*}
\]

While both \( \varphi \) and \( \psi \) satisfy the same wave equation, they are naturally subject to different boundary conditions. In addition to the requirement of continuity of \( \varphi \) and \( \partial \varphi / \partial z \) across the surface, the vanishing of the normal component of the current density (equation (3.7)), as discussed in Chapter 1, also requires that \( \partial \psi / \partial z \) vanish at the surface. Thus for a metal occupying the negative \( z < 0 \) half-space the boundary conditions become

\[
\begin{align*}
[\varphi]_{z=0} &= 0, \quad (3.16a) \\
\left[ \frac{\partial \varphi}{\partial z} \right]_{z=0} &= 0, \quad (3.16b) \\
\left[ \frac{\partial \psi}{\partial z} \right]_{z=0^-} &= 0. \quad (3.16c)
\end{align*}
\]

where \([X]\) signifies 'the discontinuity of \( X \).

For the half-space system, the transverse spatial dependence may be taken, as usual, as \( \exp(i \mathbf{k} \cdot \mathbf{r}) \). Then the equations (3.13) to (3.15) for the quantities \( \psi(z) \), etc., where \( \psi(\mathbf{r}) = \psi(z) \exp(i \mathbf{k} \cdot \mathbf{r}) \) become, for example,
\[
\left( \frac{d^2}{dz^2} - \kappa^2 \right) \left( \beta^2 \frac{d^2}{dz^2} - \beta^2 \kappa^2 - \omega_p^2 + \omega^2 \right) \psi(z) = 0. \quad (3.17)
\]

The surface modes \( \psi_\kappa \), are identified as the solutions of equation (3.17) when

\[
\beta^2 \gamma^2 = \beta^2 \kappa^2 + \omega_p^2 - \omega^2 > 0 \quad , \quad (3.18)
\]

and thus correspond to exponentially decaying density fluctuations. The bulk modes \( \psi_{\kappa q} \), are obtained when

\[
\beta^2 q^2 = \omega^2 - \omega_p^2 - \beta^2 \kappa^2 > 0 \quad , \quad (3.19)
\]

and correspond to oscillatory density variations.

### 3.2.3 Surface Modes

The general solution of equation (3.17), subject to the condition (3.18), which remains finite as \( z \to -\infty \) is

\[
\psi_\kappa(z) = A \exp(\gamma z) + B \exp(\kappa z) \quad . \quad (3.20)
\]

The corresponding electrostatic potential and density fluctuation inside the metal are then obtained using equations (3.11) and (3.8), while outside the metal, the potential satisfies Laplace's equation and is given by

\[
\varphi_\kappa^o(z) = C \exp(-\kappa z) \quad . \quad (3.21)
\]

Application of the boundary conditions then yields the system of equations
The condition for a unique solution is then given by the secular equation which may be expanded as

$$2\omega_k^2 \gamma - \omega_p^2 (\gamma + \kappa) = 0 \quad (3.23)$$

This is simply another form for the equation (Mahanty and Paranjape 1977)

$$2\beta^2 \gamma (\gamma + \kappa) - \omega_p^2 = 0 \quad (3.24)$$

and yields the well known surface plasmon relation (Ritchie and Wilems 1969),

$$\omega_k^2 = \frac{1}{\kappa} [\omega_p^2 + \beta^2 \kappa^2 + \beta \kappa (2\omega_p^2 + \beta^2 \kappa^2)] \quad (3.25)$$

Solution of equations (3.22) for the relationships between the constants then gives the un-normalised set of normal mode solutions. In terms of the normalisation constant $N = \frac{A}{k},$ yet to be determined, these are given inside the metal by

$$\psi_k (\mathbf{r}) = -N_k \exp(i \kappa \mathbf{r}) [\kappa \exp(\gamma \mathbf{z}) - \gamma \exp(\kappa \mathbf{z})], \quad (3.26)$$

$$\varphi_k (\mathbf{r}) = -\frac{m}{\epsilon} N_k \exp(i \kappa \mathbf{r}) [\omega_p^2 \exp(\gamma \mathbf{z}) - \omega_k^2 \gamma \exp(\kappa \mathbf{z})], \quad (3.27)$$
\[ \xi_k^\pm(n) = -n_0 \kappa (\gamma^2 - \kappa^2) N_k \exp(\pm i k \cdot \rho) \exp(\gamma z), \quad (3.28) \]

while outside the metal,
\[ \phi_k^o(n) = -\frac{m}{e} N_k \exp(\pm i k \cdot \rho) \left( \omega_p^2 - \omega^2 \right) \exp(-\kappa z). \quad (3.29) \]

The negative sign is defined here so that the normal mode displacement vector, which will be used in normalisation, is then given by
\[ \xi_k^\pm(n) = N_k \exp(\pm i k \cdot \rho) \left\{ \pm \kappa \exp(\gamma z) - \gamma \exp(\kappa z) \right\} \]
\[ + \hat{n}_3 \gamma \kappa \left[ \exp(\gamma z) - \exp(\kappa z) \right] \} \quad (3.30) \]

### 3.2.4 Bulk Modes

The general solution of equation (3.17), now subject to the condition (3.19), is
\[ \psi_{\kappa q}(z) = P \cos qz + Q \sin qz + R \exp(\kappa z), \quad (3.31) \]

which again can be used to obtain \( \phi_{\kappa q} \) and \( n_{\kappa q} \) inside the metal. Outside, the potential is now written
\[ \phi_{\kappa q}(z) = S \exp(-\kappa z) \quad (3.32) \]

and the boundary conditions (3.16) yield the system of equations
There are now an infinite number of solutions to this set of equations, representing a continuum of bulk modes labelled by the continuous index $q > 0$. The bulk mode frequencies are simply given, from equation (3.19), by

$$\omega_{\kappa q}^2 = \omega_p^2 + \beta^2 (\kappa^2 + q^2)$$  \hspace{1cm} (3.34)

This is nothing but the usual bulk plasmon dispersion relation with $\kappa^2 + q^2 = k^2$, and the obvious physical significance of $q$ is that of the wavevector component of the bulk oscillations, normal to the surface. The magnitude of $q$ thus also defines the direction of the bulk wave relative to the surface. As a consequence of the surface, it may be seen that these bulk modes are characterised by standing waves, as against the travelling wave motion for an infinite sample (Barton 1976).

The equations (3.33) can be solved for three of the coefficients in terms of the fourth, say $P$. Defining a normalisation constant $M_{\kappa q} = -P$, the various normal mode solutions for the bulk modes then become, with the definition $Q_{\kappa q} = 2\omega_{\kappa q}^2 - \omega_p^2$,

$$\psi_{\kappa q}(\vec{r}) = - M_{\kappa q} \exp(i\vec{\kappa} \cdot \vec{r}) \left[ \cos qz + \frac{\kappa^2}{Q_{\kappa q}} \sin qz - \frac{\omega_p^2}{Q_{\kappa q}} \exp(\kappa z) \right],$$  \hspace{1cm} (3.35)
\[ \varphi_{\kappa q}(\mathbf{\hat{r}}) = -\frac{m}{e} \frac{\omega_p^2}{\kappa q} \exp(i\mathbf{k}_q \cdot \mathbf{\hat{r}}) \left[ \cos qz + \frac{\kappa_0^2}{q Q_{\kappa q}} \sin qz - \frac{\omega_p^2}{Q_{\kappa q}} \exp(\kappa z) \right], \] (3.36)

\[ n_{\kappa q}(\mathbf{\hat{r}}) = n_o (q^2 + \kappa_0^2) \frac{\kappa q}{M_{\kappa q}} \exp(i\mathbf{k}_q \cdot \mathbf{\hat{r}}) \left[ \cos qz + \frac{\kappa_0^2}{q Q_{\kappa q}} \sin qz \right], \] (3.37)

\[ \varphi^0_{\kappa q}(\mathbf{\hat{r}}) = -\frac{m}{e} \frac{M_{\kappa q}}{\kappa q} \exp(i\mathbf{k}_q \cdot \mathbf{\hat{r}}) \frac{\omega_p^2}{\kappa q} \frac{(\omega^2 - \omega_p^2)}{Q_{\kappa q}} \exp(-\kappa q), \] (3.38)

and

\[ \hat{\xi}_{\kappa q}(\mathbf{\hat{r}}) = \frac{M_{\kappa q}}{\kappa q} \exp(i\mathbf{k}_q \cdot \mathbf{\hat{r}}) \left\{ i\mathbf{k} \left[ \cos qz + \frac{\kappa_0^2}{q Q_{\kappa q}} \sin qz - \frac{\omega_p^2}{Q_{\kappa q}} \exp(\kappa q) \right] \right. \\
- qh_3 \left[ \sin qz - \frac{\kappa_0^2}{q Q_{\kappa q}} \left[ \cos qz - \exp(\kappa q) \right] \right \}. \] (3.39)

3.2.5 Normalisation

The normalisation conditions which give the constants \( N_\kappa \) and \( M_{\kappa q} \) are derived as follows. Following Barton (1978b), and replacing the surface and bulk subscripts by the general index \( \lambda \), equation (3.11) may be written

\[ -\beta^2 v^2 \psi_\lambda = \frac{e}{m} \varphi_\lambda + \omega^2 \psi_\lambda. \] (3.40)

Multiplying the complex conjugate of equation (3.40) on the right by \( v^2 \psi^*_\lambda' \) and integrating over the negative half-space, as signified by the prime on the integral, gives

\[ -\beta^2 \int d^3 r \left( v^2 \psi^*_\lambda \right) (v^2 \psi^*_\lambda') = \int d^3 r \left( \frac{e}{m} \varphi^*_\lambda + \omega^2 \psi^*_\lambda \right) (v^2 \psi^*_\lambda'). \] (3.41a)

Similarly, relabelling equation (3.40) by \( \lambda' \) and multiplying on the left by \( v^2 \psi^*_\lambda \) gives, after integration,
The right hand sides of equations (3.41) can now be equated, giving

\[ -\beta^2 \int d^3r \left( \nabla^2 \psi^*_\lambda \nabla^2 \psi_{\lambda'} \right) = \int d^3r \left( \nabla^2 \psi^*_\lambda \left( \frac{e}{m} \varphi_{\lambda'} + \omega^2_{\lambda'} \psi_{\lambda'} \right) \right) . \] (3.41b)

But from equations (3.8) and (3.9) follows the identity

\[ \nabla^2 \varphi = 4\pi \rho \nabla^2 \psi \]

and hence the first term in square brackets in equation (3.42) vanishes, leaving

\[ \int d^3r \left( \omega^2_{\lambda} \left( \nabla^2 \psi^*_\lambda \right) \psi_{\lambda} - \omega^2_{\lambda'} \psi^*_\lambda \nabla^2 \psi_{\lambda} \right) = 0 . \] (3.43)

Each term is now integrated by parts with the first term, for example, becoming

\[ \int d^3r \omega^2_{\lambda} \nabla \cdot \left( \nabla \psi^*_\lambda \right) = \int d^3r \nabla \cdot \left( \omega^2_{\lambda} \nabla \psi^*_\lambda \right) \]

\[ -\int d^3r \nabla \cdot \left( \omega^2_{\lambda} \psi_{\lambda} \right) \nabla \psi^*_\lambda \]

Use of the divergence theorem on the first of these terms will then yield a surface integral over \[ \omega^2_{\lambda} \psi_{\lambda} \partial \psi^*_\lambda / \partial z , \] the integral vanishing because \[ \partial \psi / \partial z \] itself vanishes on the surface (equation (3.16c)). The same is done for the second term in equation (3.43) with the results combining as

\[ (\omega^2_{\lambda} - \omega^2_{\lambda'}) \int d^3r \left( \nabla \psi^*_\lambda \right) \cdot \nabla \psi_{\lambda'} = 0 . \] (3.44)
The separate surface and bulk orthogonality conditions then follow as

\[ \int d^2 \rho \int_0^0 dz \ \xi^*_\kappa \xi_{\kappa'} = \delta_{\kappa \kappa'}, \quad (3.45) \]
\[ \int d^2 \rho \int_{-\infty}^0 dz \ \xi^*_{\kappa \kappa'} \xi_{\kappa' q q'} = \delta_{\kappa \kappa'} \delta_{q q'}, \quad (3.46) \]

while it is easily verified that surface and bulk modes are mutually orthogonal.

Substituting equations (3.30) and (3.39) into equations (3.45) and (3.46) respectively, then gives the normalisation constants

\[ N^2_\kappa = \frac{2 \omega^2_p (2 \omega^2 - \omega^2_p)}{8 \pi^2 \kappa^3 (\omega^2 - \omega^2_p)^2 (2 \omega^2 + \omega^2_p)} \quad , \quad (3.47) \]

and after some lengthy algebra,

\[ M^2_{\kappa q} = \frac{\beta^4 q^2 (2 \omega^2 - \omega^2_p)}{2 \pi^3 (\omega^2 - \omega^2_p) [(2 \omega^2 - \omega^2_p)^2 - 4 \beta^2 \kappa^2 \omega^2]} \quad . \quad (3.48) \]

These differ from Barton's (1976, 1978b) results only by a factor \((2m \omega^2_\lambda)^{-1}\) which he has introduced with quantisation; that is, through the definition of the creation and annihilation operators.
3.3 PERTURBATION BY AN EXTERNAL CHARGE

3.3.1 Expansion in Normal Modes

In equation (3.10), $\varphi$ is the total electrostatic potential due to both the density fluctuations and any external charge configuration. Thus in the absence of an external source, the equations for the normal modes are

$$
\omega_{\lambda}^2 \xi_{\lambda} + \beta^2 \nabla^2 (\nabla \cdot \xi_{\lambda}) + \frac{e}{m} \nabla \varphi_{\lambda} = 0
$$

(3.49)

where $\lambda \equiv \kappa$ or $\kappa q$ for surface and bulk modes respectively. A point charge $Q$, at $\hat{r} = \hat{r}_o$, and oscillating with a frequency $\omega$, will give rise to an external potential $\varphi_{ext}(\hat{r},\hat{r}_o) \exp(-i\omega t)$. The equation for the perturbed displacement vectors and induced potential is then

$$
\frac{\partial^2 \xi}{\partial t^2} - \frac{e^2}{2m} (\nabla \cdot \xi (\hat{r},t)) + \frac{e}{m} \nabla \varphi (\hat{r},t) = - \frac{e}{m} \nabla \varphi_{ext}(\hat{r},\hat{r}_o) \exp(-i\omega t)
$$

(3.50)

The new $\xi$ and $\varphi_i$ are obtained by first expanding them in terms of the normal modes of the metal half-spaces, thus

$$
\xi(\hat{r},t) = \int d^2 \kappa S(\kappa,t) \xi_{\kappa} (\hat{r}) + \int d^2 \kappa \int_0^\infty dq B(\kappa,q,t) \xi_{\kappa q} (\hat{r})
$$

(3.51)

$$
\varphi_i(\hat{r},t) = \int d^2 \kappa S(\kappa,t) \varphi_{\kappa}^{(0)} (\hat{r}) + \int d^2 \kappa \int_0^\infty dq B(\kappa,q,t) \varphi_{\kappa q}^{(0)} (\hat{r})
$$

(3.52)
where, in equation (3.52), the appropriate normal modes $\varphi_\lambda$ or $\varphi_\lambda^0$ are used, depending on whether the induced potential is sought inside or outside the metal. Substituting equations (3.51) and (3.52) into equation (3.50) and using the equations of the form (3.49) as definitions, gives

$$
\int d^2k \frac{\partial^2}{\partial t^2} + \omega_k^2 \ S(\kappa,t) \ \xi_\kappa(\vec{r}) + \int d^2k \int_0^\infty dq \left( \frac{\partial^2}{\partial t^2} + \omega_{kq}^2 \right) B(\kappa,q,t) \ \xi_{kq}(\vec{r})
$$

$$
= \frac{e}{m} \vec{\varphi}_{ext}(\vec{r},\vec{r}_o) \ \exp(-i\omega t) \ . \ (3.53)
$$

It is trivial to show that the time dependence of $S(\kappa,t)$ and $B(\kappa,q,t)$ must be that of the external source, and hence the above equations can all be written in time independent form, with the result

$$
\int d^2k \frac{\partial^2}{\partial t^2} - \omega_k^2 \ S(\kappa) \ \xi_\kappa(\vec{r}) + \int d^2k \int_0^\infty dq \left( \omega_{kq}^2 - \omega^2 \right) B(\kappa,q) \ \xi_{kq}(\vec{r})
$$

$$
= \frac{e}{m} \vec{\varphi}_{ext}(\vec{r},\vec{r}_o) \ . \ (3.54)
$$

The external potential due to the point charge can be written in Fourier representation as

$$
\varphi_{ext}(\vec{r},\vec{r}_o) = 4\pi Q \int \frac{d^3k \ \exp[i\vec{k}.(\vec{r}-\vec{r}_o)]}{(2\pi)^3 (k_3^2 + k^2)} \ , \ (3.55)
$$

and hence, after the $k_3$ integral is performed for $\varphi_{ext}$ existing inside the metal, $z < 0 < z_o$,

$$
\vec{\varphi}_{ext}(\vec{r},\vec{r}_o) = Q \int \frac{d^2k}{2\pi k} \ \exp[i\vec{k}.(\vec{r}_0 - \vec{r}_o) + \kappa(z-z_o)](\vec{k} + \kappa \hat{z}) \ . \ (3.56)
$$
3.3.2 Evaluation of the Expansion Coefficients

(i) Surface Coefficients \( S(\kappa) \)

Taking the dot product of the surface mode displacement vector \( \hat{\xi}_{k'}^*(\vec{r}) \) with equation (3.54) and integrating over the negative half-space, the orthonormality condition (3.45) and the mutual orthogonality of surface and bulk modes, then yield the result

\[
S(\kappa) = \frac{e}{m(\omega^2_{k'} - \omega^2)} \int d^2p \int^0_{-\infty} ds \ \hat{\xi}_{k'}^*(\vec{r}) \cdot \hat{\varphi}_{\text{ext}}(\vec{r},\vec{r}_o) .
\]

These integrals are easily performed using the explicit relations (3.30) and (3.56) for \( \hat{\xi} \) and \( \hat{\varphi}_{\text{ext}} \), with the result

\[
S(\kappa) = \frac{4\pi eQ}{m} N_k \exp(-i[k_o \cdot \vec{p} - \kappa z_o]) \ \frac{\gamma}{\omega^2 (\omega^2_{k} - \omega^2)} . \tag{3.57}
\]

(ii) Bulk Coefficients \( B(\kappa, q) \)

Carrying out the identical procedure, using \( \hat{\xi}_{k'}^*, \hat{\varphi}_{\text{ext}} \) gives

\[
B(\kappa, q) = \frac{e}{m(\omega^2_{kq} - \omega^2)} \int d^2p \int^0_{-\infty} ds \ \hat{\xi}_{kq}^*(\vec{r}) \cdot \hat{\varphi}_{\text{ext}}(\vec{r},\vec{r}_o) .
\]

\[
= \frac{4\pi eQ}{m} M_{kq} \exp(-i[k_o \cdot \vec{p} - \kappa z_o]) \ \frac{(\omega^2_{kq} - \omega^2)}{(\omega^2_{kq} - \omega^2)(\omega^2_{kq} - \omega^2)} . \tag{3.58}
\]
3.4 INTERACTIONS WITH A METAL SURFACE

3.4.1 The Induced Potential

The potential arising from the density fluctuations induced in the metal by the external charge \( Q \), is given by equation (3.52). Of interest is the potential outside the metal, for which the normal mode functions \( \phi^o_\kappa \) and \( \phi^o_{\kappa q} \) given by equations (3.29) and (3.38) respectively are to be used. The surface and bulk contributions may be considered separately by defining

\[
\phi^o_\kappa (r) = \phi^o_{Is}(r) + \phi^o_{Ib}(r),
\]

where

\[
\phi^o_{Is}(r) = \int d^2 \kappa \ S(\kappa) \ \phi^o_\kappa (r),
\]

\[
\phi^o_{Ib}(r) = \int d^2 \kappa \int_0^\infty dq \ B(\kappa, q) \ \phi^o_{\kappa q} (r).
\]

These are then given explicitly by

\[
\phi^o_{Is}(r) = -\frac{Q_0^2}{2\pi} \int d^2 \kappa \ \exp[i \cdot (r - r') - \kappa (x_0 + z_0)] \ \mu^o_s(\kappa, \omega),
\]

\[
\phi^o_{Ib}(r) = -\frac{Q_0^2}{2\pi} \int d^2 \kappa \ \exp[i \cdot (r - r') - \kappa (x_0 + z_0)] \ \mu^o_b(\kappa, \omega),
\]

where

\[
\mu^o_s(\kappa, \omega) = \frac{1}{\nu(\kappa, \omega)} \left[ \frac{\omega^2 + 2\beta^2 \kappa^2 - 2\omega^2}{\beta \kappa (3\omega^2 + 2\beta^2 \kappa^2 - 2\omega^2)} - \frac{\beta \kappa (3\omega^2 + 2\beta^2 \kappa^2 - 2\omega^2)}{(2\omega^2 + 2\beta^2 \kappa^2)^{1/2}} \right],
\]

\[
\mu^o_b(\kappa, \omega) = \frac{1}{\nu(\kappa, \omega)} \left[ \frac{\omega^2 + 2\beta^2 \kappa^2 - 2\omega^2}{\beta \kappa (3\omega^2 + 2\beta^2 \kappa^2 - 2\omega^2)} - \frac{\beta \kappa (3\omega^2 + 2\beta^2 \kappa^2 - 2\omega^2)}{(2\omega^2 + 2\beta^2 \kappa^2)^{1/2}} \right].
\]
\[ \mu_b(\kappa, \omega) = \frac{\kappa \beta^4}{\pi} \int_0^\infty dq \ q^2 \left[ (\omega^2_{\kappa q} - \omega^2) (\beta^2 q^2 + \omega^2)(\beta^2 q^2 + \beta^2 q^2) \right]^{-1} \] (3.64)

\[ = \frac{1}{v(\kappa, \omega)} \left[ -2\beta k (\omega^2 + \beta^2 q^2 - \omega^2) \frac{1}{q^2} + \frac{\beta k (3\omega^2 + 2\beta^2 q^2 - 2\omega^2)}{(2\omega^2 + \beta^2 q^2)^{1/2}} \right] \]

; if \( \omega^2 < \omega^2 p + \beta^2 q^2 \) \hspace{1cm} (3.65a)

\[ = \frac{1}{v(\kappa, \omega)} \left[ -2\beta k \text{sgn}(\omega) \left( \omega^2 - \omega^2_p - \beta^2 q^2 \right)^{1/2} + \frac{\beta k (3\omega^2 + 2\beta^2 q^2 - 2\omega^2)}{(2\omega^2 + \beta^2 q^2)^{1/2}} \right] \]

; if \( \omega^2 > \omega^2 p + \beta^2 q^2 \) \hspace{1cm} (3.65b)

and where

\[ v(\kappa, \omega) = \frac{\omega^2}{p} - 4\omega^2 (\omega^2_p + \beta^2 q^2 - \omega^2) \]

\[ = 4(\omega^2_k - \omega^2) (\beta^2 q^2 - \omega^2) \hspace{1cm} (3.66) \]

Here, \( \omega_k \) is the surface plasmon frequency given by equation (3.25), which may also be written

\[ \omega^2_k = \left\{ \frac{1}{2} (2\omega^2_p + \beta^2 q^2)^{1/2} + \beta k \right\}^2 \] (3.67)

and

\[ \beta^2 q^2_k = \frac{1}{2} [\omega^2_p + \beta^2 q^2 - \beta k (2\omega^2_p + \beta^2 q^2)^{1/2}] \]

\[ = \left\{ \frac{1}{2} (2\omega^2_p + \beta^2 q^2)^{1/2} - \beta k \right\}^2 \] . \hspace{1cm} (3.68)

The complex term in equation (3.65b) is obtained when the integrand in equation (3.64) has singularities, by using the Dirac identity, after a small imaginary part of the same sign as \( \omega \) is reintroduced to phenomenologically account for the causal damping of the plasmons. It is
simply the analytic continuation of the corresponding term in equation (3.65a) and indicates that that part of the induced potential arising from those bulk plasmons with frequencies less than that of the external source, will lag in phase behind the external potential.

It is easily demonstrated that the only poles of \( u_s(\kappa, \omega) \) arise from the factor \((\omega - \omega_\kappa)\) in \( v(\kappa, \omega) \), corresponding to the fact that in the absence of the external source, oscillations may be self-sustained with the characteristic surface plasmon frequencies \( \omega_\kappa \). Similarly, the poles of the integrand in equation (3.64) for \( u_b(\kappa, \omega) \) are given by \( \omega = \omega_{b\kappa} \), the characteristic bulk plasmon frequencies. The results (3.62) and following equations are new in that while Barton (1976, 1978b) has given the same decomposition formally within his quantum mechanical treatment, he explicitly gives only the static \((\omega = 0)\) results for which the continuation (3.65b) is not required.

Neither is this continuation required in the evaluation of vdW interactions which can be written in terms of an integral over complex frequencies (Mahanty and Ninham 1976). In fact various treatments of the vdW problem, which consider only charge density fluctuations of the surface nature, give identical overall results to those obtained here for the vdW interaction (§3.4.3) as well as for the interaction with a point charge oscillating with a frequency \( \omega < \omega_p \) (§3.4.2).

This equivalence arises with the cancellation of terms between equations (3.63) and (3.65a). To illustrate
this, in the corresponding result for $\varphi_I$ obtained by Mahanty and Paranjape (1977), the integrand is simply

$$\mu(\kappa, \omega) \equiv D^{-1}(\kappa, \omega) = \left[ 2\beta^2 \gamma(\gamma+\kappa) - \omega^2 \right]^{-1}$$

(3.69)

where $\gamma$ is defined by equation (3.18). On rationalising the denominator, this becomes

$$\mu(\kappa, \omega) = \frac{1}{v(\kappa, \omega)} \left[ \omega^2 + 2\beta^2 \kappa^2 - 2\omega^2 - 2\beta \kappa \omega^2 + \beta^2 \kappa^2 - \omega^2 \right]$$

(3.70)

which is just the sum of $\mu_s(\kappa, \omega)$ and $\mu_b(\kappa, \omega)$ defined by equations (3.63) and (3.65a) respectively. The much simpler and more direct method of Mahanty and Paranjape (1977) can thus be used to obtain the response function $D^{-1}(\kappa, \omega)$ for real $\gamma$, with the continuation to complex $\gamma$ having been demonstrated above to be trivial. Their approach then directly lends itself to the evaluation of the overall interactions involving a metal surface, its only disadvantage being (Mahanty and Summerside 1979, Barton 1976) that it obviously does not give the detailed information concerning the normal mode density fluctuations inside the metal, these becoming important in Chapter 5. Here, the explicit contributions to $\varphi_I$ can now be used to investigate the explicit roles of both surface and bulk plasmons in the interactions of a point charge and a molecule with a metal surface.
3.4.2  Point Charge near a Metal Surface

The energy of the external charge in the induced field is given by

\[ E(z_o) = \frac{1}{2} \int d^3r \varphi_I(\vec{r}) \rho_\delta(\vec{r} - \vec{r}_o) = \frac{1}{2} Q \varphi_I(\vec{r}_o) \]  \hspace{1cm} \text{(3.71)}

where \( \varphi_I(\vec{r}_o) \) is the induced potential calculated in the previous section, evaluated at the position of the point charge. The surface and bulk contributions can be immediately written down as

\[ E_{s,b}(z_o) = -\frac{Q^2 \omega_p}{2 \beta} \int_0^\infty d\kappa \exp(-2\kappa z_o) \mu_{s,b}(\kappa, \omega) \]  \hspace{1cm} \text{(3.72)}

Barton (1976) has obtained these explicit contributions quantum mechanically in the static (\( \omega = 0 \)) limit. In this limit they add to give Newns' (1969b) static result

\[ E(z_o) = -\frac{Q^2 \omega_p}{2 \beta} \int_0^\infty dx \exp(-2\omega z_o x/\beta) [(x^2+1)^{1/2} - x]^2 \]  \hspace{1cm} \text{(3.73)}

an equivalent result having also been obtained by Sidyakin (1970).

Since for large \( z_o \), the integrals in equation (3.72) are dominated by small \( \kappa \), the asymptotic forms may be obtained by first expanding \( \mu_s \) and \( \mu_b \) in powers of \( \kappa \). The final results are then given by

\[ E_s(z_o) = -Q^2 \left\{ \frac{2 \omega_s}{\lambda z_o} - \frac{\beta \omega_s (3\omega - \omega^2)}{\lambda^2 z_o^2} + \frac{8\beta^2 \omega_s^4}{\lambda^3 z_o^3} + O[(\lambda z_o)^{-4}] \right\} \]  \hspace{1cm} \text{(3.74a)}
\[ E_b(z_o) = -Q^2 \left\{ \frac{\beta \omega}{s (3\omega^2 - \omega^2)} - \frac{2\beta \omega^2 (2\omega^2 - \omega^2)^{1/2}}{\lambda z_o^2} \right\} \]

where \( \lambda = 4(\omega^2 - \omega_s^2) \) and \( \omega_s^2 = \frac{\omega_p^2}{2} \). Some of the general features of these and the following results will be discussed below. While the expansion for \( E_s(z_o) \) is valid for all frequencies of the external source, only the case \( \omega < \omega_p \) has been given for \( E_b(z_o) \) as this reduces to Barton's (1976) static expansion. The expansion valid near \( \omega = \omega_p \) for \( E_b(z_o) \) has not been given in view of Barton's (1978a, b) discussion concerning the splitting of the spectrum about such resonances (see discussion following equation (3.82) below).

### 3.4.3 Molecule near a Metal Surface

Following Mahanty and Paranjape (MP 1977), the vDW energy of interaction of a molecule, polarisability \( a(\omega) \), at \( r_o \) outside the metal, can be written (Mahanty and Ninham 1976)

\[ V(z_o) = -\frac{\hbar}{2\pi} \int_0^{\pi} d\xi a(i\xi) \, \text{Tr} \, G(r_o, r_o; i\xi) \quad , \]  

(3.75)

where \( \omega = i\xi \) and the dyadic Green's function is obtained from the induced potential as

\[ G(r, r_o; \omega) = -(\nabla \nabla^*_o) \varphi_I(r, r_o; \omega) \quad . \]

Then from equations (3.62), the surface and bulk contributions to the integrand of equation (3.75) are given
As in MP (1977) the simple oscillator model for the polarisability,

\[ a(i\xi) = \frac{\alpha(0) \omega_o^2}{\omega_o^2 + \xi^2} \]  

(3.78)

may be used to obtain asymptotic forms for the vdW energy. The explicit surface and bulk contributions are, defining \( \sigma = \omega_o + \omega_s \),

\[ V_s(z_o) = -\frac{\hbar \alpha(0) \omega_o \omega_s}{8\sigma z_o^3} \left\{ 1 - \frac{3\beta (3\omega_o + 2\omega_s)}{4\omega_s \sigma z_o} \right\} \]

\[ + \frac{3\beta^2 (8\omega_s^2 + 9\omega_s \omega_o + 3\omega_o^2)}{8\omega_s^2 \sigma z_o^2} + O[(\alpha z_o)^{-3}] \]  

(3.79a)

\[ V_b(z_o) = -\frac{\hbar \alpha(0) \omega_o \omega_s}{8\sigma z_o^3} \left\{ \frac{3\beta (3\omega_o + 2\omega_s)}{4\omega_s \sigma z_o} - \frac{3\beta \omega_s \omega_o}{\pi \sigma z_o} \right\} + O[z_o^{-3}] \]  

(3.79b)

where

\[ \chi = \int_0^\infty d\xi \frac{(\xi^2 + \omega_p^2)^{1/2}}{(\xi^2 + \omega_o^2)(\xi^2 + \omega_s^2)^2} \]  

(3.80)

Again, the sum \( V_s + V_b \) is identically the result obtained by MP (1977). The integral \( \chi \) must be evaluated for the various values of \( \omega_o \) relative to \( \omega_s \) and \( \omega_p \), and defining \( \eta = 2(\omega_o^2 - \omega_s^2) \), is found to have the following forms:
while for the special cases,
\[ \chi = \frac{2}{\omega_p^2} \] if either \( \omega_o = \omega_s \) or \( \omega_p \).

(3.82)

While evaluation of \( \chi \) for these special resonance cases in the asymptotic region was possible, it has been pointed out (Mavroyannis and Hutchinson 1977, Mavroyannis 1977, Barton 1978a, b) that when \( \omega_o = \omega_s \), a perturbation expansion is not adequate because of the splitting of the spectrum at this frequency. The position and widths of the two peaks have been investigated by these authors.

3.4.4 Discussion

The equivalence of the end results of the normal mode analysis with previous studies has been established. In the static limit, the results of Lennard-Jones (1932), Newns (1969b), Sidyakin (1970) and Heinrichs (1973a) are encompassed while the leading terms in the asymptotic expansions have been derived by Bardeen (1940) and Mukhopadhyay and Mahanty (1975). However, there are some important aspects of the surface/bulk breakdown which deserve mention.

In the local approximation (\( \beta = 0 \)) all bulk
contributions vanish and it is only in this limit that the statements of, for instance, Mahan (1972) and Ritchie (1972) that surface plasmons alone give rise to the image force, become correct. In fact, in view of the cancellation of terms in $\mu(\kappa, \omega)$ on adding equations (3.63) and (3.65b), certain explicit terms arising from the surface oscillations have previously been unnoticed.

In the asymptotic expansions of $E(z_0)$ and $V(z_0)$, surface plasmons do give the main contribution, since they give rise to the leading term. For smaller separation distances a numerical evaluation of the surface and bulk contributions in equations (3.72) and (3.77) is required, but the fact demonstrated by Heinrichs (1973a), that the force on an external charge remains finite, even for $z_0 \rightarrow 0$, can be seen to arise from the balancing of terms of surface and bulk origin in the combined result for $\mu(\kappa, \omega)$, given in equation (3.70).

3.5 SURFACE AND BULK CONTRIBUTIONS IN PLASMON DISPERSION FOR TWO COUPLED METAL SLABS

A useful illustration of the role of surface and bulk plasmons is in the coupling of two metal half-spaces, separated by a vacuum. The contributions are easily evaluated within the hydrodynamic normal mode analysis presented here. In the generalisation to a two-metal system, the normal modes and normalisation constants for
metal 1, occupying the negative half-space, are given in §§3.2. For metal 2, occupying the half-space \( z > d \), the normal mode displacement potentials are given by

\[
\psi^{(2)}_{\kappa} (r) = - N^{(2)}_{\kappa} \exp(i \kappa \cdot \rho) \left\{ \kappa \exp[-\gamma_2 (z-d)] - \gamma_2 \exp[-\kappa (z-d)] \right\},
\]

\( m \) \( 0 \) \( (\ref{eq:3.83a}) \)

\[
\psi^{(2)}_{\kappa \kappa q_2} (r) = - M^{(2)}_{\kappa \kappa q_2} \exp(i \kappa q_2 \cdot \rho) \left\{ \cos \gamma_2 (z-d) - \frac{k^{\omega^2}}{p_2} \frac{q_2^2}{q_2 (2 \omega^2 \kappa q_2 - \omega^2 p_2)} \right\}
\times \left[ \sin \gamma_2 (z-d) + \frac{q_2^2}{\kappa} \exp[-\kappa (z-d)] \right], \quad (\ref{eq:3.83b})
\]

where the surface and bulk normal mode frequencies are given by

\[
2 \omega_2^2 + \omega_2^2 (\gamma_2 + \kappa) = 0 \quad , \quad (\ref{eq:3.84a})
\]

\[
\omega_2^2 = \omega_2^2 + \beta_2^2 \kappa^2 + \beta_2^2 q_2^2 \quad . \quad (\ref{eq:3.84b})
\]

The normalisation constants \( N^{(2)}_{\kappa} \) and \( M^{(2)}_{\kappa \kappa q_2} \) are the same as for metal 1 (equations (3.47) and (3.48)) with the subscript interchanges \( (1 \rightarrow 2) \).

For the coupled metals, expansions for the perturbed displacement vectors, etc., are made for each metal in terms of the corresponding normal modes for that metal, with expansion coefficients \( S_1(\kappa) \) and \( B_1(\kappa, q_1) \) in metal 1, and \( S_2(\kappa) \) and \( B_2(\kappa, q_2) \) in metal 2. Thus, the hydrodynamic equations for the coupled modes are

\[
- \frac{\beta^2}{\beta t^2} \ddot{\xi}_1 + \beta_1^2 \nabla \cdot (\nabla \cdot \dot{\xi}_1) + \frac{e}{m} \nabla \dot{\varphi}_1 = - \frac{e}{m} \nabla \dot{\varphi}_2 \quad . \quad (\ref{eq:3.85a})
\]
where, for example,
\[
\hat{\xi}_1(\mathbf{r}, t) = \int d^2 \kappa \, S_1(\kappa, t) \, \hat{\xi}_\kappa^{(1)}(\mathbf{r})
\]
\[
+ \int d^2 \kappa \int_0^\infty d q_1 \, B_1(\kappa, q_1, t) \, \hat{\xi}_\kappa^{(1)}(\mathbf{r}) .
\]

The external potentials on the right hand sides of equations (3.85) are now the induced potentials, arising from the mutually induced density fluctuations in the other metal. They involve expansions over the normal modes of the potential existing outside the corresponding metal (that is, functions of the type given in equations (3.29) and (3.38)). Thus, for example
\[
\varphi_2^0(\mathbf{r}, t) = \int d^2 \kappa \, S_2(\kappa, t) \, \varphi_\kappa^{(2)}(\mathbf{r})
\]
\[
+ \int d^2 \kappa \int_0^\infty d q_2 \, B_2(\kappa, q_2, t) \varphi_\kappa^{(2)}(\mathbf{r}) .
\]

Following the identical procedure to that in §3.3.2, the four equations connecting the expansion coefficients are obtained thus,
\[
(\omega_{\kappa_1}^2 - \omega^2) S_1(\kappa) = - 2\pi^2 \exp(-\kappa d) \, 2\kappa \omega^2 M_1^{(1)} \left[ S_2(\kappa) N_2^{(2)} + A_2(\kappa) \right] ,
\]
\[
(\omega_{\kappa_2}^2 - \omega^2) B_1(\kappa, q_1) = - 2\pi^2 \exp(-\kappa d) \, 2\kappa \omega^2 M_1^{(1)} \left[ S_2(\kappa) N_2^{(2)} + A_2(\kappa) \right] ,
\]

with two further equations symmetric in the subscripts 1 and 2, and where
The equations (3.88) are easily solved to give a determinantal equation which may be expanded as

$$1 - \left[ \mu_s(k,\omega) + \mu_b(k,\omega) \right] \left[ \mu_s^2(k,\omega) + \mu_b^2(k,\omega) \right] \times \frac{\omega_p^2 \omega_{p_2}^2}{\exp(-2kd)} = 0 ,$$

or

$$1 - \mu_s(k,\omega) \mu_2(k,\omega) \frac{\omega_p^2 \omega_{p_2}^2}{\exp(-2kd)} = 0 .$$

where the $\mu_s, b$'s are defined by equations (3.63) to (3.65). Using their equivalent forms, equation (3.69), the dispersion formula for the surface plasmons in the coupled system becomes, with the further simplification to identical metals,

$$[2\beta^2 \gamma(y+\kappa) - \omega_p^2]^2 - \omega_p^4 \exp(-2kd) = 0 .$$

This easily factorises to give the symmetric ($\omega_+$) and antisymmetric ($\omega_-$) plasmon dispersion relations (Heinrichs 1973a)
\[ \omega_1^2 = \hbar \{ \omega_p^2 (1 \pm \exp(-\kappa d)) + \beta^2 \kappa^2 \\
+ \beta \kappa [2 \omega_p^2 (1 \mp \exp(-\kappa d)) + \beta^2 \kappa^2]^{1/2} \} \quad (3.93) \]

This was also obtained from the general retarded formula (2.55) in §2.4.1. The important point here is the obvious role again played by the bulk normal modes, which therefore also enter into the vdW interaction between the two metal half-spaces.
Plasmon Dispersion in Two-Metal Systems

4.1 INTRODUCTION

4.1.1 Introductory Remarks

Of widespread interest for the practical use of metals is the effect on the properties of a metal substrate by a coating of another metal. Such a coating affects in particular the adsorptive and catalytic activities of the substrate by altering the characteristic collective modes of the system as a whole. Specifically, there will now be plasmon modes associated with the interface of the substrate and film coating. The aims of this chapter are firstly to study the collective modes associated with an interface between two different metals and then to consider the effect on these modes when the metals are cleaved and separated (Summerside 1979). Fundamental to this study is the question of boundary conditions for these systems. These are discussed in §§4.2. To simplify the algebra, two metallic half-spaces are considered, but as indicated below, the
general results should be of direct applicability, at least qualitatively, to systems involving thin films.

The bimetallic interface plasmon was predicted by Stern and Ferrell (1960), in the local approximation, to have a frequency \( \bar{\omega} \) given by

\[
\bar{\omega}^2 = \frac{1}{2} (\omega_{pl1}^2 + \omega_{pl2}^2),
\]

and the first experimental verification of this mode was given by Miller and Axelrod (1965). In this chapter the full curve for the interface plasmon, including spatial dispersion, is derived using the more realistic boundary conditions of Forstmann and Stenschke (1977, 1978) which allow electrons to flow across the interface (§§4.2). It is shown that a similar mode, also starting at \( \bar{\omega} \), exists when the metals are cleaved and separated by introducing specularly reflecting boundaries at the surfaces. The frequency dispersion curves of these two modes are identical when the metals are in contact only in the local approximation and are then given by equation (4.1), but the latter corresponds to a different type of density fluctuation and has a dependence on the separation distance. It is argued that the commonly observed interface mode is, in fact, that which is obtained using Forstmann and Stenschke's boundary conditions, and hence that the nature of the 'interface' mode has been misunderstood.

On cleaving and separating the metals, additional modes are introduced, and in particular a new 'image' plasmon, \( \omega_{im} \), representing a symmetric mode in the density
fluctuations, is predicted. This arises from the image of the denser metal 2 ($\omega_{p2} > \omega_{p1}$) forming as a result of the density response of the bulk electrons in metal 1, and is independent of the less dense metal. The generalisation of the well known symmetric ($\omega_+$) and antisymmetric ($\omega_-$) surface plasmons, seen for two identical metals, are also derived. The generalised upper branch $\omega_+$, only appears if $\omega_{p1} > \omega_{p2}/\sqrt{2}$ and forms the continuation of $\omega_{im}$ below the bulk continuum region of the less dense metal. If $\omega_{p1} < \omega_{p2}/\sqrt{2}$, the image plasmon replaces, in full, the generalised $\omega_+$ branch.

4.1.2 Existence of the Interface Mode and Preliminary Discussion

The existence of interface modes is governed by two main criteria; the diffuseness of the interface and the thickness of the two metal components. In Chapter 1 the effect of surface diffuseness (a surface density profile) on the surface plasmons was discussed. These general effects will also pertain to the interface plasmons through the blurring and roughness of the interface arising from the construction of the substrate surface and deposition of the film coating. The effects should, however, be minimal in experimental situations which naturally aim at preparing clean surfaces and regular interfaces.

Of far greater importance for the bimetallic interface is the blurring arising from the relative diffusivities of the metals in each other. In the early electron energy loss (ELS) experiments of Miller and Axelrod (1965), it was to this factor that was attributed the fact that the predicted Mg-Al interface mode was not
observed, while the $Bi-Mg$ mode was. They quote the solubilities at 150°C of $Mg$ in $Al$ as 3.35% (atomic per cent of $Mg$), of $Al$ in $Mg$ as 1.6%, while the solubility of $Bi$ in $Mg$ is less than 0.01% and is considered negligible for $Mg$ in $Bi$. In further support of this argument they quote the average diffusion length of $Al$ in $Mg$ at 150°C, taken over an observation time of 50 seconds, as 24Å!

Miller and Axelrod concluded that either no clearly defined interface existed or that the region of diffusion effectively created two interfaces at its extremities and hence that there may exist interfering modes which their energy loss experiments could not discern from the pure bulk losses.

The latter possibility was given fruition in optical (attenuated total reflection, ATR) experiments on $MgF_2-Ag$ layered films by Kovacs and Scott (1977). They successfully accounted for the blurring of the interface in an empirical way by introducing a distinct interface layer with some third effective dielectric constant and which was parametrised by its thickness.

In this chapter an ideal interface is assumed to exist, in that although the boundary conditions to be discussed relax the infinite potential barrier model to allow continuity of the electron current density across the interface, no atomic diffusion is allowed to occur.

The other general requirement for the existence of well defined interface modes is that the film/substrate components be thick enough to exhibit bulk features; that is, to allow collective bulk and surface oscillations. Brillson (1977) has observed such features in $Al$ films as
thin as 5Å. Experimentally, this requirement will usually be well satisfied, and indeed experimental thin films are generally thick enough so that the results given here for two metal half-spaces should be qualitatively applicable to systems involving thin films.

4.1.3 Boundary Conditions

In the study of metal surfaces, and in particular the longitudinal surface plasmons, the appropriate boundary condition for the infinite barrier model of a metal-vacuum interface is that the normal component of the current density vanish at the surface. This corresponds to specular reflection of the electrons by the surface barrier and has been discussed in detail in Chapter 1. When the vacuum (or dielectric) is replaced by another metal, this boundary condition is no longer correct. That this is so can be simply illustrated by considering the system of two identical metal half-spaces, separated by a vacuum (Chapters 2 and 3). For this system there exist the well-known symmetric and antisymmetric surface plasmon branches $\omega_{\pm}$. These modes are obtained using the condition of vanishing current at the two surfaces. This is an obvious failure when the metals are brought into contact, because instead of simply obtaining an infinite bulk sample, the system now corresponds to one which is unphysically cleaved by an infinite barrier, and the surface modes $\omega_{\pm}$ are still predicted.

Forstmann and Stenschke (1977) derived a more appropriate set of boundary conditions for the bimetallic
interface within the hydrodynamic jellium model, from a consideration of the energy density. An outline of the derivation, neglecting absorption arising from the finite lifetimes of the disturbances is given as follows. In terms of the current density, the hydrodynamic equation may be written

$$\frac{\partial \mathbf{j}}{\partial t} = \frac{\omega^2}{4\pi} \mathbf{E} - \beta^2 \nabla \mathbf{n} \quad , \quad (4.2)$$

and hence, taking the dot product with $\mathbf{j}$,

$$\frac{\partial}{\partial t} (\frac{1}{2} |\mathbf{j}|^2) = \frac{\omega^2}{4\pi} \mathbf{E} \cdot \mathbf{j} + \beta^2 \mathbf{j} \cdot \nabla \mathbf{n}$$

$$= \frac{\omega^2}{4\pi} \mathbf{E} \cdot \mathbf{j} + \beta^2 \mathbf{j} \cdot \nabla \mathbf{n} - \frac{\partial}{\partial t} (\frac{1}{2} \beta^2 \mathbf{n}^2) \quad . \quad (4.3)$$

The continuity equation for the energy of the electromagnetic fields is

$$\mathbf{E} \cdot \mathbf{j} + \nabla \cdot (\omega^2 \mathbf{E} \times \mathbf{H}) = \frac{-1}{8\pi} \frac{\partial}{\partial t} (\mathbf{E} \cdot \mathbf{D} + \mathbf{B} \cdot \mathbf{H}) \quad . \quad (4.4)$$

Equating the expressions for $\mathbf{E} \cdot \mathbf{j}$ from equations (4.3) and (4.4) yields

$$- \frac{\partial}{\partial t} \left[ \frac{1}{8\pi} \mathbf{E} \cdot \mathbf{D} + \frac{1}{8\pi} \mathbf{B} \cdot \mathbf{H} + \frac{2\pi}{\omega} |\mathbf{j}|^2 + \frac{2\pi}{\omega} \beta^2 \mathbf{n}^2 \right]$$

$$= \nabla \cdot \left[ \frac{\omega^2}{4\pi} \mathbf{E} \times \mathbf{H} + \frac{4\pi}{\omega} \beta^2 \mathbf{j} \mathbf{n} \right] \quad . \quad (4.5)$$

From the usual pill-box and closed-circuit arguments
at the interface, Maxwell's equations and the equation of charge continuity yield the continuity of the tangential and normal components of \( \mathbf{E} \), and the continuity of the normal component of \( \mathbf{J} \). For a metal-vacuum interface the latter reduces to the usual vanishing of \( j_z \) at the surface. For a metal-metal interface, use of the pill-box argument on equation (4.5) leads to the continuity of the normal component of the energy current vector on the right hand side of that equation. In conjunction with the other three boundary conditions this then requires that \( \beta^2 n/\omega^2 \) or \( \beta^2 n/n_o \) be continuous (the latter assuming, as in the free electron approximation, equal effective masses).

It should be pointed out that while these boundary conditions relax the unrealistic infinite barrier model, the hydrodynamic equation plays an integral role in the derivation, and so the fourth boundary condition is exact only in the hydrodynamic model. Further, the relaxation is only to the extent of allowing electrons to flow across the boundary, and so the interface blurring associated with atomic diffusion is not accounted for. The latter factor, as mentioned above, will only act to modify or damp out the ideal interface mode, which is the subject of investigation here.

It is shown that the boundary conditions of Forstmann and Stenschke (1977) lead to the correct evaluation of the interface plasmon dispersion and the nature of the density fluctuations involved. Unfortunately, Forstmann and Stenschke (1978) misused their boundary condition by not considering the appropriate regions of \( \omega-k \) space, and their result was
not a physical solution for the interface mode. The fact that in the nonretarded limit it gave the correct starting point $\tilde{\omega}$ (equation (4.1)) was, as will be shown, only a fortunate coincidence associated with the limit $\kappa = 0$.

4.1.4 General Formalism and Discussion of Regions of $\omega - \kappa$ Space

In the normal mode analysis of Chapter 3 the solutions for the density fluctuations obeying the linearised hydrodynamic equation were categorised as bulk or surface modes, depending on whether the frequency was above or below the bulk continuum bound given by

$$\omega^2_b(\kappa) = \omega^2_p + \beta^2 \kappa^2 .$$ (4.6)

For the system of two nonidentical metals there are now three distinct regions of $\omega - \kappa$ space to be considered. These are defined by

$$\omega^2 < \omega^2_{b1}(\kappa) < \omega^2_{b2}(\kappa) \quad ; \text{region I} \quad ,$$

$$\omega^2_{b1}(\kappa) < \omega^2 < \omega^2_{b2}(\kappa) \quad ; \text{region II} \quad ,$$

$$\omega^2 > \omega^2_{b2}(\kappa) \quad ; \text{region III} \quad ,$$ (4.7)

where the $\omega^2_{b,j}$'s are defined by equation (4.6) and the case $\omega^2_{p2} > \omega^2_{p1}$ is arbitrarily chosen, with metal 1 occupying the negative half-space $z < 0$, and metal 2 the half-space $z > d$.

It is convenient to work with the displacement potential introduced in Chapter 3, and which satisfies the equation
\[
\left( \frac{d^2}{dz^2} - \kappa^2 \right) \left( \frac{d^2}{dz^2} - \gamma^2 \right) \psi(z) = 0 ,
\]

where

\[
\beta^2 \gamma^2 = \beta^2 \kappa^2 + \omega_p^2 - \omega^2 > 0 \quad \text{for} \quad \omega^2 < \omega_b^2(\kappa) ,
\]

\[
\beta^2 q^2 = \omega^2 - \omega_p^2 - \beta^2 \kappa^2 > 0 \quad \text{for} \quad \omega^2 > \omega_b^2(\kappa) .
\]

The electrostatic potential and density fluctuation may then be obtained, as in §3.2.1, from the relations

\[
\varphi(z) = \frac{m}{\varepsilon} \left( \omega^2 + \beta^2 \frac{d^2}{dz^2} - \beta^2 \kappa^2 \right) \psi(z) ,
\]

\[
n(z) = n_o \left( \frac{d^2}{dz^2} - \kappa^2 \right) \psi(z) .
\]

It is instructive to note that the density fluctuation may also be obtained from its wave equation

\[
\left( \frac{d^2}{dz^2} - \gamma^2 \right) n(z) = 0 .
\]

From equation (4.11) it is obvious that solutions for frequencies \( \omega < \omega_b(\kappa) \) will correspond to exponentially decaying density fluctuations, representing surface-type modes, while for \( \omega > \omega_b(\kappa) \) the solutions correspond to oscillatory bulk-type fluctuations. Thus in region I, the solutions represent pure surface modes, exponentially bound at the surface of both metals, or on both sides of the interface. In region II, exponentially bound modes in metal 2 are correlated with oscillatory modes in metal 1, while region III represents the pure bulk continuum region with
oscillatory density fluctuations in both metals. Only regions I and II will be discussed, as these contain the important surface and interface modes, respectively.

To illustrate the assignment of coefficients, the general solutions of equation (4.8) are written

\[ \psi_1 = A \exp(\gamma_1 z) + C \exp(\kappa z) , \text{ in region I , } (4.12) \]
\[ = A \cos(q z) + B \sin(q z) + C \exp(\kappa z) , \text{ in region II , } (4.13) \]
\[ \psi_2 = P \exp(-\gamma_2 z) + R \exp(-\kappa z) , \text{ in regions I and II . } (4.14) \]

The electrostatic potentials inside the metals are then given by equation (4.9) while between the separated metals, Laplace's equation gives

\[ \varphi_0 = E \exp(\kappa z) + F \exp(-\kappa z) . \] (4.15)

4.2 BIMETALLIC INTERFACE

4.2.1 Region I: Absence of Localised Modes

The boundary conditions of continuity of \( \varphi, \partial \varphi / \partial z \), \( n \partial \psi / \partial z \) and \( \beta^2 n / n_0 \), applied to the solutions for region I, obtained from equations (4.12) and (4.14), lead to the determinantal equation
This is equivalent to the nonretarded reduction of Forstmann and Stenschke's (1978) result and may be expanded as

\[
\begin{align*}
(\omega_{p1}^2 + \omega_{p2}^2 - 2\omega^2) \left[ \gamma_1 \omega_{p2}^2 \left( \omega_{p1}^2 - \omega^2 \right) + \gamma_1 \omega_{p1}^2 \left( \omega_{p2}^2 - \omega^2 \right) \right] \\
- \kappa \omega^2 \left( \omega_{p2}^2 - \omega_{p1}^2 \right)^2 = 0 .
\end{align*}
\] (4.17a)

A little algebra yields the alternative useful form

\[
\begin{align*}
\omega_{p1}^2 \beta_1^2 (\gamma_1 + \kappa) [2\beta_2^2 (\gamma_2 + \kappa) - \omega_{p2}^2 + \omega_{p1}^2] \\
+ \omega_{p1}^2 \beta_2^2 (\gamma_2 + \kappa) [2\beta_1^2 (\gamma_1 + \kappa) - \omega_{p1}^2 + \omega_{p2}^2] = 0 ,
\end{align*}
\] (4.17b)

from which it is obvious that if either \( \omega_{p1} \) or \( \omega_{p2} \) is zero, the equation for the surface plasmon dispersion curve for the remaining single metal half-space is obtained (Mahanty and Paranjape 1977) as

\[
2\beta_j^2 \gamma_j (\gamma_j + \kappa) - \omega_{pj}^2 = 0 .
\] (4.18)

More importantly, equation (4.17) has no real roots in region I and hence there are no modes localised at the interface and decaying exponentially in both metals. The fact that for \( \kappa = 0 \), equation (4.17) has the solution (4.1), is an unphysical coincidence and the source of Forstmann...
and Stenschke's (1978) error in applying the retarded generalisation of equation (4.17) to region II where it is simply not valid.

4.2.2 Region II: Interface Mode

The correct interface mode is obtained by applying the same boundary conditions to the solutions (4.13) and (4.14) for region II. With the extra constant in equation (4.13), this now yields the system of equations

\[
\begin{pmatrix}
\omega_{p1}^2 & 0 & \omega_{p2}^2 & -\omega_{p2}^2 & -\omega_{p2}^2 \\
0 & \omega_{p1}^2 q_1 & \omega_{p2}^2 c_1 & \omega_{p2}^2 c_2 & \omega_{p2}^2 c_2 \\
0 & \omega_{p1}^2 q_1 & \omega_{p2}^2 c_1 & \omega_{p2}^2 c_2 & \omega_{p2}^2 c_2 \\
\omega_{p1}^2 - \omega_{p2}^2 & 0 & 0 & \omega_{p2}^2 - \omega_{p2}^2 & 0
\end{pmatrix}
\begin{pmatrix}
A \\
B \\
C \\
P \\
R
\end{pmatrix} = 0.
\]

(4.19)

This system has an infinite number of solutions, representing a continuum in region I. The relationships between the coefficients are easily obtained and of particular interest is the result

\[
A = B \omega_{p1}^2 q_1 (\omega_{p2}^2 - \omega_{p1}^2) (\omega_{p2}^2 p_2 + \omega_{p1}^2 - 2\omega_{p2}^2) K^{-1}(\kappa),
\]

(4.20)

where

\[
K(\kappa) = \kappa \omega_{p2}^2 (\omega_{p2}^2 - \omega_{p1}^2)^2 - \gamma_2 \omega_{p2}^2 (\omega_{p2}^2 - \omega_{p1}^2) (\omega_{p2}^2 + \omega_{p1}^2 - 2\omega_{p2}^2).
\]

(4.21)

If \(K(\kappa)\) vanishes, it can be shown that \(B\) must also vanish for \(A\) to remain an arbitrary finite constant. Thus the condition

...
corresponds to an interface plasmon mode, \( \omega_I(\kappa) \), embedded in the continuum and representing an exponentially decaying density fluctuation in metal 2 and a pure cosine (\( B = 0 \)) fluctuation in metal 1. It is this mode, which starts at \( \bar{\omega} = \left[ \frac{1}{2} (\omega_{p1}^2 + \omega_{p2}^2) \right]^{1/2} \) which was first observed by Miller and Axelrod (1965). The full dispersion curve for \( \omega_I(\kappa) \) is plotted in figure 4.1, and it is further discussed in §§4.3.

Before considering the case of two separated metals, the statement following equation (4.21) requires some justification. The following discussion is also necessary to sort out the physics from the mathematics involved. The factor \( (\omega_{p1}^2 - \omega^2) \) in equation (4.20) can be absorbed into the definition of \( K(\kappa) \) since \( \omega = \omega_{p2}^2 \) is also a solution of equation (4.22). In the numerical evaluation of \( \omega_I(\kappa) \), this is simply avoided using L'Hospital's rule.

The factor \( (\omega_{p2}^2 + \omega_{p1}^2 - 2\omega^2) \) vanishes simultaneously with \( K(\kappa) \), only at \( \kappa = 0 \). However, such occurrences associated with the limit \( \kappa = 0 \) must be regarded with great caution in the nonretarded limit. To illustrate this it must be remembered that the axis \( \kappa = 0 \) actually corresponds to the photon line in the limit \( c = \infty \). In reality, the longitudinal plasmon curves will not meet the photon line, as is seen in the identical behaviour of the retarded and nonretarded surface plasmon curves for a single half-space (figure 1.1). The true (retarded) curve becomes asymptotic with the photon line \( \omega = c\kappa \) at small \( \kappa \), bending down towards the origin. This asymptotic behaviour associated with the
Caption for Figure 4.1

Bimetallic interface mode $\omega_I(\kappa)$ for $\omega_{p1} = 0.85 \omega_{p2}$. In all figures of this chapter, the solid curves $\omega_{bj}(\kappa)$, equation (4.6), define the regions I, II, III and the dotted curves $\omega_{sj}(\kappa)$, equation (4.18), are the asymptotic surface plasmon curves for the isolated metals. The free electron parameters for Al are used for metal 2.
Figure 4.1

\[ \frac{\omega}{\omega_{p2}} \]

\[ \frac{\beta_2 \kappa}{\omega_{p2}} \]

\(\omega_{b2}\), \(\omega_I\), \(\omega_{b1}\), \(\omega_{s2}\), \(\omega_{s1}\)
transverse character of the surface plasmon is missed in
the nonretarded analysis which predicts a zero-\( \kappa \) limit of
\( \omega = \omega_p/\sqrt{2} \). Similarly, the coincidence of the factors
\((\omega_{p2}^2 + \omega_{pl}^2 - 2\omega^2)\) and \(K(\kappa)\) at \( \kappa = 0 \) is only a mathematical
consequence of the neglect of the finite velocity of light.
The factor \((\omega_{p2}^2 + \omega_{pl}^2 - 2\omega^2)\) will therefore be considered
to have no physical significance and will be neglected in
the following analysis.

Finally, the factor \( q_1 = \beta_1 \left( \omega^2 - \omega_{pl}^2 - \beta_{1\kappa}^2 \right)^{-1} \), which
represents the lower bound of the bulk continuum for metal 1,
ever vanishes simultaneously with \( K(\kappa) \) and does not influence
the statement following equation (4.21). However, if the
same reasoning is used, then the vanishing of \( q_1 \) must also
require that \( \Lambda = 0 \) and hence correspond to a pure sine
density fluctuation in metal 1. This is obviously
contradictory and misleading, since the term \( \sin q_1 z \) itself
vanishes for \( q_1 = 0 \). The concept of \( q_1 = 0 \) requires
further explanation.

The neglect of this \( q_1 = 0 \) 'mode' can be justified
by demonstrating that it is a null mode, or equivalently, by
simply defining the curve given by \( q_1 = 0 \) to be included in
the surface region I. In support of this statement, three
arguments are given as follows.

It can be demonstrated that \( q = 0 \) corresponds to a
null mode for the single metal half-space simply by
inspecting the bulk normal mode solutions (3.35) to (3.39).
Recalling that \( M_{\kappa q} \) involves a factor \( q \) (equation (3.48)),
all terms in these solutions with the multiplicative factor
\( q = 0 \) will vanish automatically. The remaining \( \sin qz \)
terms vanish by definition, but it is interesting that even for \( q = 0 \), before the \( \sin qx \) term is taken to zero, the external potential \( \varphi_{kq}^0 \) is already vanishing and hence the coupling with this mode would be negligible.

The justification for defining the curve \( q = 0 \) as part of the surface region also follows from a previous example, this time for the two identical separated metal slabs. If the behaviour of the surface plasmon branches \( \omega_\pm \), given by equation (3.93), is followed as a function of the separation distance, it is first noted that the two branches are degenerate and independent for \( d = \infty \), when they simply correspond to the surface plasmon curves for the isolated metal half-spaces. As \( d \) decreases, the correlation of the electrons in the two metals causes the splitting in the branches and at \( d = 0 \) the upper branch actually gives the line \( \omega^2 = \omega_p^2 + \beta^2 \kappa^2 \), or \( q = 0 \).

These arguments provide a concrete foundation for the problem at hand. It is finally a simple exercise to show that \( q = 0 \) also gives a null mode in the present case, since having demanded that \( \Lambda = 0 \), it is found that the amplitudes \( P \) and \( R \) in metal 2, as well as the coefficient \( C \) in metal 1, are simply related to \( \Lambda \) as, for example, \( P = \Lambda (\omega_{p1}^2 - \omega^2)/(\omega_{p2}^2 - \omega^2) \).
4.3 TWO SEPARATED METALS

4.3.1 Region I: Surface Modes

The metals are now assumed to be cleaved and separated by the introduction of specularly reflecting surfaces at $z = 0$ and $z = d$. This is commonly referred to as the classical infinite barrier model (CIBM). In region I, application of the boundary conditions of continuity of $\varphi$ and $\partial \varphi / \partial z$ and vanishing of $n_0 \partial \psi / \partial z$ at the surfaces yields a determinantal equation which can be expanded as

$$[2\beta^2_{11}(\gamma_1 + \kappa) - \omega^2_{pl}][2\beta^2_{22}(\gamma_2 + \kappa) - \omega^2_{p2} - \omega^2_{pl} \omega^2_{p2} \exp(-2\kappa d) = 0. \ (4.23)$$

For identical metals, this gives the result (equation (3.92)) for the well-known symmetric and antisymmetric modes for that system.

The general result (equation (4.23)) always has at least one root $\omega_- (\kappa)$ (figures 4.2 and 4.3), starting at $\omega = 0$ and approaching the surface plasmon curve $\omega_{s1} (\kappa)$ given by equation (4.18) for metal 1. $\omega_- (\kappa)$ is the generalisation of the antisymmetric branch $\omega_-$. If $\omega_{pl} < \omega_{s2} (\omega_s = \omega_p / \sqrt{2})$, it is easily shown, both analytically and numerically, that this is the only real root in region I (figure 4.2). However, if $\omega_{pl} > \omega_{s2}$ (figure 4.3), there is always some value of $d$, beyond which a second root $\omega_+ (\kappa)$, appears below $\omega_{b1} (\kappa)$. This is part of the generalised upper symmetric branch $\omega_+$, seen for identical metals. In the limit $d = \infty$, equation (4.23) gives the two independent surface plasmon dispersion relations, with $\omega_- (\kappa)$ becoming the surface plasmon
Caption for Figure 4.2

Plasmon modes for two separated metals for the case $\omega_p < \omega_{s2}$ ($\omega_p = 0.6\omega_p$). At $d = 0$ (figure 4.2a), $\omega_{im}(\kappa)$ coincides with $\omega_{b2}(\kappa)$. The lower branch $\omega_-(\kappa)$ (dashed curve), always exists in region I while for $\omega_p < \omega_{s2}$, $\omega_{sin}(\kappa)$ and $\omega_{im}(\kappa)$ (solid curves) are always defined in region II, with $\omega_{sin}(\kappa) < \omega_{im}(\kappa)$. No pure surface upper branch $\omega_+(\kappa)$ appears.

Caption for Figure 4.3

Plasmon modes for two separated metals for the case $\omega_p > \omega_{s2}$ ($\omega_p = 0.85\omega_p$). The lower branch $\omega_-(\kappa)$ (dashed curve) goes to the origin as in figure 4.2. $\omega_{sin}(\kappa)$ and $\omega_{im}(\kappa)$ (solid curves) now dip below $\omega_{b1}(\kappa)$, with the surface mode $\omega_+(\kappa)$ (dashed curve) appearing by $d = 3\lambda_0$, and being continuous with $\omega_{im}(\kappa)$ across $\omega_{b1}(\kappa)$. Analysis of equations (4.26) and (4.27) shows that the algebraic solutions for $\omega_{sin}(\kappa)$ and $\omega_{im}(\kappa)$ would intersect at $\omega = \omega_p$, but in region II the inequality $\omega_{sin}(\kappa) < \omega_{im}(\kappa)$ always holds.
Figure 4.2 (a)

\[ \frac{\omega}{\omega_p^2} \]

\[ \omega_{b_2}, \omega_{im} \]

\[ \omega_{s_1} \]

\[ \omega_{s_2} \]

\[ \omega_{b_1} \]

\[ \omega \]

(a) \( d = 0 \)

\( \frac{\beta_2 \kappa}{\omega_p^2} \)
Figure 4.2 (b) Figure 4.2 (c)

\[ \frac{\omega}{\omega_{p2}} \]

\( \omega_{b2} \)
\( \omega_{im} \)
\( \omega_{s2} \)
\( \omega_{b1} \)
\( \omega_{s1} \)
\( \omega_{-} \)

(b) \( d = 5 \, \text{Å} \)
(c) \( d = 10 \, \text{Å} \)
Figure 4.3 (a)

\[ \frac{\omega}{\omega_{p2}} \]

\[ \omega_{b2}, \omega_{im} \]

\[ \omega_{s2} \]

\[ \omega_{s1} \]

\[ \omega_{n} \]

(a) \( d = 0 \)
curve $\omega_{s1}(\kappa)$ and $\omega_+(\kappa)$ forming the portion of the metal 2 surface plasmon curve, $\omega_{s2}(\kappa)$, only up to the curve $\omega_{b1}(\kappa)$.

To complete the picture, region II must now be considered.

4.3.2 Region II: Mixed-Mode Continuum and the Image Plasmon

In region II, application of the boundary conditions, including the vanishing normal currents, to the solutions corresponding to equations (4.13) to (4.15) now yields the system of equations

$$\begin{pmatrix}
\omega_{p1}^2 - \omega_{q1}^2 & -1 & -1 & 0 \\
0 & (\omega_{p1}^2 - \omega_{q1}^2) & -1 & 1 & 0 \\
0 & 0 & \exp(\kappa d) & \exp(-\kappa d) & \omega_2^2 - \omega_{p2}^2 \\
0 & 0 & \exp(\kappa d) & -\exp(-\kappa d) & (\omega_{p2}^2 - \omega_2^2) \gamma_2
\end{pmatrix} \begin{pmatrix}
A \\
B \\
E' \\
F' \\
P'
\end{pmatrix} = \begin{pmatrix}
0
\end{pmatrix} \tag{4.24}
$$

where $E'(F') = (\varepsilon/m) \kappa E(F)$ and $P' = P \exp(-\gamma_2 d)$. As in the bimetallic interface problem, the infinite number of solutions to equations (4.24) represents a continuum of modes which are oscillatory in metal 1 and exponentially decaying in metal 2.

Solution of equations (4.24) for the relationships between the coefficients now gives

$$A \omega_{p1}^2 \kappa J_2(\kappa) = -Bq_1 J_1(\kappa) \tag{4.25}$$

where

$$J_1(\kappa) = (\omega_{p1}^2 - 2\omega_{q1}^2) [2\beta_2^2 \gamma_2 (\gamma_2 + \kappa) - \omega_2^2] - \omega_{p1}^2 \omega_{p2}^2 \exp(-2\kappa d) \tag{4.26}$$

$$J_2(\kappa) = 2\beta_2^2 \gamma_2 (\gamma_2 + \kappa) - \omega_{p2}^2 + \omega_{p2}^2 \exp(-2\kappa d) \tag{4.27}$$
The conditions

\begin{align}
J_1(\kappa) &= 0 \quad , \\
J_2(\kappa) &= 0 \quad ,
\end{align}

(4.28)  
(4.29)

correspond to special modes embedded in the continuum and represent pure sine (A = 0) and cosine (B = 0) density fluctuations respectively, in metal 1. Again, this statement must be justified by first noting that the factor $q_1$ in equation (4.25) plays the same role as in equation (4.20) where it was shown to be of no physical significance. Secondly, it is easily shown that $J_1(\kappa)$ and $J_2(\kappa)$ never vanish simultaneously in region II. In fact, if the solutions of equations (4.28) and (4.29) were to be continued into region I, substitution of $\omega = \omega_{pl}$ into both shows that they would intersect on this line.

The solution of equation (4.28), which will be denoted $\omega_{\text{sin}}(\kappa)$, is similar to the bimetallic interface mode $\omega_1(\kappa)$ insofar that it starts at $\bar{\omega}$ (equation (4.1)). However, it has the extremely important difference that it now represents a sinusoidal density fluctuation and is thus nodal at the surface of metal 1. In addition, it has a dependence on the separation distance as illustrated in figures 4.2 and 4.3. If $\omega_{pl} < \omega_{s2}$ (figure 4.2), $\omega_{\text{sin}}(\kappa)$ is always defined in region II. However, if $\omega_{pl} > \omega_{s2}$ (figure 4.3), then beyond some value of $d$, there is always a range of values of $\kappa$ for which part of the curve is lost below $\omega_{bl}(\kappa)$. A further point, which will become significant later, is that there is no analogue of $\omega_{\text{sin}}(\kappa)$
continuing below the curve \( \omega_{b1}(\kappa) \), into region I. Finally, it should be noted that for \( d = 0 \), equation (4.28) does not reduce to equation (4.17a) for the bimetallic interface mode, the latter being obtained only when the reflecting surfaces are removed.

The result for the cosine mode, equations (4.27) and (4.29), is particularly noteworthy in that it corresponds to the upper branch for a system of two identical metals separated by a distance \( 2d \) (see equation (3.92) and its factorised form, equation (2.56)). This represents a perfect, image result, with metal 2 effectively seeing its own image as a result of the density response of the bulk electrons in the less dense metal 1. The solution to equation (4.29) will thus be referred to as the 'image' plasmon, \( \omega_{im}(\kappa) \), and is explicitly given by (see equation (2.57))

\[
\omega_{im}(\kappa) = \frac{1}{\beta_2} \left\{ \frac{\omega_{p2}^2 (1 + \exp[-2\kappa d]) + \beta_2^2 \kappa^2}{\omega_{p2}^2 (1 - \exp[-2\kappa d]) + \beta_2^2 \kappa^2} + \beta_2 \kappa \right\}.
\] (4.30)

While \( \omega_{im}(\kappa) \) is distinct and unique in its own right, it will become evident that it also serves to complete the analogue of the upper symmetric branch \( \omega_{+} \), in region II. Starting at \( \omega_{p2} \), \( \omega_{im}(\kappa) \) has a dependence on the separation distance similar to \( \omega_{sin}(\kappa) \), dipping downwards with increasing \( d \), but again will only meet the curve \( \omega_{b1}(\kappa) \) if \( \omega_{p1} > \omega_{s2} \) (figure 4.3). When this occurs the surface mode \( \omega_{+}(\kappa) \) appears in region I and is in fact continuous (though not in slope) with \( \omega_{im}(\kappa) \) across the bulk curve. This fact
is easily seen analytically by substituting \( \omega = \omega_{b1}(\kappa) \) into equations (4.23) and (4.29), both of which then reduce to the relation

\[
2\beta_2^2 \gamma_{21}(\gamma_{21} + \kappa) - \omega_{p2}^2 + \omega_{p2}^2 \exp(-2\kappa d) = 0 , \tag{4.31}
\]

where

\[
\beta_2^2 \gamma_{21} = (\beta_2^2 - \beta_1^2) \kappa^2 + \omega_{p2}^2 - \omega_{p1}^2 . \tag{4.32}
\]

The existence of real roots, \( \kappa(d) \), of equation (4.31) also gives the condition for \( \omega_{im}(\kappa) \) actually meeting the curve \( \omega_{b1}(\kappa) \) and hence the onset of the pure surface mode \( \omega_+(\kappa) \).

In the limit \( d = \infty \), equation (4.29) reduces to the surface plasmon relation (4.18) for metal 2. Thus the continuity is preserved, with \( \omega_+(\kappa) \) forming that portion of \( \omega_{s2}(\kappa) \) lying in region I and \( \omega_{im}(\kappa) \) completing this surface plasmon curve above \( \omega_{b1}(\kappa) \), in region II. If \( \omega_{p1} < \omega_{s2} \), \( \omega_{im}(\kappa) \) reduces to the entire curve \( \omega_{s2}(\kappa) \) and as mentioned earlier, \( \omega_+(\kappa) \) never appears.

It is important to make some further observations concerning the relative magnitudes of the plasmon modes \( \omega_{sin}(\kappa) \) and \( \omega_{im}(\kappa) \), and of the continuum in which they lie. Recalling that all modes in region II are oscillatory bulk-type modes in metal 1 \( (n_1 \sim \text{Acos}q_1z + \text{Bsin}q_1z) \) and exponentially decaying in metal 2 \( (n_2 \sim \text{Pexp}(-\gamma_2d)) \), it is easily found from equation (4.24) that

\[
\frac{1}{2} P (\gamma_2 - \kappa)(\omega_{p2}^2 - \omega^2)^{-1} = A \omega_{p1}^2 \kappa J_1^{-1}(\kappa) \exp[(\gamma_2 - \kappa)d] \\
= - B q_1 J_2^{-1}(\kappa) \exp[(\gamma_2 - \kappa)d] . \tag{4.33}
\]
Thus at the surface of metal 2 \((z = d)\), the density fluctuations behave, in terms of the amplitudes in metal 1, as

\[
n_2 \sim A J_1^{-1}(\kappa) \exp(-\kappa d) \\
\sim -B J_2^{-1}(\kappa) \exp(-\kappa d) \quad .
\]

(4.34)

From equation (4.34) it is seen that anywhere in the continuum such that neither \(J_1(\kappa)\) nor \(J_2(\kappa)\) is zero, \(n_2\) decays relative to \(n_1\) as \(\exp(-\kappa d)\). Thus the general continuum of exponentially decaying modes in metal 2 are forced oscillations, coupled to the bulk modes of metal 1, and vanish as the metals are separated to infinity. Meanwhile, the continuum remains as part of the ordinary bulk continuum of metal 1, with the relation \((d = \infty)\)

\[
A \omega_{p1}^2 \kappa = -B q_1 (\omega_{p1}^2 - 2\omega^2) \quad ,
\]

(4.35)

previously obtained (Barton 1976, Summerside and Mahanty 1978, and equation (3.35)) for the bulk normal mode functions for a single metal half-space. At the same time, for increasingly large \(d\) both \(J_1(\kappa)\) and \(J_2(\kappa)\) tend to zero along the curve \(\omega_{s2}(\kappa)\). At \(d = \infty\), when they become zero simultaneously on \(\omega_{s2}(\kappa)\), both \(A\) and \(B\) (and hence \(n_1\)) must vanish, with \(P\) becoming an independent normalisation constant for the discrete surface normal mode \(\omega_{s2}(\kappa)\), in metal 2.

Finally, it is important to note from equation (4.33) that, since it can be shown that the function \(J_1(\kappa)\) is positive definite in region II when \(J_2(\kappa)\) vanishes (that is,
along the curve \( \omega_{im}(\kappa) \), then \( P \) and \( A \) are of opposite sign, because of the factor \( (\omega_{pl}^2 - \omega^2) \). Thus the image plasmon mode is indeed a symmetric mode, in consistency with its role as part of the generalisation of the upper branch \( \omega^+, \) in region II.

### 4.4 CONCLUDING DISCUSSION

Using the dielectric continuum model, Stern and Ferrell (1960) predicted that a plasma wave with constant resonant frequency \( \bar{\omega} \), given by equation (4.1), existed at the interface between two metals characterised by the local dielectric functions

\[
\varepsilon_j(\omega) = 1 - \frac{\omega_{pj}^2}{\omega^2} \quad . \tag{4.36}
\]

They effectively considered the cleaved (CIBM) interface of §§4.3, the non-local generalisation of their result thus being given by equations (4.26) and (4.28) for the mode \( \omega_{\text{sin}}(\kappa) \), with \( d = 0 \),

\[
(\omega_{pl}^2 - \omega^2) [2\beta_2^2 \gamma_2 (\gamma_2 + \kappa) - \omega_{pj}^2] - \omega_{pl}^2 \omega_{p2}^2 = 0 \quad . \tag{4.37}
\]

However, as discussed earlier, the infinite barrier model for the interface is not always realistic, as is borne out by the fact that Miller and Axelrod (1965) failed to observe the \( Mg-Al \) interface mode, attributing this to the blurring
of the interface, which could not occur for the CIBM. Commonly observed interface modes (for example, Bi-Mg (Miller and Axelrod 1965), Al-CdSe and Al-CdS (Brillson 1977), Ag-MgF$_2$ (Kovacs and Scott 1977), Al-Ag (Lopez-Rios et al 1978)) more likely correspond to the curve $\omega_I(\kappa)$ given by equations (4.21) and (4.22) for the more realistic bimetallic junction, since in these experiments the interface is formed by the deposition of one metal onto the substrate to build up a layer. In the case where two thin films are simply brought into contact mechanically, only partial electron transfer would be expected, in which case a mixture of modified interface and surface modes might be observed.

The curves for $\omega_I(\kappa)$ and $\omega_{\sin}(\kappa, d=0)$, given by equations (4.22) and (4.37) respectively, are plotted in figure 4.4. While these equations correspond to different boundary conditions, both reduce to the straight line result (4.1) predicted by Stern and Ferrell (1960) in the local ($\beta = 0$) approximation. Thus it is a combination of both spatial dispersion and boundary conditions which accounts for their different behaviour. As expected, however, these effects are irrelevant for the infinite wavelength ($\kappa = 0$) oscillation, with both curves starting at the predicted value.

In conclusion, with regard to the generalisation of this work to include retardation and systems involving thin films, which are amenable to experimental study, the following remarks may be made. Firstly, it is expected that the inclusion of retardation should only affect the
Caption for Figure 4.4

Comparison of interface modes $\omega_1(\kappa)$ and $\omega_{\sin}(\kappa,d=0)$, given by equations (4.22) and (4.37) respectively. Their different behaviour is due to both the boundary conditions and the effect of spatial dispersion. Here, $\omega_{p1} = 0.85\omega_{p2}$. 
curves $\omega_{-}(\kappa)$ and $\omega_{\text{im}}(\kappa)/\omega_{+}(\kappa)$ in the same manner as for identical metals, studied in Chapter 2 (Summerside and Mahanty 1979), as well as introducing the transverse electromagnetic modes. Secondly, the effect of boundary conditions and spatial dispersion on the interface mode (figure 4.4) should be evident in studies on thin films, bearing in mind that the experimental reflectance (ATR) or energy loss (ELS) data would need to be interpreted using a non-local dielectric function. Finally, a similar splitting should occur for the surface modes of two unlike thin metallic films. As is well known (Economou 1969, Ritchie 1973), a thin film, by virtue of its two surfaces, supports two types of surface oscillations, normal and tangential to the surfaces. An experimental and theoretical investigation of the coupling of these modes at a bimetallic junction and through a thin dielectric medium is required.
5.1 INTRODUCTION

5.1.1 Preliminary Remarks

Energy losses suffered by charged particles on reflection from or transmission through metal samples provide a useful method for studying the dielectric properties of metals. Such losses occur through various mechanisms such as interband transitions, electron-electron scattering, Bragg reflection and plasmon excitation. In this chapter the emphasis is on the force, arising from plasmon excitation, on a charged particle moving outside a spatially dispersive metal. Experimentally, such a study is achieved by firing electrons, say, at a metal surface, with a small normal component of velocity so as to reduce or eliminate penetration and hence eliminate energy losses by Bragg reflection and collisions. To achieve this, the electrons, which are necessarily of high speed, are fired at grazing incidence. In energy loss experiments, the use of 10 - 20 keV electrons ensures that the changes in energy and
momentum are only small fractional changes and so the electrons
may be considered as point charges with well defined paths. In
other words, the energy and momentum of the incident electron
are much higher than those of the characteristic excitations
under consideration, so that the recoil of the electron may be
neglected. As pointed out by Lucas and Sunjić (1972), even
when penetration of the metal by the charged particle is
eliminated there will be three distinct contributions to the
energy loss spectrum arising from elastic or specular
reflections, ionisation of true secondary electrons and the
characteristic losses considered here.

The moving charge will induce density fluctuations in
the metal and hence set up an opposing field which tends to
alter its velocity. The above 'fast particle' approximation
presents formal difficulties when the incident particle has a
velocity component normal to the surface, since in order to
correctly describe the reflection process, the opposing force
must be included self-consistently. Because of this difficulty
it is usually assumed that the particle has a well defined path
before and after reflection. For example, Chan and Richmond
(1976b) take the position of the particle as \( \mathbf{r} = \mathbf{v}_\parallel t + \mathbf{v}_\perp |t| \),
which may describe fairly well the forces involved well before
or after the reflection time \( t = 0 \); that is, when the particle
is at a large distance from the surface. A more appropriate
device used by Gumhalter and Newns (1975, Muscat 1976),
introduced a constant external force, causing the charge to move
in a parabolic path, the force being large enough so that some
minimum distance of approach without penetration was achieved.
Again, no account was given of the effect of the field, which
gives rise to this force, on the metal and hence on the induced potential.

An alternative approach, aimed at applicability to grazing incidence, was given by Muscat and Newns (1977), following the formalism applied by Takimoto (1966) to the case of a moving charge near a thin metallic film. Muscat and Newns considered only motion of the charge parallel to the surface of a semi-infinite metal and then introduced a small angle perturbation to account for grazing incidence. Their approach is developed here to include spatial dispersion, while the range of the velocity $v$ of the charged particle is still restricted to the non-relativistic region so that only electrostatic effects are considered.

Very recently, Barberán et al (1979) also attempted such a generalisation. However, in attempting to also include single particle effects, they used an approximate form for the surface plasmon dispersion relation and overlooked several important aspects of the effect of spatial dispersion, particularly the role of bulk plasmons.

5.1.2 Introduction to the Moving Charge Problem

The opposing force on the moving external charge in general has components $F_\perp$ normal to, and $F_\parallel$ in the direction of the particle's motion. This resolution is unique in that it is now well known (Gumhalter and Newns 1975, Muscat and Newns 1977, Barberán et al 1979) that only those surface plasmons whose phase velocity $v_p$ is less than the velocity $v$ of the particle contribute to $F_\parallel$ while only those with $v_p > v$ will contribute to $F_\perp$. In obtaining expressions for the force
components in the local limit, Muscat and Newns (1977) found that $F_{\parallel}^{loc}$ vanishes only when the velocity of the external charge becomes zero and that the transverse force $F_{\perp}^{loc}$ then reduces to the classical image force for a stationary charge, $-Q^2/4\pi^2$.

The inclusion of spatial dispersion introduces the role of bulk plasmons, ignored in previous investigations of this problem. The separate contributions of surface and bulk plasmons to the dynamical image force are conveniently handled using the normal mode decomposition of Chapter 3. The resolution into $F_{\parallel}$ and $F_{\perp}$ seen for surface plasmons also holds for bulk plasmons, but now in terms of the phase velocities parallel to the surface, and both the magnitude and direction of the bulk plasma oscillation wavevectors are now important.

With the inclusion of spatial dispersion, which is intimately related to the fact that the metallic electrons have a finite velocity (see Chapter 1), it is shown that $F_{\parallel}$ in fact vanishes when $v \leq \beta$, where $\beta$ is of the order of the Fermi velocity of the metallic electrons and is given by $\beta = (3/5)^{1/3} v_F$ (equation (1.16)). For these velocities all plasmon phase velocities are greater than $v$ and the only force on the charge is the velocity-dependent 'image' force $F_{\perp}$ which, for $v \to 0$, gives the well known static non-local image result of Newns (1969b). For $v > \beta$, the condition $\omega_{\kappa}/\kappa = v$, where $\omega_{\kappa}$ is the surface plasmon frequency, gives the limiting wavenumber $\kappa_s = \omega_s/[v(v-\beta)]^{1/2}$ for the surface plasmons contributing to $F_{\parallel}$ and $F_{\perp}$, compared to the corresponding limit $\kappa_s^{loc} = \omega_s/v$ in the local ($\beta = 0$) approximation (Muscat and Newns 1977). For the longitudinal bulk plasmons, which have the well known
dispersion relation $\omega_{kq}^2 = \omega_p^2 + \beta^2 k^2$ where $\hat{k} = (\hat{k}, q)$, the limiting condition $\omega_{kq}/k = \nu$ leads to rather more complicated conditions relating the wavevector components parallel and normal to the surface. These conditions, given in §5.3.4, are simply related to the fact that the induced density fluctuations associated with bulk plasmons are able, by virtue of the additional degree of freedom, to disperse downwards into the metal in response to the moving charge.

The origin of the force components and the fact that the moving charge does work only against $F_\parallel$ may be interpreted, on the basis that $F_\parallel$ and $F_\perp$ derive from the excitation of real and virtual surface plasmons respectively (Muscat and Newns 1977). A much clearer physical picture follows from the analysis of the induced density in §§5.4. As for the force components, the induced density may also be separated into that part $n_{\parallel}(\hat{r})$ involved in 'slow' plasma oscillations with phase velocities $v_p < \nu$ and that part $n_{\perp}(\hat{r})$ involved in 'fast' oscillations, with $v_p > \nu$. It is shown that $n_{\perp}(\hat{r})$ remains symmetrically distributed beneath the moving charge and corresponds to the total induced charge $-Q$. While the centroid of $n_{\perp}(\hat{r})$ remains at a constant distance below the surface, the velocity dependence of $F_\perp$ is seen to arise from the actual shape of $n_{\perp}(\hat{r})$ through the dependence on $\nu$ of its second moment. That part of the induced density $n_{\parallel}(\hat{r})$, contributes no net induced charge as it is antisymmetrically centred beneath the moving charge, thus forming a net opposing dipole with axis parallel to $\hat{v}\text{sgn}(Q)$. 
5.2 DYNAMICAL IMAGE POTENTIAL AND INDUCED DENSITY

5.2.1 Formalism

In Chapter 3 the linearised hydrodynamic equation of motion

\[ mn_o \frac{\partial \psi}{\partial t} = - en_o \hat{E} - mB^2 \hat{V} n \]  

(5.1)

was solved in terms of the displacement potential \( \psi \) defined in equation (3.5), and which is related to the induced density fluctuation as

\[ n = n_o \nabla^2 \psi \]  

(5.2)

While the normalisation procedure of Chapter 3 requires the displacement vector \( \hat{\xi} = - \hat{V} \psi \), the discussion here will be given in terms of the more relevant induced density and image or induced potential. With the usual assumption that \( n(\hat{\rho}) = n(s) \exp(i \hat{\rho} \cdot \hat{\rho}) \), appropriate for the planar geometry, the wave equation (3.13) for the induced density becomes

\[ \beta^2 \frac{d^2 n}{dz^2} - \beta^2 \kappa^2 - \omega_p^2 + \omega^2 \]  

(5.3)

The solution of equation (5.3) corresponding to the conditions

\[ \beta^2 \gamma^2 = \beta^2 \kappa^2 + \omega_p^2 - \omega^2 > 0 \]  

(5.4)

and

\[ \beta^2 q^2 = \omega^2 - \omega_p^2 - \beta^2 \kappa^2 > 0 \]  

(5.5)
are denoted \( n_{\kappa} \) and \( n_{\kappa q} \) respectively, for the exponentially decaying surface and oscillatory bulk normal mode density fluctuations (see equations (3.28) and (3.37)). The corresponding normal mode potential functions inside the metal are related to \( n \) by

\[
\nabla^2 \varphi = 4\pi n n
\]

and

\[
\nabla^2 \psi = n/n_0
\]

while outside the metal, \( \varphi \) is the matching solution of Laplace's equation. All of these normal mode functions are given in equations (3.26) to (3.30) and (3.35) to (3.39). Application of the boundary condition of vanishing of the normal component of the current density at the surface \( z=0 \) (or equivalently, vanishing of \( \partial \psi/\partial z \) at \( z = 0 \)) leads to the well known dispersion relations for the discrete surface plasmon and continuum of bulk modes,

\[
\omega_{\kappa}^2 = \frac{1}{2}[\omega_p^2 + \beta^2 \kappa^2 + \beta \kappa(2\omega_p^2 + \beta^2 \kappa^2) \frac{h}{p}] = \{\frac{1}{2}[(2\omega_p^2 + \beta^2 \kappa^2) \frac{h}{p} + \beta \kappa]\}^2
\]

and

\[
\omega_{\kappa q}^2 = \omega_p^2 + \beta^2 \kappa^2 + \beta^2 q^2
\]

where the continuous index \( q > 0 \) represents the normal component of the wavevector \( \vec{k} = (\kappa, q) \) for the bulk plasma.
oscillations. The explicit factorisation for $\omega_k$ given in equation (5.7) (also noted by Heinrichs (1975), but previously overlooked, attention being given rather to a small $\kappa$ expansion) is very useful in the detailed analysis required to obtain many results of this chapter.

A charged particle $Q$, initially at $\vec{r}_o = (\vec{p}_o, z_o)$ outside the metal and moving with constant velocity $\vec{v} = (\vec{v}, 0)$ parallel to the metal surface ($v_F << v << c$), will give rise to the nonretarded Coulomb potential

$$\varphi_{ext}(\vec{r}, t) = \frac{Q}{|\vec{r} - \vec{r}_o - \vec{v}t|}$$

$$= \frac{4\pi Q}{(2\pi)^3} \int \frac{d^3k}{k^2} \exp \left[ i\vec{k}.(\vec{r}-\vec{r}_o) - i\vec{k}.\vec{v}t \right] , \quad (5.9)$$

for which the Fourier frequency component is simply

$$\varphi_{ext}(\vec{r}, \omega) = \frac{4\pi Q}{(2\pi)^2} \int \frac{d^3k}{k^2} \exp \left[ i\vec{k}.(\vec{r}-\vec{r}_o) \right] \delta(\omega - \vec{k}.\vec{v}) .$$

$$\quad (5.10)$$

### 5.2.2 Induced Density and Image Potential

In the normal mode expansions of the type (3.51) and (3.52), the time dependence of each component is determined as $\exp(i\omega_o t)$ where $\omega_o = \omega_o(\kappa) = \vec{k}.\vec{v}$. The various normalised functions giving the surface and bulk contributions to the induced density and to the induced potential existing outside the metal are then given, in time-independent form, by

$$\eta_s(\vec{r}, t) = \frac{\omega_o^2}{\varepsilon} \int \frac{d^2k \exp[i\vec{k}.(\vec{r}-\vec{r}_o-\vec{v}t) + \gamma_k z - k z_o] \beta_k (\gamma_k + \kappa)}{(2\pi)^2 (\omega_k^2 - \omega_o^2) T(\kappa)} ,$$

$$\quad (5.11)$$
\[ \eta_{\beta}(r,t) = \frac{\omega^2 p}{4e} \int \frac{d_k}{(2\pi)^2} \exp[i k \cdot (r - r_o - \mathbf{vt}) - \kappa s_o] \times \int_0^\infty \frac{dq}{2\pi} \frac{\beta^2 q^2}{(\omega - \omega_o)^2} \frac{(2\omega^2 - \omega^2) \cos qz + (\kappa \omega^2/q) \sin qz}{(\beta^2 q^2 + \omega^2) (\beta^2 q^2 + \omega^2)} , \quad (5.12) \]

where

\[ T(\kappa) = (2\omega^2 + \beta^2 \kappa^2)^{1/2} , \quad (5.13) \]

\[ \beta^2 \gamma^2 = \frac{1}{2} [\omega^2 + \beta^2 \kappa^2 - \beta \kappa (2\omega^2 + \beta^2 \kappa^2)^{1/2}] = \{\frac{1}{2} [(2\omega^2 + \beta^2 \kappa^2)^{1/2} - \beta \kappa]\}^2 , \quad (5.14) \]

and the potentials, as given in Chapter 3 (equations (3.62)), may be written

\[ \varphi_{\text{Is},b}(r,t) = -\omega^2 p \int \frac{d_k}{2\pi \kappa} \exp[i k \cdot (r - r_o - \mathbf{vt}) - \kappa (z + z_o)] \mu_{\text{Is},b}(\kappa, \omega_o) \, , \quad (5.15) \]

where \( \mu_{\text{s}} \) and \( \mu_{\text{b}} \) are given by equations (3.63) to (3.66). An alternative useful form of \( \mu_{\text{s}} \), which explicitly shows its singularities, is

\[ \mu_{\text{s}}(\kappa, \omega) = \frac{\beta \gamma}{(\omega^2 - \omega_o^2) T(\kappa)} . \quad (5.16) \]

The contributions to the induced potential may be combined as

\[ \varphi_{\text{I}}(r,t) = -\omega^2 p \int \frac{d_k}{2\pi \kappa} \exp[i k \cdot (r - r_o) - \kappa (z + z_o)] \times \int_0^\infty \frac{d\omega}{\omega} \exp(-i\omega t) \delta(\omega - d_k) \frac{\exp(-i\omega t)}{D(\kappa, \omega)} \, , \quad (5.17) \]

where
\[ D^{-1}(\kappa, \omega) = \mu_s(\kappa, \omega) + \mu_b(\kappa, \omega) \]
\[ = [2\beta^2 \gamma(\gamma+\kappa) - \omega_p^2]^{-1} \] \hspace{1cm} (5.18)

is analytically continued as indicated in §3.4.1 when \( \gamma \) becomes complex. In the local (\( \beta=0 \)) limit, this reduces to

\[ D^{loc}(\omega) = 2(\omega_s^2 - \omega^2) \] \hspace{1cm} (5.19)

and equation (5.17) reduces to the result of Muscat and Newns (1977). Equation (5.17) is readily obtained for real \( \gamma \) much more directly using the method of Mahanty and Paranjape (1977). While the continuation to complex \( \gamma \) is trivial, as pre-empted in §3.4.1, their method bypasses the information contained in equations (5.11) and (5.12) for the induced density, which is of central importance in this chapter.

5.3 FORCE ON THE MOVING CHARGE

5.3.1 General Expression for the Force

From equation (5.17), the force experienced by the moving charge after a time \( t \) is simply

\[ \vec{F}(z_o) = -Q \frac{\partial \phi_I(\vec{r}, t)}{\partial \vec{r}} \bigg|_{\vec{r} = \vec{r}_0 + \vec{v}t} \]
\[ = \omega_p^2 Q^2 \int \frac{d^2 \kappa}{2\pi} \exp(-2\pi \omega_o) \frac{(i\kappa - \kappa_3)}{2\pi} D(\kappa, \omega_o) \] \hspace{1cm} (5.20)

where again, \( \omega_o = \kappa \cdot \vec{v} \). As usual, the components of the force
longitudinal and transverse with respect to the particle's motion are evaluated separately from the general expressions

\[ F_{\parallel}(z_o) = \frac{\omega^2 Q^2}{2\pi} \int_0^\infty dk \kappa \exp(-2kz_o) \int_0^{2\pi} \frac{d\theta \ i \ \cos \theta}{D(k, \kappa \nu \cos \theta)}, \quad (5.21) \]

\[ F_{\perp}(z_o) = \frac{\omega^2 Q^2}{2\pi} \int_0^\infty dk \kappa \exp(-2kz_o) \int_0^{2\pi} \frac{d\theta}{D(k, \kappa \nu \cos \theta)}. \quad (5.22) \]

Since the \( \theta \) integrations inevitably separate the surface and bulk contributions, it is convenient to use the explicit decomposition of \( D^{-1}(\kappa, \omega) \) with equations (5.16) for \( \mu_s(\kappa, \omega) \) and (3.64) for \( \mu_b(\kappa, \omega) \). Further to this preliminary analysis, it will be noted that in general, \( \mu_s \) and \( \mu_b \) may have poles within the range of integration. The contributions from these points are handled by reintroducing a small imaginary part and using the Dirac identity in the form

\[ \frac{1}{x - i\eta} = P\left(\frac{1}{x}\right) + i\pi \text{sgn}(\eta) \delta(x) \quad (5.23) \]

where \( x = (\omega_k^2 - \omega^2) \) or \( (\omega_k^2 - \omega^2) \) and \( \eta \) has the same sign as \( \omega \), consistent with a phenomenological damping of the plasmons (Takimoto 1966).

5.3.2 Longitudinal or Parallel Force

The contributions to \( F_{\parallel} \) from surface and bulk plasmons may be separated by writing equation (5.21) as

\[ F_{\parallel,s,b}(z_o) = \frac{\omega^2 Q^2}{2\pi} \int_0^\infty dk \kappa \exp(-2kz_o) \int_0^{2\pi} \mu_{s,b}(k, \kappa \nu \cos \theta) \ i \ \cos \theta. \quad (5.24) \]

When \( \nu < \beta \), neither \( \mu_s \) nor \( \mu_b \) will have any singularities and
the oddness of the principal part integrand renders the $\theta$ integral zero. Thus

$$F_{\parallel, b}(s_o) = 0 ; \quad \nu < \beta . \quad (5.25)$$

For $\nu > \beta$, the only remaining non-zero terms in $F_{\parallel, b}$ arise from the singular term in the Dirac identity $(5.23)$. The $\theta$ integrals are then trivially performed using the identity

$$\delta[f(\theta)] = \sum \frac{\delta(\theta - \theta_i)}{|f'(\theta_i)|} , \quad (5.26),$$

where the $\theta_i$ are the zeros of $f(\theta) = \omega^2 - \kappa^2 v^2 \cos^2 \theta$, (where $\lambda$ indicates the appropriate label $\kappa$ or $\kappa q$) and are given by

$$\theta_i = \cos^{-1}\left( \pm \frac{\omega_\lambda}{\kappa v} \right) . \quad (5.27)$$

The occurrence of these points is governed by the condition on the argument that $\omega_\lambda/\kappa < \nu$ corresponding to the requirement that the plasmon phase velocity parallel to the surface be less than the velocity $\nu$ of the moving charge. For surface plasmons, the solution $\kappa(v)$ of the equation $\omega_\kappa = \kappa v$, is given by

$$\kappa_s = \frac{\omega_s}{[v(v-\beta)]^\frac{1}{2}} \quad (5.28)$$

and determines the lower limit on the wavenumbers for the surface plasmons which will contribute to $F_{\parallel}$. The corresponding condition for bulk plasmons involves the normal wavevector component through the solution $q \equiv q_0(\kappa)$ of the
equation \( \omega_{\kappa q} = \kappa \nu \), given by

\[
\beta^2 q_o^2(\kappa) = \kappa^2 (\nu^2 - \beta^2) - \omega_p^2 < 0 .
\] (5.29)

This immediately gives the condition on the bulk plasmon wavevector component parallel to the surface, that \( \kappa > \kappa_b \)

where

\[
\kappa_b = \frac{\omega_p}{\sqrt{(\nu^2 - \beta^2)^2}} .
\] (5.30)

Having determined the ranges of wavenumbers in which the singularities of \( \mu_s \) and \( \mu_p \) will occur, the \( \theta \) integrations in equations (5.24) are straightforward and give the results

\[
F_{|| s}(z_o) = -\frac{\omega_s^2 Q_s^2}{\nu} \int_{\kappa_s}^{\infty} d\kappa \frac{\exp(-2\kappa z_o)}{T(\kappa)} \frac{2\beta \gamma_\kappa}{(\kappa^2 \nu^2 - \omega_p^2)^{1/2}} ,
\] (5.31)

and

\[
F_{|| p}(z_o) = -\frac{\omega_s^2 Q_s^2}{\nu} \int_{\kappa_b}^{\infty} d\kappa \frac{\exp(-2\kappa z_o)}{T(\kappa)} \frac{2}{\pi} \int_0^{q_o(\kappa)} \frac{dq \Re(\kappa,q)}{(q_o^2 - q^2)^{1/2}}
\] (5.32a)

\[
= -\frac{\omega_s^2 Q_s^2}{\nu} \int_{\kappa_b}^{\infty} d\kappa \frac{\exp(-2\kappa z_o)}{T(\kappa)} \left[ \frac{\omega_\kappa}{(\kappa^2 \nu^2 - \beta^2 \gamma_\kappa^2)^{1/2}} - \frac{\beta \gamma_\kappa}{(\kappa^2 \nu^2 - \omega_p^2)^{1/2}} \right] .
\] (5.32b)

where \( T(\kappa) \) is defined by equation (5.13) and

\[
R(\kappa,q) = \frac{\omega_\kappa^2}{\beta^2 q^2 + \omega_\kappa^2} - \frac{\beta^2 \gamma_\kappa^2}{\beta^2 q^2 + \beta^2 \gamma_\kappa^2} .
\] (5.33)
5.3.3 Transverse or Normal Force

Again, the surface and bulk contributions may be separated by writing equation (5.22) as

\[
F_{L, s, b}(z_0) = \frac{\omega_s^2}{2\pi} \int_0^\infty d\kappa \exp(-2\kappa z_0) \int_0^{2\pi} d\theta \mu_{s, b}(\kappa, \kappa \cos \theta) .
\] (5.34)

It is now the singular parts of \( \mu_{s, b} \) which produce an odd \( \theta \)-integrand and the limits \( \kappa_s, \kappa_b \) and \( q_0 \) now determine the appropriate wavenumber ranges for which the plasmon phase velocities are greater than \( v \). The manner in which these limits now arise may be illustrated by considering the surface contribution which becomes

\[
F_{L, s}(z_0) = -2\omega_s^2 \int_0^\infty d\kappa \frac{\beta \gamma_k}{T(\kappa)} \exp(-2\kappa z_0) \frac{2\pi}{2} \int_0^{\frac{\kappa \pi}{2}} \frac{d\theta}{\omega_k^2 - \kappa^2 v^2 \cos^2 \theta} .
\] (5.35)

The \( \theta \) integral is a standard one whose principal value vanishes if \( \omega_k < \kappa v \) or \( \kappa > \kappa_s \). A similar integral for the bulk term gives the non-vanishing condition \( \omega_k q > \kappa v \) with the implied conditions on the wavenumber components as indicated in equation (5.37) below. The results for the surface and bulk contributions to the normal force become, for \( v > \beta \),

\[
F_{L, s}(z_0) = -\omega_s^2 \int_0^{\kappa_s} d\kappa \kappa \exp(-2\kappa z_0) \frac{2\beta \gamma_k}{T(\kappa)} \omega_k^2 \left( \omega_k^2 - \kappa^2 v^2 \right) \frac{1}{q_0^2}
\] (5.36)

and

\[
F_{L, b}(z_0) = -\omega_s^2 \left\{ \int_0^{\kappa_b} d\kappa \kappa \exp(-2\kappa z_0) \frac{2}{T(\kappa)} \int_0^{\infty} \frac{dq}{\omega_{kq} \left( q^2 + q_{1, q_0}^2 \right) \frac{1}{q_0^2}} \right. \\
+ \left. \int_0^{\kappa_b} d\kappa \kappa \exp(-2\kappa z_0) \frac{2}{T(\kappa)} \int_0^{\infty} \frac{dq}{\omega_{kq} \left( q^2 - q_{1, q_0}^2 \right) \frac{1}{q_0^2}} \right\} ,
\] (5.37)

where \( q_{1, q_0}^2 = -q_{0}^2 \) is positive in the first term of equation...
(5.37), while for \( \nu < \beta \), the second term in equation (5.37) vanishes and the limits \( \kappa_s \) and \( \kappa_p \) are both replaced by infinity. The limits in equations (5.36) and (5.37) again have the significance that only those plasmons whose phase velocity parallel to the surface is greater than \( \nu \), will contribute to \( F_\perp \). The distinct and important role played by the normal component of the bulk plasmon wavevector is illustrated by comparing equation (5.32a) with the second term in equation (5.37). For \( \kappa > \kappa_b \), those bulk plasmons whose wavevectors make an angle with the surface smaller than

\[
\theta_b = \tan^{-1} \frac{q_0(\kappa)}{\kappa} \tag{5.38}
\]

will have \( \nabla \equiv \omega \kappa q / \kappa < \nu \) and contribute to \( F_\parallel \), while those which have larger normal components \( q \), and thus make an angle with the surface \( \theta > \theta_b \) contribute to \( F_\perp \). Physically, this is easily understood in terms of the induced density discussed in §5.4, and the description can be summarised by saying that those electrons involved in bulk plasma oscillations with \( \kappa > \kappa_b \) and 'large' \( q > q_0(\kappa) \) are able to respond, by virtue of the additional degree of freedom normal to the surface, so that the associated density fluctuation remains symmetrically distributed beneath the moving charge.

5.3.4 Reduction to and Asymptotic Corrections to the Local Limit

In the spatially non-dispersive approximation \( (\beta = 0) \), all bulk contributions vanish along with \( \nu_b \) and the local results of Muscat and Newns (1977) follow directly from equations (5.31) and (5.36). The parallel force becomes
The first form, equation (5.39a), explicitly contains the appropriate limit $\kappa_{loc} = \omega_s / \nu$ and the second is obtained with the variable change $x = \kappa \upsilon / \omega_s$, with $\alpha = 2 \omega_s z_o / \nu$, and where $K_0$ is the zeroth order modified Bessel function (e.g., Gradshteyn and Ryzhik 1965, Abramovitz and Stegun 1970). (An error of a factor of 2 should be noted in the expression for $F_{\parallel loc}$ by Muscat and Newns 1977), this factor being required to obtain their subsequent result for the surface plasmon excitation probability.)

The normal force is given in the local limit by

$$F_{\parallel loc}(z_o) = -\frac{\omega_s^2 Q^2}{\nu} \int_{\kappa_{loc}}^{\infty} \frac{dk}{\kappa_{loc}} \frac{\exp(-2\kappa z_o)}{(\kappa^2/2 - \omega_s^2/2)^{1/2}}$$

(5.39a)

$$= -\frac{\omega_s^2 Q^2}{\nu^2} \int_1^\infty dx \frac{\exp(-\alpha x)}{(x^2 - 1)^{1/2}}$$

(5.39b)

$$= -\frac{\omega_s^2 Q^2}{\nu^2} K_0(\alpha)$$

The expressions (5.40b) are those given by Muscat and Newns (1977) and it is a simple matter to show that when $\upsilon = 0$, the static classical image result $F_{\parallel im}(z_o) = -Q^2/4z_o$ is obtained.

While the more general non-local expressions for the
force components cannot be integrated analytically, it is possible to obtain asymptotic corrections to the local results in the limits of large $v/\beta$ and large $z_0$. This derivation also clearly demonstrates the region of validity of the local results and will be illustrated for the parallel force given by equations (5.31) and (5.32b). Considering first the surface contribution, the variable change $y = \beta k/\omega_s$ transforms equation (5.31) to

$$F_{\parallel s}(z_0) = -\frac{2\omega_s^2}{\beta v} \int_0^\infty \frac{dy \exp(-2s_0 \omega_s y/\beta) A(y)}{\left(\frac{\omega_s^2 y^2}{\beta^2} - 1\right)^{1/2}}$$

where $2\beta y_k/T(\kappa)$ transforms as $A(y)$, $\omega_k$ as $\omega_y$, and $V_s = [v(v-\beta)]^{1/3}$.

For sufficiently large $v$, such that the lower limit on the integral is much less than unity ($\beta/V_s << 1$), the main contribution will come from small $y$ in the range $\beta/V_s < y < 1$. In making a small $y$ expansion, the square root factor may only be expanded internally with respect to $1/\omega_y^2 = (1-y+3y^2)/\omega_s^2$. Keeping only the leading term for $\omega_y$ within the square root, the appropriate expansion becomes

$$F_{\parallel s}(z_0) = \frac{\omega_s^2}{\beta v} \int_0^\infty \frac{dy \exp(-2s_0 \omega_s y/\beta)}{(v y/\beta^2 - 1)^{1/2}} \left[1 - y + \frac{3y^2}{8}\right].$$

The final variable change to $x = yV_s/\beta$ then gives, with $\alpha_s = 2s_0 \omega_s/V_s$,

$$F_{\parallel s}(z_0) = -\frac{\omega_s^2}{v^2} \int_1^\infty \frac{dx \exp(-\alpha_s x)}{(x^2 - V_s^2/\beta^2)^{1/2}} \left[1 - \frac{\beta V_s}{x} + \frac{3\beta^2}{8V_s^2} x^2\right].$$

The local result of Muscat and Newns (1977) emerges as the
leading term only after making the final approximation that \( V_s/\nu = 1 \). Including only the first correction term, the asymptotic form for the surface contribution to the parallel force becomes

\[
F_{\parallel S}(z_o) = -\frac{\omega_s^2 Q^2}{\nu^2} \left[ K_0 (a) - \frac{\beta}{\nu} K_1 (a) \right] . \tag{5.43}
\]

A similar analysis gives, for the bulk contribution,

\[
F_{\parallel b}(z_o) = -\frac{\omega_s^2 Q^2}{\nu^2} \int_{1}^{\infty} dx \exp \left( -\alpha_{b} x \right) \left( \frac{\beta x}{V_b} - O \left( \frac{\beta x}{V_b} \right)^5 \right) , \tag{5.44}
\]

where \( V_b = [(\nu^2 - \beta^2)/2]^{1/2} = \nu/\sqrt{2} \), and while an expression in terms of elementary or special functions is not forthcoming, this will only tend to cancel the correction term in equation (5.43). In view of the approximation \( \beta << \nu \) already made, the correction terms will naturally be very small. The derivation of equation (5.43) does, however, emphasise the approximations implicit in the local limit, the results of which can therefore only be regarded as quantitative in the limits of large \( \nu \) and \( z_o \).

5.3.5 The Static Limit and Final Comments

The local limits obtained above all derive from only the surface plasmon contributions. It may also be noted that if the hydrodynamic surface plasmon frequency (equation (5.7)) is used in the results of Barberán et al (1979), only those surface contributions are obtained and so their results also lead directly to those of Muscat and Newns (1977). The importance of the bulk contributions, not included by Barberán
may be seen in deriving the static image force, with spatial dispersion included. With $v = 0$, the $q$ integral in equation (5.37) becomes straightforward and the separate static contributions $F_{\perp s,b}$ combine to give, with the variable change $x = \beta \kappa / \omega_p$,

$$F(z_o; v=0) = -\frac{\omega_p^2}{\beta^2} \int_0^\infty dx x \exp(-ax) \left[ (x^2+1) \frac{1}{2} - x \right]^2$$

(5.45)

where now $a = 2\omega_p z_o / \beta$. This corresponds to the interaction energy of a stationary point charge with a spatially dispersive metal (Newns 1969b),

$$E(z_o) = -\frac{\omega_p^2}{2\beta} \int_0^\infty dx \exp(-ax) \left[ (x^2+1) \frac{1}{2} - x \right]^2$$

(5.46)

Corrections to the static result for small $v$ are obtained by making the appropriate expansion of $D^{-1} \equiv \mu_s + \mu_b$, with the combined result

$$F(z_o; v<<\beta) = -\frac{\omega_p^2}{\beta^2} \int_0^\infty dx x \exp(-ax) \left[ (x^2+1) \frac{1}{2} - x \right]^2 \left\{ 1 + \frac{[(x^2+1) \frac{1}{2} - x]^2}{2(x^2+1) \frac{1}{2}} \frac{2(x^2+1) \frac{1}{2} + x}{2(x^2+1) \frac{1}{2}} \left( \frac{v}{\beta} \right)^2 \right\}$$

$$+ O\left( \frac{v^4}{\beta^4} \right)$$

(5.47)

Of particular interest here is the sign on the correction terms, indicating that for small $v << \beta$, the 'image' force $F_{\perp}$ increases with increasing $v$. Again, this may be understood in terms of the induced charge density distribution. Although, as indicated in §5.4.1, the induced density remains
symmetrically distributed beneath the moving charge for these velocities, it is obvious (equations (5.11) and (5.12)) that the form of this distribution is still dependent on $v$. It will also be shown that both the total induced charge and its centre of mass are independent of $v$. The above effect must be understood in terms of the actual shape of $n(\vec{r})$ and it is indicated in §5.4.1 that through the velocity dependence of its second moment, $n(\vec{r})$ tends to peak beneath the moving charge with increasing $v$. While this trend continues for all $v$, $F_\parallel$ decreases again for $v > \beta$ as low phase velocity plasmons are eliminated, with a net spreading of the distribution due to the increased weight of the contributions from large $\nu_p$ or long wavelength plasmons.

5.4 ANALYSIS OF THE INDUCED DENSITY

5.4.1 Moments of the Induced Density

Equations (5.11) and (5.12) may be written as

\[
n_{s,b}(\vec{r}',z) = \frac{\omega_p^2}{\varepsilon} \int_0^\infty \frac{d\kappa \kappa \exp(-\kappa z)}{(2\pi)^2} \left(2\pi\right)^2 \int_0^{2\pi} d\phi \exp(i\kappa \cos(\phi)) N_{s,b}(\kappa,\kappa\nu \cos(\theta))
\]

where the time dependence is contained in the origin

$(\vec{r'} - \vec{r}_o - \vec{v}t, z) = 0$ which now lies directly beneath the moving charge and $N_{s,b}'$ which also contain the $z$-dependence, are self-evident. The angles $\theta$ and $\phi$ are related by $\phi = \theta - \eta$. 

where $n = \cos^{-1}(\hat{\rho}', \hat{v})$ is fixed.

Integration of equations (5.48) over the negative half-space gives, for the total induced charge,

$$Q_s = -\varepsilon \int d^2 \rho' \int_0^0 dz \ n_s(\hat{\rho}', z) = -Q$$  \hspace{1cm} (5.49)

and

$$Q_b = 0$$  \hspace{1cm} (5.50)

Thus the total induced charge is the negative of, and is independent of the nonrelativistic velocity of, the external charge and is contained in the density fluctuations associated with surface plasmons. Although at first surprising, equation (5.50) does not contradict the fact that $n_b(\hat{v})$ contributes to $F_L$, since examination of equation (5.12) indicates that the density associated with bulk plasmons in fact has a multipolar character, with overall neutrality.

The first moment of $n_s(\hat{\rho}', z)$ gives the centre of mass of the net induced charge, $\langle R_s \rangle = (0,0,-\beta/\omega_s)$, where $\beta/\omega_s$ is of the order of the Thomas-Fermi screening length. In the local limit this corresponds to the fact that the induced charge resides entirely on the surface ($n^{1oc}(z) \sim \delta(z)$). As for $\langle R_s \rangle$, it is easily shown that the first moment of the bulk charge is also independent of $v$. The velocity dependence of the forces arises in the second moments of $n(\hat{\rho}', z)$ which indicate a peaking of the charge distribution beneath the moving charge, with increasing $v$. This effect is illustrated qualitatively by the increasing magnitude of the central peak of the induced charge at $\hat{\rho}' = 0$ in equations (5.48) or
equivalently in equation (5.59) below.

5.4.2 Symmetry Considerations and Origin of the Force Components

The distinct origins of the force components $F_{||}$ and $F_{\perp}$ can be clearly understood in terms of the symmetry properties of the induced charge density. The general form of the $\theta$ integrals in equations (5.48) may be written

$$I(\rho', \eta) = \int_0^{2\pi} d\theta \exp[i\kappa\rho'\cos(\theta-\eta)] f(\cos\theta) \quad (5.51)$$

With the variable change to $\theta-\pi$ in the range $(\pi, 2\pi)$ followed by the change to $\pi-\theta$ in the range $(\pi, 2\pi)$, $I(\rho', \eta)$ takes the form

$$I(\rho', \eta) = 2[I_+(\rho', \eta) + I_-(\rho', \eta)] \quad (5.52)$$

where

$$I_+(\rho', \eta) = \int_0^{\pi/2} d\theta \cos(\kappa\rho'\cos\theta\cos\eta) \cos(\kappa\rho'\sin\theta\sin\eta)$$

$$\times [f(\cos\theta) + f(-\cos\theta)] \quad (5.53)$$

and

$$I_-(\rho', \eta) = \int_0^{\pi/2} d\theta \sin(\kappa\rho'\cos\theta\cos\eta) \cos(\kappa\rho'\sin\theta\sin\eta)$$

$$\times [f(\cos\theta) - f(-\cos\theta)] \quad (5.54)$$

The following identities are easily verified:

$$I_\pm(\rho', \eta) = I_\pm(\rho', -\eta) \quad (5.55)$$

$$I_\pm(\rho', \eta) = \pm I_\pm(\rho', \eta + \pi) \quad (5.56)$$
If \( f(\cos \theta) \) is an even function of \( \cos \theta \), then \( I_- \) vanishes and from equations (5.55) and (5.56), \( I_0 = I_+ \) corresponds to a symmetric density distribution with respect to inversion about both axes \( n = 0 \) and \( n = \frac{\pi}{2} \) in any plane parallel to the surface. In addition, on comparing equations (5.53) and (5.57), \( I_+ \) has an absolute maximum at \( \rho' = 0 \), directly beneath the moving charge. When \( f(\cos \theta) = -f(-\cos \theta) \), then \( I_0 = I_- \) is antisymmetric about, and vanishes on, the axis \( n = \frac{\pi}{2} \). The corresponding antisymmetric charge distribution will contribute no net charge.

In the expression for the surface and bulk charge densities, \( f(\cos \theta) \) is given by \((\omega^2 - \kappa^2 \nu^2 \cos^2 \theta)^{-1} \) where \( \lambda \equiv \kappa \) and \( \kappa \nu \) respectively. When there are no singularities, \( f(\cos \theta) \) is even and the symmetric density \( n_\perp \) will give rise to \( F_\perp \). When singularities occur, only the imaginary parts \( i\pi \text{sgn}(\cos \theta) (\omega^2 - \kappa^2 \nu^2 \cos^2 \theta) \) contribute, leading to the antisymmetric charge distribution \( n_\parallel \) which in turn gives rise to \( F_\parallel \). Thus, for example,

\[
n_{\perp}(\rho', n, z) = \frac{\omega^2}{e} \int_0^{\frac{\pi}{2}} d\theta \left[ f(\cos \theta) + f(-\cos \theta) \right], \quad (5.57)
\]

\[
I_+(0, n, z) = I_-(0, n, z) = 0. \quad (5.58)
\]

and

\[
I_+(\rho', \frac{\pi}{2}, z) = \int_0^{\frac{\pi}{2}} d\theta \cos(\kappa \rho' \cos \theta \cos n) \cos(\kappa \rho' \sin \theta \sin n), \quad (5.59)
\]
where \( \theta_s = \cos^{-1}(\omega_\kappa / \kappa v) \). Note also that the induced charge
\(-e n_{s\parallel}(\rho', 0, z) = e n_{s\parallel}(\rho', \pi, z)\) is of the same sign as \( Q \) in front of the moving charge. An equivalent analysis gives the bulk terms \( n_{b\parallel} \) and \( n_{b\perp} \) with the corresponding limits \( \kappa_b \) and \( q_o(\kappa) \) as in equations (5.32) and (5.37) for \( F_\parallel \) and \( F_\perp \).

### 5.5 CONCLUDING REMARKS

The approach of Takimoto (1966) and Muscat and Newns (1977) has been extended here to study the effects of spatial dispersion on the force on a charge moving with constant velocity parallel to a metal surface. The notable effects of the nonlocality of the dielectric response of the metal are the inclusion of the contributions from bulk plasmons and the introduction of the physically important limits \( \kappa_s = \omega_s / [\nu(\nu - \beta)]^{1/2} \) (compared to \( \omega_s / \nu \) in the local approximation) on the surface plasmon wavenumbers and \( \kappa_b = \omega_p / (\nu^2 - \beta^2)^{1/2} \) and \( q_o(\kappa) = [\kappa^2(\nu^2 - \beta^2) - \omega_p^2]^{1/2} / \beta \) for bulk plasmons, separating their contributions to the longitudinal and transverse force components. These limits are connected with the results that \( F_\parallel \) vanishes when \( \nu \leq \beta \), with the induced density fluctuations in the metal then remaining symmetrically distributed beneath the moving charge.
charge, and the shape of this symmetric distribution giving rise to the velocity dependence of $F_\perp$. For $v > \beta$ the existence and origin of the force components $F_\parallel$ and $F_\perp$ can be understood in terms of the lack of symmetry of the induced density, rather than simply as resolved components of an 'image' force resulting from a charge distribution with centre of mass which lags behind the moving charge.

The results are easily extended to obtain the probability of plasmon excitation for very small angle grazing incidence as done by Barberán et al (1979) for the surface plasmon contributions. For the bulk contribution, equation (5.32a) must be used with the factor $\omega_{kq}$ introduced into the $q$ integral which then requires numerical evaluation.

Although, as indicated above, the results of Barberán et al (1979) only reproduce the surface contributions given here, and thus do not reduce to the same static limit (Newns 1969b), a clearer picture of the effects of single particle excitations on the results of this chapter is desired. In addition, the inclusion of retardation is expected to introduce some lag, and hence asymmetry, in the induced density so that there would no longer be a clear distinction for the contributions to $F_\parallel$ and $F_\perp$ on the basis of plasmon phase velocities. However, the usefulness of the hydrodynamic model, in this case within the nonretarded limit, is highlighted in this important problem in giving a clear physical basis on which these other effects can be evaluated.
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